

# PNCS-ESG 2018

15<sup>th</sup> International Conference on the Physics of Non-Crystalline Solids & 14<sup>th</sup> European Society of Glass Conference

9 - 13 July 2018 - Saint Malo



# PROGRAM





## PNCS – ESG 2018 WELCOME !

Dear Colleagues !

It is our great pleasure to welcome you all to the 15<sup>th</sup> International Conference on the Physics of Non-Crystalline Solids (PNCS) and the 14<sup>th</sup> European Society of Glass Conference (ESG), organized by USTV (Union for Glass Science and Technology) and University Rennes 1. We will host more than 400 glass scientists from industrial and academic laboratories coming from 34 countries.

Highlights of the congress features 9 Plenary lectures: Stephen Elliott (University of Cambridge), Annie Pradel, (University of Montpellier), Jianrong Qiu (Zhejiang University), Alicia Duran (Instituto de Ceramica y Vidrio), Edgar Zanotto (Federal University of São Carlos), Hajime Tanaka (University of Tokyo), Kathleen Richardson (Center for Research and Education in Optics and Lasers), Daniel Ricoult (Corning), Neville Greaves (University of Cambridge). Recipients of three prestigious prizes will be presented: the Otto Schott Award, the SGT Alastair Pilkington Award and the USTV Award. The scientific program includes 47 sessions covering 26 important topics and 264 oral papers. 2 poster sessions are organized and includes 78 posters. We also highly encourage you to visit the Exhibition space at the heart of the conference.

We would like to take the opportunity to thank our many sponsors for their generosity: CEA, Corning, Perking Elmer, Horiba, Schott, Thorlabs, AGC, IXBLUE, AMTS, Land Ametek, Heraeus, Lumasense Technologie, Linseis, Air Product, Journal of Non-Crystalline Solids, Andor, Saint-Gobain, Glass Service, Quartz and Institut de Physique du Globe de Paris. We want also to express thanks to our partners: International Commission on Glass, The American Ceramics Society, and Glass Worldwide.

Bienvenue, Welcome to St-Malo, and we hope that all participants in the St Malo Glass-Meeting will be delighted by the location on the seafront, the quality of the food and especially the many gourmet regional specialists, and also the high scientific quality of the presentations.

L. Cormier , X.H. Zhang, D.R. Neuville



PLATINUM SPONSOR

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## **DGG – USTV Meeting 2019**

**Nürnberg  
13-15 May 2019**

**Orléans  
June 2020**

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All information on  
[www.ustverre.fr](http://www.ustverre.fr) or <http://www.hvg-dgg.de>**

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**Second conference on the limits of elemental  
characterization in materials with food contact: a  
scientific and industrial constraint (REACH)**

**Organized by USTV, the French Glass Federation,  
and TC02 Durability & Analysis of International Commission on Glass**

**22-23 Novembre 2018  
Institut de physique du globe de Paris, 1 rue Jussieu, 75005 Paris**

**All informations: [www.ustverre.fr](http://www.ustverre.fr)**



## GENERAL ONSITE INFORMATION

### Convention Centre Rooms

PNCS-ESG 2018 is being held in Saint-Malo, France. Registration, posters, talks, exhibition and refreshments are in Le Palais du Grand Large de Saint-Malo. Oral sessions will take place in rooms on the 2<sup>nd</sup> and 3<sup>rd</sup> floors. Plenary sessions will take place in the Amphithéâtre Chateaubriand.

### Coffee Breaks & Lunches

Refreshments, coffee, tea ... will be available in the Salle du Grand Large around 10:30 and the afternoon around 16:00. Lunches will be served on table in Rotonde Jacques Cartier (2<sup>nd</sup> floor) and Rotonde Surcouf (3<sup>rd</sup> floor) from 12:30 – 14:00 on Monday, Tuesday, and Thursday, and 12:45 – 14:00 on Wednesday. A lunch bag will be available Friday noon on request.

### Wireless Internet Access

Please use WiFi sparingly, because bandwidth is finite and this will speed connection times for others delegates. All delegates may access the wireless internet on all floors of the Congress Centre.

The conference network name is **PNCS-ESG\_WIFI** and the password is **pncsesg2018**.

### Registration & Help Desk Opening Times

Registration and the Help Desk will be open at the entrance of the Congress Center from 16:00 – 20:00 on Sunday and 08:00 - 18:30 on Monday, Tuesday and Thursday. The Help Desk will be open from 08:00 – 14:00 on Wednesday and Friday.

### Name Badges

Please be sure to wear your name badge at all times. Admission to Le Palais du Grand Large and all sessions will require identification by your badge. If you lose your name badge please visit the Help Desk.

### Lost & Found

All items found in the Congress Centre should be brought to the Help Desk.

### Insurance & Responsibility

Liability insurance is the responsibility of each individual delegate. Delegates should have their own medical coverage. The Organising Committee assumes no responsibility for accident, losses, damage, delays, or any modifications to the program arising from unforeseeable circumstances. It accepts no responsibility for travel or accommodation arrangements. The participant acknowledges that he/she has no right to lodge damage claims against the USTV or Le Palais du Grand Large should the conference proceeding be hindered or prevented by unexpected political or economic events, or should the non-appearance of speakers or other reasons necessitate program changes.

### Smoking Policy

For the comfort of delegates, all rooms used by the conference have been designated as non-smoking areas, including the stairwells and the entrance of Le Palais du Grand Large de Saint-Malo.

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## ORAL PRESENTATION INSTRUCTIONS

### Oral Presentation Times

Sessions with oral presentations will take place on Monday, Tuesday and Thursday from 08:30-12h30 and 14:00-18:30. On Wednesday and Friday, oral presentations will take place from 08:30-12h30.

### Uploading your talk

You may upload your talk in the room on the day of your presentation. Presenters can upload from 08:15 in the morning before the sessions, or during the coffee break and lunch break. We do recommend that all presenters bring their talk on a USB.

### Talk Timing

Speakers should arrive at their allocated room no less than 20 minutes before the start of the first presentation in order to meet with the chairperson. All presentations must be given in English, which is the official language of the Conference. Oral presentations are allocated 15 minutes, invited speakers 30 minutes and plenary lectures 45 minutes. 15-minute talks should be finished after 12 minutes, and 30-minute invited talks after 25 minutes, to leave time for discussion. The chairperson will give a first signal after 10 minutes, a warning after 12 minutes and prevent further talking after 15 minutes. It is essential for the success of the conference that the speakers keep strictly to this scheme to ensure that all parallel sessions are synchronized.

### Mobile Phones, Pagers, Cameras and Video Cameras

Delegates are required to mute or turn off their cell phones and pagers during oral presentations. **No photography or videoing** is permitted in any of the oral sessions or at the poster sessions without the permission of the relevant oral presenter or authors of the poster.



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## POSTER PRESENTATION INSTRUCTIONS

### Poster Presentation Times

There will be 2 afternoon sessions for poster presentations on Monday and Thursday. Posters should be put up from lunch time on Monday. The materials required to attach each poster to the board will be supplied. Posters should be removed at the end of the second poster session on Friday (around 10:30). Posters not collected by this time will be removed by the conference organizers and recycled.

### Poster Locations

The posters will be displayed in the *CHARCOT* and *BOUVET* rooms located between the entrance hall of the Congress Center and the *Rotonde Jacques Cartier* (1<sup>st</sup> floor). Poster board numbers are given in the Program Volume (See page 73).

### Poster Size

The poster boards are large enough to fit a size A0 poster in portrait orientation (this is 33.1" × 46.8" or 841mm × 1189mm). Oversize posters will not be displayed.

### Poster Etiquette

The poster sessions are from 14:45-16:30 on Monday and from 16:30-18:00 on Thursday. Delegates should expect to be available by their poster for most of this time.

### Cameras & Video Cameras

**No photography or videoing** is permitted at any of the poster sessions without the permission of the authors of the poster.



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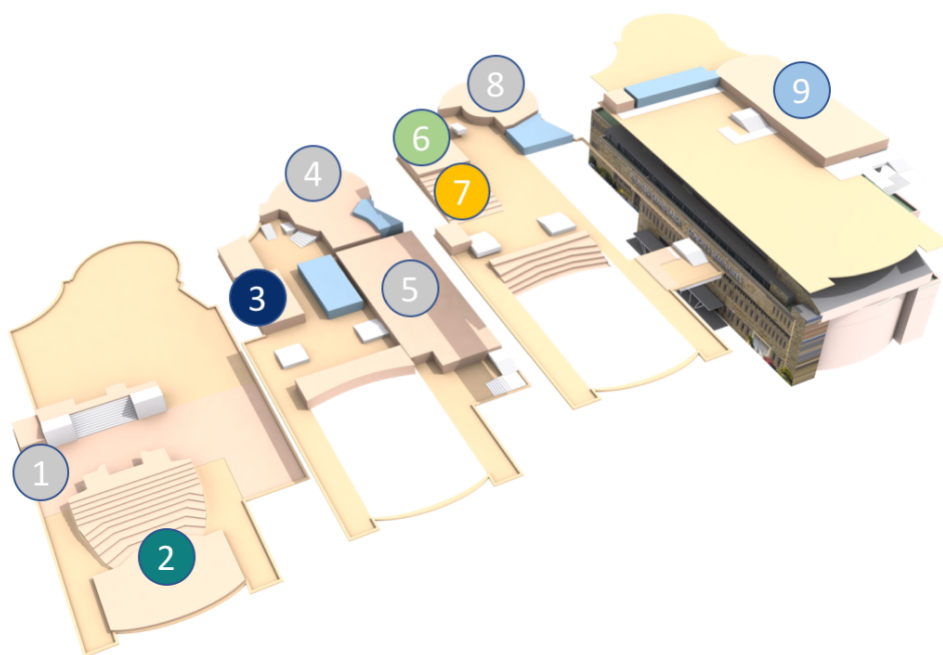
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# CONGRESS CENTER



ENTRANCE	1	REGISTRATION HELP DESK
CHATEAUBRIAND	2	PLENARY LECTURES
BOUVET / CHARCOT	3	POSTERS
Rotonde Jacques CARTIER	4	LUNCH
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LE GRAND LARGE	5	COFFEE EXHIBITORS
VAUBAN	6	PARALLEL SESSIONS
MAUPERTUIS	7	
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# CONFERENCE PROGRAM AT A GLANCE

	SUNDAY	MONDAY	TUESDAY
08:30		OPENING	PARALLEL SESSION 2
09:00		PLENARY 1	STRUCTURE 2 PRESSURE, DENSIFICATION GLASS TECHNOLOGY SIMULATION MODELING DURABILITY, DISSOLUTION, CORROSION
10:30		COFFEE BREAK	COFFEE BREAK
11:00		PLENARY 2	PARALLEL SESSION 3
12:30		LUNCH	LUNCH
14:00		OTTO SCHOTT AWARD POSTER SESSION	PARALLEL SESSION 4
16:00			STRUCTURE 4 DYNAMICS, EXCITATIONS, RELAXATION HERITAGE 1 GLASS-CERAMICS 1 SPECIAL GLASSES CROSS-CUTTING
16:30	REGISTRATION WELCOME RECEPTION	PARALLEL SESSION 1	COFFEE BREAK
18:30		STRUCTURE 1 AWARD IONIC EXCHANGE FURNACE ELABORATION 1 WASTE GLASSES	PARALLEL SESSION 5
19:30			STRUCTURE 5 BIOLASSES 1 PROPERTIES 2 THIN FILMS & GLASS SURFACE 1 MECHANICAL PROPERTIES 1
20:30			

## 1st FLOOR

CHATEAUBRIAND

## 2nd FLOOR

MAUPERTUIS

VAUBAN

## 3rd FLOOR

LAMENNAIS 1&2

LAMENNAIS 3

LAMENNAIS 4&5



**WEDNESDAY**

**THURSDAY**

**FRIDAY**

PLENARY 3	PARALLEL SESSION 6					AWARD	PARALLEL SESSION 9				
	SIMULATION, MODELING 2	WASTE GLASSES 2	HERITAGE 2	IONIC DIFFUSION & CONDUCTIVITY	BIOGLASSES 2		FIBERS 1	STRUCTURE 6	OPTOELECTRONICS AND OPTICAL PROPERTIES 2	TELLURITE	THERMODYNAMICS
COFFEE BREAK	COFFEE BREAK						COFFEE BREAK				
PLENARY 4	PARALLEL SESSION 7					FIBERS 2	PARALLEL SESSION 10				
	PHASE CHANGE MATERIALS	WASTE GLASSES 3	THIN FILMS & GLASS SURFACE 2	OPTOELEC. AND OPTICAL PROPERTIES 1	BIOGLASSES 3		STRUCTURE 7	FURNACE ELABORATION 2	PROPERTIES 3		
LUNCH	LUNCH						CLOSING				
FREE AFTERNOON OR EXCURSIONS	PARALLEL SESSION 8										
	CHALCOGENIDE	MECHANICAL PROP. 2	LASER INTERACTION	GLASS-CERAMICS 2							
	POSTER SESSION										
BANQUET											



## PLENARIES

Monday 9th July, 09:00, Amphithéâtre Chateaubriand

**Stephen Elliott**

Cambridge University

*Understanding the atomistic origin of the ultra-rapid crystallization and radiation hardness of the phase-change non-volatile memory material,  $\text{Ge}_2\text{Sb}_2\text{Te}_5$ , via ab-initio molecular dynamics simulations*

Monday 9th July, 09:45, Amphithéâtre Chateaubriand

**Annie Pradel**

Institut Charles Gerhardt

*Crystallization and phase separation in chalcogenide glasses*

Monday 9th July, 11:00, Amphithéâtre Chateaubriand

**Jianrong Qiu**

State Key Laboratory of Modern Optical Instrumentation, Zhejiang University

*Control of metastable state of glass*

Monday 9th July, 11:45, Amphithéâtre Chateaubriand

**Alicia Duran**

Instituto de Ceramica y Vidrio

*Transparent oxyfluoride nano-glass ceramics: Processing is the key*



## PLENARIES

Wednesday 11th July, 08:30, Amphithéâtre Chateaubriand

### **Edgar Zanotto**

Center for Research, Technology, and Education in Vitreous Materials,  
Department of Materials Engineering, Federal University of São Carlos  
*Homogeneous Crystal Nucleation in Deeply Supercooled Glass-Forming  
Liquids – Open Issues*

Wednesday 11th July, 09:15, Amphithéâtre Chateaubriand

### **Hajime Tanaka**

Institute of Industrial Science – The University of Tokyo  
*Impact of structural ordering in supercooled liquids on glassy slow  
dynamics and glass-forming ability*

Wednesday 11th July, 09:15, Amphithéâtre Chateaubriand

### **Kathleen Richardson**

CREOL – University of Central Florida  
*Advances in infrared optics: novel materials towards next-generation  
components and devices*

Wednesday 11th July, 11:15, Amphithéâtre Chateaubriand

### **Daniel Ricoult**

CORNING  
*Moving to the Glass Age*

Wednesday 11th July, 12:00, Amphithéâtre Chateaubriand

### **Neville Greaves**

Cambridge University  
*Hybrid Glasses and Melts*



## AWARDS

Monday 9th July, 14:00, Amphithéâtre Chateaubriand

### **OTTO SCHOTT RESEARCH AWARD**

Awarded to **C.A. Angell**

*The Otto Schott Research Award alternates with the Carl Zeiss Research Award every year in recognition of excellence in scientific research and motivational support for cooperation between scientific research and industry. The Stifterverband für die deutsche Wissenschaft innovation agency for the German science system is responsible for the two research awards, which invites contenders from across the world – matching the SCHOTT AG and CARL ZEISS AG sphere of activity. Award winners have included German scientists in physics and chemistry along with scientists from a variety of European countries, the USA, Russia, Japan and China.*

Monday 9th July, 18:00, Amphithéâtre Chateaubriand

### **PILKINGTON AWARD**

Awarded to **M. Smedskjaer**

The SGT-Alastair Pilkington Award is designed to encourage and recognise excellent work in glass research or innovation achieved by someone who, like Sir Alastair, has come relatively recently into the field of glass studies. This Award is not restricted to hard science or engineering – it spans all dimensions of glass studies, creativity and research; glass art as well as glass science, conservation and museum studies as well as engineering, history and design as well as molecular dynamics.

Friday 13th July, 08:30, Amphithéâtre Maupertuis

### **USTV Ph-D AWARD**

Awarded to **A. Barnini**

Each year, the USTV Ph-D Award recognizes a young researcher who has completed a doctoral thesis in a French doctoral school in one of the fields of glass science: basic or applied research ranging from material sciences (Chemistry, Physics, ...) to Earth's sciences.





## SOCIAL EVENTS

### **Icebreaker Welcome Reception**

Sunday 8<sup>th</sup> July: 18:00 – 20:30

Location: Palais du Grand Large – Rotonde Jacques CARTIER

*The Icebreaker Welcome Reception is the perfect time to catch up with colleagues that you haven't seen over the year, and meet new people in your field. All delegates are warmly invited and encouraged to attend.*

### **Visit of the Mont Saint-Michel Abbey**

Wednesday 11<sup>th</sup> July: 14:00 – 19:00

Meeting Point: Entrance Hall of the Congress Center Le Palais du Grand Large

*A magical island topped by a gravity-defying medieval monastery, the Mont-Saint-Michel counts among France's most stunning sights. For centuries one of Europe's major pilgrimage destinations, this holy mount is now a UNESCO World Heritage Site, as is its breathtaking bay. A two hour visit of the famous Mont-Saint-Michel Abbey is proposed.*

### **Visit of a Medieval City - Dinan**

Wednesday 11<sup>th</sup> July: 14:00 – 19:00

Meeting Point: Entrance Hall of the Congress Center Le Palais du Grand Large

*City of Art and History, **Dinan** has majestically crossed the centuries as a history book. Of various periods buildings open their doors to tell you. The city overlooking the Rance, which carves its valley. Rance sometimes calm and peaceful sometimes meandering to become a marine river. This excursion includes a 2 hour walk in downtown Dinan with a specialized guide to discover this amazing medieval city. It also includes a stop at the Rance Tidal Power Station.*

### **PNCS-ESG Banquet**

Thursday 12<sup>th</sup> July: 19:30 – 23:00

Location: Salle Le Grand Large - Le Palais du Grand Large



## OUR PARTNERS

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# Conference Schedule

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# MONDAY 9<sup>th</sup> JULY

## TIMETABLE

08:30 - 09:00 › **OPENING CEREMONY**

Auditorium CHATEAUBRIAND

CHATEAUBRIAND

### PLENARY LECTURE 1

*Session Chair: Xiang-Hua ZHANG*

09:00 › **Stephen Elliott**, *University of Cambridge, UK*

Understanding the atomistic origin of the ultra-rapid crystallization and radiation hardness of the phase-change non-volatile memory material, Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>, via *ab initio* molecular-dynamics simulations

09:45 › **Annie Pradel**, *Institut Charles Gerhardt Montpellier, France*

Crystallization and phase separation in chalcogenide glasses

10:30 - 11:00 › **COFFEE BREAK**

Salle LE GRAND LARGE

CHATEAUBRIAND

### PLENARY LECTURE 2

*Session Chair: Laurent CORMIER*

11:00 › **Jianrong Qiu**, *State Key Laboratory of Modern Optical Instrumentation, Zhejiang University, China*

Control of metastable state of glass

11:45 › **Alicia Duran**, *Instituto de Ceramica y Vidrio, Spain*

Transparent oxyfluoride nanoglass ceramics: Processing is the key

12:30 - 14:00 › **LUNCH**

Rotondes Jacques CARTIER & SURCOUF

CHATEAUBRIAND

### OTTO SCHOTT AWARD

*Session Chair: Roland LANGFELD*

14:00 › **C. Austen Angell**

*Arizona State University, USA*

**SCHOTT**  
glass made of ideas

14:45 – 16h30 › **POSTER SESSION & COFFEE BREAK**

*BOUVET & CHARCOT Rooms*

16:30 – 18h30 › **PARALLEL SESSIONS 1**

	CHATEAUBRIAND	LAMENNAIS 1&2	LAMENNAIS 3	LAMENNAIS 4&5
	STRUCTURE 1	IONIC EXCHANGE	FURNACE AND ELABORATION 1	WASTE GLASSES 1
16:30 – 16:45	A. HANNON	T. GROSS	A.J. FABER	M. HARRISON
16:45 – 17:00				
17:00 – 17:15	V. MICHAELIS	H. HASSANI	S. FRANCHITTO	A-L. CHABAUTY
17:15 – 17:30	G. HENDERSON	P. MARQUES	S. TIOZZO	E. NIENHUIS
17:30 – 17:45	E. BUROV	G. MACRELLI	J. KLOUZEK	I. GIBOIRE
17:45 – 18:00	G. TRICOT	C. RAGOEN		
18:00 – 18:15	PILKINGTON AWARD	H. GOVER	F. PIGEONNEAU	S. KROEKER
18:15 – 18:30		J. WU	E. ALEJANDRO	

# MONDAY 9<sup>th</sup> JULY - PM

CHATEAUBRIAND

## STRUCTURE 1

*Session Chair: Benoit RUFFLE*

*Room: CHATEAUBRIAND*

- 16:30 › **Invited: Alex Hannon**, *ISIS Facility*  
The bond valence method applied to glass structure
- 17:00 › **Vladimir Michaelis**, *University of Alberta*  
Dissolvable borophosphate glasses: unravelling changes in short and medium range structure with solid state NMR spectroscopy
- 17:15 › **Grant Henderson**, *Earth Sciences, University of Toronto*  
Raman fitting of the high frequency NBO bands in alkali silicate glasses
- 17:30 › **Ekaterina Burov**, *Surface du Verre et Interfaces*  
Local glass structure modification during diffusion views by Raman spectroscopy
- 17:45 › **Gregory Tricot**, *Laboratoire de Spectrochimie Infrarouge et Raman*  
1D/2D NMR investigation of the Pyrex glass

CHATEAUBRIAND

## PILKINGTON AWARD

*Session Chair: Bill BROOKES, President of the SGT*

*Room: CHATEAUBRIAND*

- 18:00 › **Morten Smedskjaer**  
*Dept of Chemistry and Bioscience, Aalborg University*
- Improving the damage resistance of oxide glasses from knowledge of their structural response to densification



## IONIC EXCHANGE

*Session Chair: Monique COMTE*

*Room: LAMENNAIS 1&2*

LAMENNAIS 1&2

- 16:30 › **Invited: Timothy Gross**, *Corning Research and Development Corporation*  
Mechanics of Ion Exchanged Glass
- 17:00 › **Hamid Hassani**, *University of Trento*  
Influence of processing temperature and time on the structure evolution and mechanical properties of ion exchanged soda lime silicate glass
- 17:15 › **Paulo Marques**, *CORNING SAS*  
Chemical strengthening of magnesium doped LAS glass ceramics
- 17:30 › **Guglielmo Macrelli**, *Isoclima SpA R&D Department*  
Calculation of residual stress in Alkali Silicate glasses after Ion Exchange
- 17:45 › **Céline Ragoen**, *AGC*  
Structural adaptation in Na<sup>+</sup>/K<sup>+</sup> ion exchanged glasses leading to a relaxation of the compressive stress
- 18:00 › **Hande Gover**, *Dept. of Mater. Sci. and Eng., Sheffield*  
Strengthening of Alkali Alkaline Earth Silicate Glasses by Ion Exchange
- 18:15 › **Jingshi Wu**, *Corning Incorporated*  
Boron effects on chemical strengthened glass

# MONDAY 9<sup>th</sup> JULY - PM

## FURNACE AND ELABORATION 1

*Session Chair: Nicola FAVARO*

*Room: LAMENNAIS 3*

LAMENNAIS 3

- 16:30 › **Invited: AnneJans Faber**, *CelSian Glass & Solar*  
Transition to CO2 neutral glass furnaces: technological options and challenges
- 17:00 › **Sophie Franchitto**, *HERAEUS*  
Platinum equipment for manufacturing of high quality glasses
- 17:15 › **Simone Tiozzo**, *Stazione Sperimentale del Vetro*  
SSV's integrated approach for the assessment of quality and reliability of refractory materials
- 17:30 › **Invited: Jaroslav Klouzek**, *University of Chemistry and Technology*  
Interaction of Gas Phase and Glass during Melting Process
- 18:00 › **Franck Pigeonneau**, *MINES ParisTech CEMEF*  
Nucleated bubbles in glass former liquids undergoing coalescence and growth
- 18:15 › **Estela Alejandro**, *Vidrala*  
Improving batch caking and melting properties by using calcined lime. An industrial experience



## WASTE GLASSES 1

*Session Chair: Elise REGNIER*

*Room: LAMENNAIS 4&5*

- 16:30 › **Invited: Mike Harrison**, *National Nuclear Laboratory*  
Vitrification of Waste Containing High Content of Molybdenum and Sodium
- 17:00 › **Anne Lise Chabauty**, *Unité de Catalyse et de Chimie du Solide, CEA, DEN, DE2D/SEVT/LDMC*  
Radioactive iodine conditioning in silver phosphate glasses
- 17:15 › **Emily Nienhuis**, *Washington State University*  
Structure of Mixed Anion Salt Glasses from Synchrotron X-Ray Pair Distribution Functions
- 17:30 › **Invited: Isabelle Giboire**, *Lab. d'étude et Dév. de Matrices de Conditionnement*  
Rare Earth solubility limits in simplified borosilicate glass
- 18:00 › **Scott Kroeker**, *Department of Chemistry, Univ. Manitoba*  
The Effect of Phosphorus on Molybdenum Solubility in Boroaluminosilicate Glasses



**MONDAY 9<sup>th</sup> JULY - PM**

## TIMETABLE

08:30 – 10h30 › **PARALLEL SESSIONS 2**

**STRUCTURE 2** – *MAUPERTUIS*

**PRESSURE AND DENSIFICATION** – *LAMENNAIS 1&2*

**GLASS TECHNOLOGY AND FUTURE TRENDS** – *LAMENNAIS 3*

**SIMULATION, MODELING 1** – *LAMENNAIS 4&5*

**DURABILITY, DISSOLUTION & CORROSION** – *VAUBAN*

10:30 - 11:00 › **COFFEE BREAK**

*Salle LE GRAND LARGE*

11:00 – 12h30 › **PARALLEL SESSIONS 3**

**STRUCTURE 3** – *MAUPERTUIS*

**OXYFLUORIDE, OXYNITRIDE GLASSES** – *LAMENNAIS 1&2*

**FURNACE AND ELABORATION 2** – *LAMENNAIS 3*

**METALLIC GLASSES** – *LAMENNAIS 4&5*

**PROPERTIES 1** – *VAUBAN*

12:30 - 14:00 › **LUNCH**

*Rotondes Jacques CARTIER & SURCOUF*

## TUESDAY 10<sup>th</sup> JULY - AM

08:30 – 10h30 › **PARALLEL SESSIONS 2**

	MAUPERTUIS	LAMENNAIS 1&2	LAMENNAIS 3	LAMENNAIS 4&5	VAUBAN
	STRUCTURE 2	PRESSURE AND DENSIFICATION	GLASS TECHNOLOGY AND FUTURE TRENDS	SIMULATION, MODELING 1	DURABILITY, DISSOLUTION & CORROSION
8:30 – 8:45	S.K. LEE	C. WEIGEL	N. FAVARO	A. CORMACK	R. HAND
8:45 – 9:00					
9:00 – 9:15	L. TORZUOLI	N. OLLIER	S. KARLSSON	S. ISPAS	M. BAUCHY
9:15 – 9:30	B. DIALLO	M. BUSCEMI	L. GALLAIS	D. RODNEY	
9:30 – 9:45	K. KANEHASHI	L. DING	X. ZHAO	G. FERLAT	H. ROGGENDORF
9:45 – 10:00		C. MARTINET			O. MAJERUS
10:00 – 10:15	D. LE CORNEC	B. RUFFLE	K. KIM	G. MOUNTJOY	F. PERRUDIN
10:15 – 10:30	A. DANEZAN	C. DEREURE	X. CAPILLA		T. FUJIMA

**STRUCTURE 2***Session Chair: Randall YOUNGMAN**Room: MAUPERTUIS*

- 08:30 › **Invited: Sung Keun Lee**, *Seoul National University*  
Direct probing of structural transitions in amorphous oxide under extreme compression and friction
- 09:00 › **Lyna Torzuoli**, *Institut de Recherche sur les Céramiques*  
Structural study of  $\text{TeO}_2\text{M}_y\text{O}_z$  glasses by X-ray total scattering and molecular dynamics
- 09:15 › **Babacar Diallo**, *CEMHTI*  
Evidence of phase separation phenomena in  $\{\text{La}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2\}$  system by high resolution NMR spectroscopy
- 09:30 › **Invited: Koji Kanehashi**, *Advanced Technology Research Laboratories, Nippon Steel & Sumitomo Metal Corporation*  
Application of multinuclear solid state NMR to structural analysis of slag and glass
- 10:00 › **Domitille Le Cornec**, *IMPMC / Association Technique de l'Industrie des Liants Hydrauliques*  
Structure and hydration of amorphous blast furnace slag
- 10:15 › **Abel Danezan**, *CEMHTI*  
Understanding of the reactivity of granulated blast furnace slags by a multiscale structural characterization

## TUESDAY 10<sup>th</sup> JULY - AM

### PRESSURE AND DENSIFICATION

*Session Chair: Anita ZEIDLER*

*Room: LAMENNAIS 1&2*

LAMENNAIS 1&2

- 08:30 › **Invited: Coralie Weigel**, *Laboratoire Charles Coulomb*  
High Pressure behaviour of v-SiO<sub>2</sub>: Brillouin and polarized Raman study
- 09:00 › **Nadège Ollier**, *Laboratoire des Solides Irradiés*  
Densification and relaxation of densified glasses under electron irradiation in silica and phosphate glasses
- 09:15 › **Michela Buscemi**, *Department of Physics, University of Bath*  
Structure of (11B<sub>2</sub>O<sub>3</sub>)<sub>0.3</sub>(GeO<sub>2</sub>)<sub>0.7</sub> glass at pressures up to 8.2 GPa
- 09:30 › **Linfeng Ding**, *Institute of Geosciences, Johannes Gutenberg University*  
Pressure dependence of density and structural relaxation of glass near the glass transition region
- 09:45 › **Christine Martinet**, *Institut Lumière Matière*  
Relaxation processes of densified silicate glasses having different thermomechanical histories
- 10:00 › **Benoit Rufflé**, *Laboratoire Charles Coulomb*  
Spectroscopy as a tool for local density measurement in vitreous silica
- 10:15 › **Corentin Dereure**, *Institut de Physique de Rennes*  
A laser shocked induced densification of silica glass studied by both experience and molecular dynamic simulation

## GLASS TECHNOLOGY AND CURRENT TRENDS

*Session Chair: Ekaterina BUROV*

*Room: LAMENNAIS 3*

LAMENNAIS 3

- 08:30 › **Invited: Nicola Favaro**, *Stazione Sperimentale del Vetro*  
Chemical Agents Exposure in the Glass Industry: assessment and main issues
- 09:00 › **Stefan Karlsson**, *RISE Research Institutes of Sweden*  
"Transparent Intelligence" for Sustainable Development
- 09:15 › **Laurent Gallais**, *Institut FRESNEL*  
CO<sub>2</sub> laser processing of fused silica surfaces for high power laser applications
- 09:30 › **Invited: Xiujian Zhao**, *State Key Laboratory of Silicate Materials for Architectures (Wuhan University of Technology)*  
Intelligent Coatings for Energy Efficient Glazing of Glasses
- 10:00 › **Kicheol Kim**, *Dept. Mat. Sci. Eng. Kunsan National University*  
Characterization of glass produced from glass wool batch containing simulated end of life LCD waste glass
- 10:15 › **Xavier Capilla**, *Institut du Verre, Paris*  
Release from glass production process and regulation constraints: what to expect ?

# TUESDAY 10<sup>th</sup> JULY - AM

LAMENNAIS 4&5

## SIMULATION, MODELING 1

*Session Chair: Akira TAKADA*

*Room: LAMENNAIS 4&5*

- 08:30 › **Invited: Alastair Cormack**, *Alfred University*  
MD Simulations of the melting of sodium and lithium metasilicates
- 09:00 › **Simona Ispas**, *Laboratoire Charles Coulomb*  
Developing interaction potentials for modelling oxide glasses
- 09:15 › **David Rodney**, *Institut Lumière Matière*  
Atomistic study of two level systems in amorphous silica
- 09:30 › **Invited: Guillaume Ferlat**, *IMPMC, Sorbonne Université*  
A novel numerical method for exploring challenging phase transitions: From liquid crystal to amorphous-amorphous transformations
- 10:00 › **Gavin Mountjoy**, *University of Kent, Canterbury*  
Using molecular dynamics to descend into the structural complexity of  $\text{EuF}_3$  doped  $\text{ZrF}_4\text{BaF}_2\text{LaF}_3\text{AlF}_3\text{NaF}$  (ZBLAN) glass



## DURABILITY, DISSOLUTION & CORROSION

*Session Chair: Jean-Pierre GUIN*

*Room: VAUBAN*

VAUBAN

- 08:30 › **Invited: Russell Hand**, *University of Sheffield*  
Glass durability under elevated pH conditions
- 09:00 › **Invited: Mathieu Bauchy**, *University of California, Los Angeles*  
Topological control on glasses' dissolution kinetics
- 09:30 › **Hans Roggendorf**, *Martin Luther University Halle Wittenberg, Inst. of Physics*  
Corrosion of sodium silicate glasses: the influence of concentration effects
- 09:30 › **Odile Majerus**, *Institut de Recherche de Chimie Paris*  
Evaluation and mechanisms of a surface treatment based on zinc salts to slow down atmospheric alteration
- 10:00 › **François Perrudin**, *Institut Jean Lamour*  
RE<sub>2</sub>O<sub>3</sub> dissolution kinetics and mechanisms in CMAS silicate melts: influence of the rare earth
- 10:00 › **Takuya Fujima**, *Faculty of Engineering, Tokyo City University*  
Formation of Hierarchical Nanoporous Layer etched on a silicate glass

## TUESDAY 10<sup>th</sup> JULY - AM

11:00 – 12h30 › **PARALLEL SESSIONS 3**

	MAUPERTUIS	LAMENNAIS 1&2	LAMENNAIS 3	LAMENNAIS 4&5	VAUBAN
	STRUCTURE 3	OXYFLUORIDE, OXYNITRIDE GLASSES	FURNACE AND ELABORATION 2	METALLIC GLASSES	PROPERTIES 1
11:00 – 11:15	R. YOUNGMAN	F. MUNOZ	I. PETERSON	A.L. GREER	R. MORETTI
11:15 – 11:30					
11:30 – 11:45	R. KADO	J. REN	J-C. WIENCKE	J. XU	L. BRIESE
11:45 – 12:00	D. MASSIOT	C. CALAHOO	K. SENESCHAL- MERZ	A. MUSIAL	JS. CHOI
12:00 – 12:15	S. SUKENAGA	K. SHINOZAKI	T. YANO	S. HARATIAN	H. JAIN
12:15 – 12:30	P. JOVARI	G. GORNI			L. KARAM

### STRUCTURE 3

*Session Chair: Charles LE LOSQ*

*Room: MAUPERTUIS*

MAUPERTUIS

- 11:00 › **Invited: Randall Youngman**, *Corning Incorporated*  
Impact of Temperature and Pressure on the Structure of Borosilicate Glasses
- 11:30 › **Kado Rikiya**, *Tokyo Institute of Technology*  
Local environment of iron ions in magnesium aluminosilicate glasses from liquid helium temperature to glass transition temperature
- 11:45 › **Dominique Massiot**, *CEMHTI*  
Chemical homogeneity and network topology from NMR experiments
- 12:00 › **Sohei Sukenaga**, *Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University*  
Structural role of aluminum cation in alkaline-earth aluminosilicate glasses
- 12:15 › **Pál Jóvári**, *Wigner Research Centre for Physics*  
Short range order in amorphous germanium tellurides

## TUESDAY 10<sup>th</sup> JULY - AM

### OXYFLUORIDE, OXYNITRIDE GLASSES

*Session Chair: Alicia DURAN*

*Room: LAMENNAIS 1&2*

LAMENNAIS 1&2

- 11:00 › **Invited: Francisco Munoz**, *Institute of Ceramics and Glass (CSIC)*  
Oxynitride phosphate glasses: new strategies of synthesis for new applications
- 11:30 › **Jinjun Ren**, *Shanghai Inst. of Opt. and Fine Mech., Chin. Acad. Sci.*  
Structural Studies of fluorophosphate Laser Glasses by Solid State NMR
- 11:45 › **Courtney Calahoo**, *Otto Schott Institute of Materials Research*  
The structural role of fluorine in ionic glasses via fluorine-19 MAS NMR
- 12:00 › **Kenji Shinozaki**, *National Inst. of Adv. Ind. Sci. and Tech.*  
Ordering of Ba site in MgF<sub>2</sub>rich barium fluoroborate glasses and their highly efficient photoluminescence
- 12:15 › **Giulio Gorni**, *Instituto de Cerámica y Vidrio (CSIC)*  
Transparent 80SiO<sub>2</sub>-20LnF<sub>3</sub> sol-gel oxyfluoride glass-ceramics for photonics

## FURNACE AND ELABORATION 2

*Session Chair: Anne-Jans FABER*

*Room: LAMENNAIS 3*

- 11:00 › **Invited: Irene Peterson**, *Corning Research and Development Corporation*  
In-situ Measurement of Reactions in a Glass-Forming Batch by Neutron  
Diffraction
- 11:30 › **Jan-Christian Wiencke**, *Arcelor Mittal R&D (FRANCE), Institut Jean Lamour*  
Behavior of a molten magnesium-aluminosilicate at elevated potentials
- 11:45 › **Karine Seneschal-Merz**, *Bundesanstalt für Materialforschung und prüfung*  
Development of low melting glasses as durable transparent enamel colors for  
the manufacture of decorated glass panels
- 12:00 › **Invited: Tetsuji Yano**, *Tokyo Institute of Technology*  
High-temperature X-ray CT approach to the vitrification reactions of glass raw  
materials

## METALLIC GLASSES

*Session Chair: Jean-Christophe SANGLEBOEUF*

*Room: LAMENNAIS 4&5*

- 11:00 › **Invited: A. Lindsay Greer**, *Univ. of Cambridge, Dept. of Mat. Sci. Metallurgy*  
Metallic Glasses
- 11:30 › **Jian Xu**, *Institute of Metal Research, Chinese Academy of Sciences*  
 $Zr_{61}Ti_2Cu_{25}Al_{12}$  bulk metallic glass: Failure under torsional loading and Mode III fracture toughness
- 11:45 › **Andrzej Musial**, *Institute of Molecular Physics, Polish Academy of Sciences*  
Glassy state formation and thermal stability in (Hf,Cr)CoB alloys
- 12:00 › **Saber Haratian**, Mechanical Eng. Dept., Technical University of Denmark  
Surface hardening of Zr-Cu based bulk metallic glasses using gaseous thermochemical treatment

## PROPERTIES 1

*Session Chair: Russel HAND*

*Room: VAUBAN*

VAUBAN

- 11:00 › **Invited: Roberto Moretti**, *IPGP, Observatoire Volcanologique et Sismologique de la Guadeloupe*  
Redox (and acid-base) properties of aluminosilicate melts: the ionic-polymeric description
- 11:30 › **Laura Briese**, *Inst. for Non-Metallic Mat., Clausthal University of Technology*  
Redox-induced precipitation of nickel and cobalt metal nanoparticles in silicate glasses
- 11:45 › **JoonSung Choi**, *Yonsei University, Martin Luther University Halle Wittenberg, Inst. of Physics*  
The effect of cation species on the sulfur solubility of CaO-FeO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> melts
- 12:00 › **Himanshu Jain**, *Lehigh University*  
A dislocation based model of rotating-lattice single crystal growth on glass surface by CW-laser
- 12:15 › **Lara Karam**, *Institut des Sciences Moléculaires*  
Microstructuring the optical properties in ionic glasses by thermal poling: the influence of the sodium content



**TUESDAY 10<sup>th</sup> JULY - AM**



## TIMETABLE

14:00 – 16h00 › **PARALLEL SESSIONS 4**

**STRUCTURE 4** – *MAUPERTUIS*  
**DYNAMICS, EXCITATIONS & RELAXATION** – *LAMENNAIS 1&2*  
**HERITAGE, HISTORY 1** – *LAMENNAIS 3*  
**GLASS-CERAMICS 1** – *LAMENNAIS 4&5*  
**SPECIAL GLASSES AND CROSS-CUTTING** – *VAUBAN*

16:00 - 16:30 › **COFFEE BREAK**

*Salle LE GRAND LARGE*

16:30 – 18h45 › **PARALLEL SESSIONS 5**

**STRUCTURE 5** – *MAUPERTUIS*  
**BIOGLASSES 1** – *LAMENNAIS 1&2*  
**PROPERTIES 2** – *LAMENNAIS 3*  
**THIN FILMS & GLASS SURFACE 1** – *LAMENNAIS 4&5*  
**MECHANICAL PROPERTIES 1** – *VAUBAN*

## TUESDAY 10<sup>th</sup> JULY - PM

14:00 – 16h00 › **PARALLEL SESSIONS 4**

	MAUPERTUIS	LAMENNAIS 1&2	LAMENNAIS 3	LAMENNAIS 4&5	VAUBAN
	STRUCTURE 4	DYNAMICS, EXCITATIONS & RELAXATION	HERITAGE, HISTORY 1	GLASS-CERAMICS 1	SPECIAL GLASSES AND CROSS-CUTTING
14:00 – 14:15	B. HEHLEN	J. DEUBENER	E. GREINER-WRONA	X. QIAO	Y. YUE
14:15 – 14:30					
14:30 – 14:45	T. CHARPENTIER	T. MORI	G. CALAS	C. LIU	C. ZHOU
14:45 – 15:00	M.R. CICONI	S. HOSOKAWA	I. MULLER	S. RIO	T. BENNETT
15:00 – 15:15	O. MAJERUS	M. BAUCHY	M. VILARIGUES	D. GALUSEK	L. WONDRACZEK
15:15 – 15:30	T. GRAMMES	D. RODNEY		E. BERNARDO	
15:30 – 15:45	T. UESBECK	C. RODRIGUEZ-TINOCO	D. GALUSKOVA	A. MOGUS-MILANKOVIC	K. JURKIEWICZ
15:45 – 16:00	M. BREHL			E. WALCH	M. STEPNIIEWSKA

**STRUCTURE 4***Session Chair: Dominique MASSIOT**Room: MAUPERTUIS*

MAUPERTUIS

- 14:00 › **Invited: Bernard Hehlen**, *Laboratoire Charles Coulomb*  
The complex Raman response of cations in aluminosilicate Glasses
- 14:30 › **Thibault Charpentier**, *NIMBE, CEA, CNRS, Univ. Paris-Saclay, CEA Saclay*  
Combined solid-state NMR and molecular dynamics study of the structure of strontium-aluminosilicate glasses
- 14:45 › **Maria Rita Cicconi**, *Friedrich-Alexander Univ., CNRS-IPGP, Géomatériaux*  
Solubility and role of iodine and xenon in silicate glasses
- 15:00 › **Odile Majerus**, *Institut de Recherche de Chimie Paris*  
Structure and crystallization in the  $B_2O_3$ - $La_2O_3$  binary and focus on the congruent lanthanum metaborate composition ( $LaB_3O_6$ )
- 15:15 › **Thilo Grammes**, *Otto-Schott Institute of Materials Research*  
Effect of a third network former on the properties of aluminosilicate glasses
- 15:30 › **Tobias Uesbeck**, *Friedrich-Alexander Universität*  
Structural investigation of  $M_2O$ - $SiO_2$ - $B_2O_3$ - $Al_2O_3$  glasses by Raman spectroscopy and the influence of thermal history
- 15:45 › **Martin Brehl**, *Friedrich-Alexander University Erlangen-Nürnberg*  
Structural investigation of glasses in the  $BaO$ - $B_2O_3$ - $SiO_2$  system with coupled Raman/Brillouin spectroscopy

## TUESDAY 10<sup>th</sup> JULY - PM

### DYNAMICS, EXCITATIONS & RELAXATION

*Session Chair: Hajime TANAKA*

*Room: LAMENNAIS 1&2*

LAMENNAIS 1&2

- 14:00 › **Invited: Joachim Deubener**, *Institute of Non-Metallic Materials, Clausthal University of Technology*  
Impact of structural water on sub-T<sub>g</sub> relaxations in glass
- 14:30 › **Tatsuya Mori**, *University of Tsukuba*  
Investigation of boson peak and fraction in protein lysozyme by terahertz time-domain spectroscopy
- 14:45 › **Shinya Hosokawa**, *Kumamoto University*  
Phonon excitations in an anisotropic metaphosphate glass
- 15:00 › **Mathieu Bauchy**, *University of California, Los Angeles*  
Stretched exponential relaxation of glasses and origin of the mixed alkali effect
- 15:15 › **David Rodney**, *Institut Lumière Matière*  
Modeling viscoelasticity and energy dissipation in Silica in the THz regime
- 15:30 › **Cristian Rodríguez-Tinoco**, *Institute of Physics, University of Silesia*  
Secondary relaxations in ultrastable glasses and their connection with structural relaxation

## HERITAGE, HISTORY 1

*Session Chair: Laurence GALOISY*

*Room: LAMENNAIS 3*

LAMENNAIS 3

- 14:00 › **Invited: Elżbieta Greiner-Wrona, Poland**  
Glass archaeometry in the aspect of cultural heritage
- 14:30 › **Georges Calas, IMPMC**  
The color of the stained glasses of the Reims Cathedral: a witness of Middle Age technologies
- 14:45 › **Isabelle Muller, Vitreous State Laboratory, The Catholic University of America**  
Identification of Factors Relevant to Preservation of Claude Laurent's Glass Flutes: Model Studies vs. Actual Observations
- 15:00 › **Invited: Márcia Vilarigues, Department of Conservation and Restoration, Faculty of Science and Technology, NOVA University of Lisbon, Research Unit VICARTE – Glass and Ceramics for the Arts, Faculty of Science and Technology, NOVA University of Lisbon**  
From words to objects: the art of glassmaking through recipes
- 15:30 › **Dagmar Galuskova, Vitrum Lauguricio – Joint Glass Center of the IIC SAS, TnU AD, and FChFT STU**  
Reconstruction of technology of layered red glass production based on chemical analysis of discovered glass fragment

## GLASS CERAMICS 1

*Session Chair: Edgar ZANOTTO*

*Room: LAMENNAIS 4&5*

- 14:00 › **Invited: Xusheng Qiao**, *Zhejiang University*  
Phase separation and crystallization strategies to enhance the luminescence of silver and rare-earth doped multiphase glass and glass-ceramics
- 14:30 › **Chao Liu**, *State Key Lab. of Silicate Mater. for Architectures, Wuhan Univ. of Technology*  
Glasses containing halide perovskite nanocrystals and their potential applications
- 14:45 › **Sandra Rio**, *Institut des matériaux Jean Rouxel, Arc, France*  
Influence of crystalline phases on optical characteristics of a glass-ceramic in the visible range
- 15:00 › **Dusan Galusek**, *Centre for functional and surface functionalized glass, Alexander Dubček University of Trenčín, Trenčín*  
Crystallization of physical properties of aluminate glasses
- 15:15 › **Enrico Bernardo**, *University of Padova, Dept. of Industrial Engineering*  
Novel Glass-ceramics from Glass Powders and Reactive Silicone Binders
- 15:30 › **Andrea Mogus-Milankovic**, *Ruder Boskovic Institute*  
Electrical transport in  $\text{Li}_2\text{O}-\text{P}_2\text{O}_5-\text{GeO}_2$  glass-ceramics
- 15:45 › **Emmanuel Walch**, *RWTH Aachen University*  
Residual stresses in  $\text{Bi}_2\text{O}_3-\text{B}_2\text{O}_3-\text{ZnO}-\text{SiO}_2$  partially crystallizing glass-enamel

## SPECIAL GLASSES AND CROSS-CUTTING

*Session Chair: Steve MARTIN*

*Room: VAUBAN*

VAUBAN

- 14:00 › **Invited: Yuanzheng Yue**, *Dept. of Chem. and Bioscience, Aalborg University, State Key Lab. of Silicate Mater. for Architectures, Wuhan Univ. of Tech.*  
Metal-Organic Framework Glass Formation and “Reordering”
- 14:30 › **Chao Zhou**, *Department of Chemistry and Bioscience, Aalborg University*  
Formation of Metal-Organic Framework Glass via Post-Synthetic Modification
- 14:45 › **Thomas Bennett**, *University of Cambridge*  
Metal-Organic Framework Liquids and Glasses
- 15:00 › **Invited: Lothar Wondraczek**, *Otto Schott Institute of Materials Research*  
Kinetics of decelerated melting
- 15:30 › **Karolina Jurkiewicz**, *Institute of Physics, University of Silesia in Katowice, Silesian Centre for Education and Interdisciplinary Research, Poland*  
The atomic structure of glassy carbon foams
- 15:45 › **Malwina Stepniewska**, *Dept. of Chemistry and Bioscience, Aalborg University*  
Glass formation and mechanical properties of melt-quenched glasses of mixed metal node Zn/Co ZIF62

## TUESDAY 10<sup>th</sup> JULY - PM

16:30 – 18h45 › **PARALLEL SESSIONS 5**

	MAUPERTUIS	LAMENNAIS 1&2	LAMENNAIS 3	LAMENNAIS 4&5	VAUBAN
	STRUCTURE 5	BIOGLASSES 1	PROPERTIES 2	THIN FILMS & GLASS SURFACE 1	MECHANICAL PROPERTIES 1
16:30 – 16:45	C. LE LOSQ	L. HUPA	H. JAIN	J. HU	T. ROUXEL
16:45 – 17:00					
17:00 – 17:15	E. CHESNEAU	S. NANDYALA	P. VAN NIJNATTEN	D. VAN DEMBROUCQ	S. BAKER
17:15 – 17:30	M. HUNAUT	A. TOURE	O. KIBRISLI	M. VLCEK	B. JODAR
17:30 – 17:45	E. BARNEY	D.A.A. SALAZAR	A. CORRIAS	G. HELSCH	B. NAVET
17:45 – 18:00	G. HENDERSON	R. LEBULLENGER	T. WELTER	A. KOVALSKIY	K. JANUCHTA
18:00 – 18:15	G. TRICOT	D. HORKAVCOVA	M. OSTERGAARD	G. CAGNOLI	C. DEREURE
18:15 – 18:30	D. HAMANI	M. POULAIN	T. NISHI		J. MECHOLSKY
18:30 – 18:45			C. EYPERT		G. SCANNELL



**STRUCTURE 5***Session Chair: Sung Keun LEE**Room: MAUPERTUIS*

- 16:30 › **Invited: Charles Le Losq**, *Research School of Earth Sciences, Australia*  
Structure, thermodynamic properties and viscosity of silicate melts:  
development of a model in the Adam and Gibbs theoretical framework
- 17:00 › **Erwan Chesneau**, *NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay*  
Structural study of sodium borate glasses combining molecular dynamics and  
nuclear magnetic resonance
- 17:15 › **Myrtille Hunault**, *Synchrotron SOLEIL*  
Uranium speciation in binary alkali-borate glasses: a multispectroscopic  
study
- 17:30 › **Emma Barney**, *Faculty of Engineering, Advanced Materials Research Group,  
University of Nottingham*  
The structure of bioactive phosphate glasses using diffraction techniques and  
EPSR modelling
- 17:45 › **Grant Henderson**, *Earth Sciences, University of Toronto*  
Stabilization of Silicate Melts through Polymerization Reactions, with  
Implications for the Redox State of the Mantle and Crust
- 18:00 › **Gregory Tricot**, *Laboratoire de Spectrochimie Infrarouge et Raman*  
1D/2D NMR investigation of borophosphate glasses
- 18:15 › **David Hamani**, *Institut de Recherche sur les Céramiques*  
New tellurite glasses within the  $\text{TeO}_2\text{NbO}_{2.5}\text{WO}_3$  system: relevant correlations  
between structural and optical properties

## TUESDAY 10<sup>th</sup> JULY - PM

### BIOGLASSES 1

*Session Chair: Robert HILL*

*Room: LAMENNAIS 1&2*

LAMENNAIS 1&2

- 16:30 › **Invited: Leena Hupa**, *Åbo Akademi University*  
In vitro and in vivo correlations of silicate-based bioactive glasses
- 17:00 › **Sooraj Nandyala**, *School of Metallurgy and Materials, Univ. of Birmingham*  
Development of Lanthanide glass-reinforced Hydroxyapatite composites:  
MG63 Cells behavior and Antimicrobial response
- 17:15 › **Adja Touré**, *Loughborough University*  
Atomic-level clustering in fluorinated phosphate-based glass
- 17:30 › **Dahiana Andrea Avila Salazar**, *Otto Schott Institute of Materials Research,  
Friedrich Schiller University*  
Structure-dissolution relationships in bioactive phosphate glasses
- 17:45 › **Ronan Lebullenger**, *University of Rennes*  
Glassy foam from cullet for biomaterials applications, comparison with 46S6  
glass
- 18:00 › **Diana Horkavcová**, *University of Chemistry and Technology Prague,  
Department of Glass and Ceramics*  
Interaction of glass-ceramic scaffold with simulated body fluid buffered by  
BES
- 18:15 › **Marcel Poulain**, *Le Verre Fluore – Verres et Céramiques – Univ. Rennes 1*  
Fluoride Fiber Lasers Sources for Medical Applications

**PROPERTIES 2***Session Chair: Yuanzheng YUE**Room: LAMENNAIS 3*

LAMENNAIS 3

- 16:30 › **Invited: Himanshu Jain**, *Lehigh University (USA)*  
Electric field-induced softening (EFIS) of alkali silicate glasses
- 17:00 › **Peter van Nijnatten**, *OMT Solutions BV*  
Measuring the difference in refractive index between tin and glass side of float glass
- 17:15 › **Orhan Kibrıslı**, *Yildiz Technical University*  
Temperature Dependent Optical and Electrical Properties of Heavy Metal Oxide Glasses
- 17:30 › **Anna Corrias**, *University of Kent*  
Ceria nanocubes stabilized in Silica Aerogels
- 17:45 › **Thorben Welter**, *Clausthal University of Technology*  
Silicate glass structures with low hydrogen permeability
- 18:00 › **Martin Østergaard**, *Section of Chemistry, Aalborg University*  
Effect of Macrostructure on Thermal Conductivity of Foam Glass
- 18:15 › **Tsuyoshi Nishi**, *Ibaraki University*  
Thermal Conductivities of  $R_2O-SiO_2$  and  $CaO-R_2O-SiO_2$  (R=Li, Na, K) Melts
- 18:30 › **Celine Eypert**, *HORIBA Scientific*  
Glass characterization by Raman microscopy, Glow Discharge Optical Emission Spectrometry and Spectroscopic Ellipsometry

## THIN FILMS & GLASS SURFACE 1

*Session Chair: Emmanuelle GOUILLART*

*Room: LAMENNAIS 4&5*

- 16:30 › **Invited: Juguang Hu**, *Inst. of Thin Film Phys. and Appl., Shenzhen University*  
Controlled crystallization of PLD amorphous CZTS thin film for photovoltaic application
- 17:00 › **Damien Vandembroucq**, *Physique et mécanique des milieux hétérogènes*  
The long memory of glass surfaces
- 17:15 › **Miroslav Vlcek**, *Center of Materials and Nanotechnologies, Faculty of Chemical Technology, University of Pardubice*  
Structuring of chalcogenide glasses thin layers
- 17:30 › **Gundula Hensch**, *Clausthal Univ. of Tech., Inst. of Non-Metallic Materials*  
Quartz inversion temperatures of LAS solid solutions of sol-gel derived glasses
- 17:45 › **Andriy Kovalskiy**, *Austin Peay State Univ., Dept. of Physics and Astronomy*  
Transient photoinduced optical effects in spin-coated chalcogenide glass thin films
- 18:00 › **Gianpietro Cagnoli**, *Laboratoire des Matériaux Avancés, Univ. Claude Bernard Lyon 1*  
Thermal noise in Gravitational Wave mirror coatings: relaxations in SiO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub> films.

**MECHANICAL PROPERTIES 1***Session Chair: Lothar WONDRAKZEK**Room: VAUBAN*

VAUBAN

- 16:30 › **Invited: Tanguy Rouxel**, *Univ. Rennes 1, IPR, Dept. of Glass Mechanics*  
The Fracture Toughness of Inorganic Glasses
- 17:00 › **Shefford Baker**, *Cornell University*  
In-Situ Raman Spectroscopy During Indentation to Study Plastic Deformation in Silicate Glasses
- 17:15 › **Benjamin Jodar**, *Institut de Physique de Rennes*  
Dynamic behavior of ZrCuAl Bulk Metallic Glasses under high pressure and high strain rate induced by laser shock
- 17:30 › **Benjamine Navet**, *AGC*  
Innovative ion implantation technologies for cutting-edge materials: Scratch resistant glass, a first case study
- 17:45 › **Kacper Januchta**, *Dept. of Chemistry and Biosciences, Aalborg University*  
Fracture toughness and indentation cracking resistance in the Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> chemical system
- 18:00 › **Corentin Dereure**, *Institut de Physique de Rennes*  
Combined Experimental and Computational Study of Damage in Silica Glass due to Laser Shock
- 18:15 › **Jack Mecholsky**, *University of Florida*  
Fractal Geometry: A Key to Understanding the Nature of Glass Fracture
- 18:30 › **Garth Scannell**, *Otto Schott Institute of Materials Research*  
Effect of Valence Change on Surface Stresses in EuPO<sub>3</sub> Glasses



**TUESDAY 10<sup>th</sup> JULY - PM**

CHATEAUBRIAND

### PLENARY LECTURE 3

*Session Chair: Daniel NEUVILLE*

*Room: CHATEAUBRIAND*

08:30 › **Edgar Zanotto**, *Center for Research, Technology, and Education in Vitreous Materials, Dept of Mat. Eng., Federal University of São Carlos, Brazil*  
Homogeneous Crystal Nucleation in Deeply Supercooled Glass-forming Liquids – Open Issues

09:15 › **Hajime Tanaka**, *Institute of Industrial Science, University of Tokyo, Japan*  
Impact of structural ordering in supercooled liquids on glassy slow dynamics and glass-forming ability

10:00 › **Kathleen Richardson**, *Center for Research and Education in Optics and Lasers, FL, USA*  
Advances in infrared optics: novel materials towards next-generation components and devices

10:45 - 11:15 › **COFFEE BREAK**

*Salle LE GRAND LARGE*

CHATEAUBRIAND

### PLENARY LECTURE 4

*Session Chair: Daniel NEUVILLE*

*Room: CHATEAUBRIAND*

11:15 › **Daniel Ricoult**, *CORNING*  
Moving to the Glass Age

12:00 › **Neville Greaves**, *Cambridge University, UK*  
Hybrid Glasses and Melts

12:45 - 14:00 › **LUNCH**

*Rotondes Jacques CARTIER & SURCOUF*

14:00 - 18:30 › **FREE AFTERNOON OR EXCURSIONS**

**WEDNESDAY 11<sup>th</sup> JULY**



## TIMETABLE

08:30 – 10h30 › **PARALLEL SESSIONS 6**

**SIMULATION, MODELING 2** – *MAUPERTUIS*

**WASTE GLASSES 2** – *LAMENNAIS 1&2*

**HERITAGE, HISTORY 2** – *LAMENNAIS 3*

**IONIC DIFFUSION & CONDUCTIVITY** – *LAMENNAIS 4&5*

**BIOGLASSES 2** – *VAUBAN*

10:30 - 11:00 › **COFFEE BREAK**

*Salle LE GRAND LARGE*

11:00 – 12h30 › **PARALLEL SESSIONS 7**

**PHASE CHANGE MATERIALS** – *MAUPERTUIS*

**WASTE GLASSES 3** – *LAMENNAIS 1&2*

**THIN FILMS & GLASS SURFACE 2** – *LAMENNAIS 3*

**OPTOELECTRONICS AND OPTICAL PROPERTIES 1** – *LAMENNAIS 4&5*

**BIOGLASSES 3** – *VAUBAN*

12:30 - 14:00 › **LUNCH**

*Rotondes Jacques CARTIER & SURCOUF*

# THURSDAY 12<sup>th</sup> JULY - AM

08:30 – 10h30 › **PARALLEL SESSIONS 6**

	MAUPERTUIS	LAMENNAIS 1&2	LAMENNAIS 3	LAMENNAIS 4&5	VAUBAN
	SIMULATION, MODELING 2	WASTE GLASSES 2	HERITAGE, HISTORY 2	IONIC DIFFUSION & CONDUCTIVITY	BIOGLASSES 2
8:30 – 8:45	P. LUCAS	R. POKORNY	A. VERNEY- CARRON	S. MARTIN	F. FAYON
8:45 – 9:00					
9:00 – 9:15	J. ZWANZIGER	A. KRUGER	G. ROISINE	E. BYCHKOV	A. KRISHNAMURTHY
9:15 – 9:30	D. VAN DEMBROUCQ	O. McGANN	S. CONTE	H. MEHRER	R. WETZEL
9:30 – 9:45	N. WILES	I. HUGON	J. GUO	A. RUIVO	X. CHEN
9:45 – 10:00	Z. ZHANG	M. NEYRET	M. VILARIGUES	L. DEL CAMPO	A. MISHRA
10:00 – 10:15	A. KORSUNSKY	E. SAUVAGE	S. POLLOCK- HILL	T. OHKUBO	D.S. BRAUER
10:15 – 10:30	G. SESE		I. HASDEMIR	J. KIEFFER	

**SIMULATION, MODELING 2***Session Chair: Guillaume FERLAT**Room: MAUPERTUIS*

- 08:30 › **Invited: Pierre Lucas**, *University of Arizona*  
On the utility of topological principles for determining the fragility of network glass-formers
- 09:00 › **Josef Zwanziger**, *Dalhousie University*  
Dispersion of the elasto-optic tensor
- 09:15 › **Damien Vandembroucq**, *Physique et mécanique des milieux hétérogènes*  
Amorphous plasticity from atomic scale to mesoscopic scale
- 09:30 › **Nicole Wiles**, *Cornell University*  
Structural Mechanisms of Plastic Deformation in Hydrostatically Compressed Calcium Aluminosilicates
- 09:45 › **Zhen Zhang**, *Laboratoire Charles Coulomb, Univ. Montpellier*  
Fracture of sodium-silicate glasses: Insights from atomistic computer simulations
- 10:00 › **Alexander Korsunsky**, *University of Oxford*  
XPDF and molecular dynamics analysis of the significance of bond angle change in the deformation of amorphous silica
- 10:15 › **Gemma Sesé**, *Universitat Politècnica de Catalunya*  
Microscopic dynamics and thermodynamics on a dipolar glass former

## WASTE GLASSES 2

*Session Chair: Mike HARRISSON*

*Room: LAMENNAIS 1&2*

- 08:30 › **Invited: Richard Pokorny**, *University of Chemistry and Technology Prague*  
Conversion of waste feed into glass – cold cap formation
- 09:00 › **Albert Kruger**, *US Department of Energy*  
Producing Desired Properties from a Broader Spectrum of Compositions for Nuclear Waste Glass
- 09:15 › **Owen McGann**, *Glass Technology Services Ltd*  
Outcomes from the application of the 'Hazmelt' thermal treatment technology to a range of simulant LLW and ILW wastestreams
- 09:30 › **Isabelle Hugon**, *CEA*  
Glass design for the vitrification of high active deposits coming from the Dismantling and Decommissioning of nuclear plant
- 09:45 › **Muriel Neyret**, *CEA Marcoule*  
Role of Platinum Group Metals on rheological and electrical properties of nuclear glass
- 10:00 › **Invited: Emilien Sauvage**, *CEA, DEN, DE2D, SEVT, LDPV*  
Cold crucible induction melting for nuclear waste vitrification: from numerical simulations to industrial operation

## HERITAGE, HISTORY 2

*Session Chair: Elzbieta GREINER-WRONA*

*Room: LAMENNAIS 3*

LAMENNAIS 3

- 08:30 › **Invited: Aurélie Verney-Carron**, *Laboratoire inter-universitaire des systèmes atmosphériques*  
Alteration mechanisms of medieval stained glass windows in atmospheric medium
- 09:00 › **Gauthier Roisine**, *Institut de Recherche de Chimie Paris*  
Investigating ancient glazing processes: Lead-glazed earthenware of Bernard Palissy (1510-1590)
- 09:15 › **Sonia Conte**, *National Research Council-Institute of Science and Technology of Ceramic Materials*  
Archaeometrical investigation of protohistoric glass from southern Italy: from Early Bronze Age to Advanced Iron Age (18<sup>th</sup>-6<sup>th</sup> century BC).
- 09:30 › **Jianyong Guo**, *Shandong University of Art and Design*  
A new style of inside painting glass sculptures
- 09:45 › **Márcia Vilarigues**, *Research Unit VICARTE – Glass and Ceramics for the Arts, Faculty of Science and Technology, NOVA University of Lisbon*  
Historical Reproduction of Grisailles: A preliminary study
- 10:00 › **Stephen PollockHill**,  
Gentilshommes verriers, mythe ou légende ?
- 10:15 › **Ilhan Hasdemir**,  
Micromechanical properties of altered surfaces or archaeological glass fragments

## IONIC DIFFUSION AND CONDUCTIVITY

*Session Chair: Annie PRADEL*

*Room: LAMENNAIS 4&5*

LAMENNAIS 4&5

- 08:30 › **Invited: Steve Martin**, *Dept. Materials Science & Engineering, Iowa State University of Science and Technology*  
New Fast Ion Conducting Glasses: Towards Enabling High Energy Density and Safe All Solid State Batteries
- 09:00 › **Eugene Bychkov**, *University of Littoral*  
Ionic conduction pathways in chalcogenide glasses: experimental evidence and modelling
- 09:15 › **Helmut Mehrer**, *University of Muenster*  
Diffusion and Ionic Conduction in Glasses
- 09:30 › **Andreia Ruivo**, *Research Unit VICARTE – Glass and Ceramics for the Arts, Faculty of Science and Technology, NOVA University of Lisbon (VICARTE)*  
Development of down converting stable and efficient materials: Silver diffusion in glass
- 09:45 › **Leire del Campo**, *CEMHTI*  
Ionic conductivity of binary alkali borate melts
- 10:00 › **Takahiro Ohkubo**, *Chiba University*  
Li conduction in Li<sub>2</sub>SP<sub>2</sub>S<sub>5</sub> glasses: insights from dynamics and polarizability
- 10:15 › **John Kieffer**, *University of Michigan, Ann Arbor*  
Structure, Ionic Mobility, and Mechanical Stiffness in Mixed-Network Former Glasses

**DURABILITY, DISSOLUTION & CORROSION**

*Session Chair: Jean-Pierre GUIN*

*Room: VAUBAN*

VAUBAN

- 08:30 › **Invited: Franck Fayon**, *CEMHTI*  
Solid-state NMR study of bioglasses
- 09:00 › **Arun Krishnamurthy**, *Department of Chemistry, University of Manitoba*  
Structure and Dissolution Behaviour of Multifunctional Borophosphate  
Bioactive Glasses
- 09:15 › **Roland Wetzel**, *Otto Schott Institute of Materials Research*  
Effect of substitution amount of magnesium and zinc on dissolution behaviour  
and thermal properties of Bioglass 45S5
- 09:30 › **Xiaoqing Chen**, *Xiangya Stomatological Hospital & School of Stomatology,  
Central South University, Dental Physical Sciences, Institute of Dentistry,  
Queen Mary University of London*  
Influence of Strontium Substitution for Calcium on the Apatite Formation  
Ability of Chloride-Containing Bioactive Glasses
- 09:45 › **Ayush Mishra**, *BioMediTech Institute and Biomedical Sciences and  
Engineering faculty*  
Albumin and fibronectin attachment on silicate and phosphate bioactive  
glasses
- 10:00 › **Invited: Delia S. Brauer**, *Otto Schott Institute of Materials Research, Friedrich  
Schiller University Jena*  
Bioactive Glasses: Controlling Dissolution & Ion Release via Modifier Ionic  
Radius

# THURSDAY 12<sup>th</sup> JULY - AM

11:00 – 12h30 › **PARALLEL SESSIONS 7**

	MAUPERTUIS	LAMENNAIS 1&2	LAMENNAIS 3	LAMENNAIS 4&5	VAUBAN
	PHASE CHANGE MATERIALS	WASTE GLASSES 3	THIN FILMS & GLASS SURFACE 2	OPTOELECTRONICS AND OPTICAL PROPERTIES 1	BIOGLASSES 3
11:00 – 11:15	M. WUTTIG	I. MULLER	E. GOUILLART	P. BINGHAM	R. HILL
11:15 – 11:30					
11:30 – 11:45	K. KONSTANTINOOU	P. HRMA	L. MONTAGNE	P. VAN NIJNATTEN	J. CHRISTIE
11:45 – 12:00	S. KOZYUKHIN	E. REGNIER	C. RODRIGUEZ-TINOCO	T. VOLOTINEN	A.T. CONTRERAS JAIMES
12:00 – 12:15	J-B. DORY	L. GALOISY	V. KOLOSOV	G. CALAS	J. MASSERA
12:15 – 12:30	G. WANG	O. BOUTY	S. PONTON	Y. SGIBNEV	A. SANTIC



**PHASE CHANGE MATERIALS**

*Session Chair: Stephen ELLIOTT*

*Room: MAUPERTUIS*

MAUPERTUIS

- 11:00 › **Invited: Matthias Wuttig**, *I. Physikalisches Institut der RWTH, Lehrstuhl für Physik neuer Materialien*  
Phase Change Materials by Design: Taming Bond No. 6
- 11:30 › **Konstantinos Konstantinou**, *Dept. of Chemistry, University of Cambridge*  
Ab initio modelling of radiation damage in amorphous phase-change memory materials: The case of  $\text{Ge}_2\text{Sb}_2\text{Te}_5$
- 11:45 › **Sergey Kozyukhin**, *Inst. General and Inorg. Chem., RAS, Tomsk State Univ.*  
Laser-Induced Modification and Formation of Periodic Surface Structures (“Ripples”) of Amorphous GST225 Phase Change Materials
- 12:00 › **Jean-Baptiste Dory**, *Université Grenoble Alpes, CEALETI*  
Ge-Sb-S-Se-Te amorphous chalcogenide thin films for nonlinear optics in the Mid-Infrared
- 12:15 › **Guoxiang Wang**, *Laboratory of Infrared Material and Devices, The Research Institute of Advanced Technologies, Ningbo University, Leibniz Institute of Surface Modification (IOM)*  
Controllable crystallization and interface microstructure stability of new phase-change films

**WASTE GLASSES 3**

*Session Chair: Albert KRUGER*

*Room: LAMENNAIS 1&2*

LAMENNAIS 1&2

- 11:00 › **Invited: Isabelle S. Muller**, *Vitreous State Lab., Catholic University of America*  
Alteration Phases on Hanford LAW Glasses after Long-Term Leaching
- 11:30 › **Pavel Hrna**, *Pacific Northwest National Laboratory*  
Boundary layer approach to heat transfer rate to cold cap
- 11:45 › **Elise Regnier**, *CEA-Marcoule*  
Crystal growth in temperature gradients
- 12:00 › **Laurence Galois**, *IMPIC*  
Evidence of two layers alteration gel in nuclear glasses containing Zr
- 12:15 › **Olivier Bouty**, *Commissariat à l'Energie Atomique - Site de Marcoule*  
New insights on the structure of borosilicate glasses containing zirconium by combining Wide Angle X-ray Scattering and atomistic simulations

**THIN FILMS & GLASS SURFACE 2***Session Chair: Juguang HU**Room: LAMENNAIS 3*

- 11:00 › **Invited: Emmanuelle Guillard**, *Unité mixte CNRS/SaintGobain (SVI)*  
Multicomponent diffusion in industrial glasses and thin films
- 11:30 › **Lionel Montagne**, *Unité de Catalyse et de Chimie du Solide*  
Investigations of phosphate and silicate glasses and glass-ceramics deposited as nanometric thin films
- 11:45 › **Cristian Rodríguez-Tinoco**, *Institute of Physics, University of Silesia*  
Emergence of a substrate-temperature-dependent dielectric process in a prototypical vapor deposited hole-transport glass
- 12:00 › **Vladimir Kolosov**, *Ural Federal University*  
Novel Transrotational Solid State Order Discovered by TEM in Crystallizing Amorphous Films and New Model of Amorphous State Based on Nanocrystals with Curved Lattice
- 12:15 › **Simon Ponton**, *Centre Inter-universitaire de Recherche et d'Ingénierie des Matériaux*  
Computational and Experimental Investigation of the Atmospheric Pressure Chemical Vapor Deposition of SiO<sub>2</sub> films from TEOS and O<sub>2</sub> and Determination of their Microstructural Characteristics and their Corrosion Resistance in Aggressive Aqueous Media.

**OPTOELECTRONICS AND OPTICAL PROPERTIES 1**

*Session Chair: Long ZHANG*

*Room: LAMENNAIS 4&5*

LAMENNAIS 4&5

11:00 › **Invited: Paul Bingham**, *Sheffield Hallam University*  
Redox in glasses: interactions with radiation

11:30 › **Peter van Nijnatten**, *OMT Solutions BV*  
Measurement of internal transmittance and refractive index of optical glasses at cryogenic temperatures

11:45 › **Tarja Volotinen**, *Uppsala University*  
Absorption spectrum analysis of Fe-Ce- and Fe-Cu-doped soda-lime-silica glasses melted with a refiner

12:00 › **Georges Calas**, *IMPMC*  
Coloration of alkali borate glasses by transition d and f elements: a review

12:15 › **Yevgeniy Sgibnev**, *ITMO University*  
Spectral-luminescent properties of silver ion-exchanged aluminosilicate glass doped with Eu<sup>3+</sup> ions

### BIOGLASSES 3

*Session Chair: Delia BRAUER*

*Room: VAUBAN*

VAUBAN

- 11:00 › **Invited: Robert Hill**, *Queen Mary University of London*  
Structure Property Relationships in OxyHalide Bioactive Glasses
- 11:30 › **Jamieson Christie**, *Loughborough University*  
Structure-bioactivity relationships of phosphate-based glass from computer modelling
- 11:45 › **Altair T. Contreras Jaimes**, *Otto Schott Institute of Materials Research, Friedrich Schiller University*  
Applications of bioactive glasses for glass ionomer cements
- 12:00 › **Jonathan Massera**, *BioMediTech Institute and Biomedical Sciences and Engineering faculty*  
Amorphous Borosilicate Bioactive Glass Scaffolds Processing and In-Vitro Dissolution
- 12:15 › **Ana Šantić**, *Ruđer Bošković Institute*  
Setting process of glass ionomer cements studied by dielectric spectroscopy

**THURSDAY 12<sup>th</sup> JULY - AM**

## TIMETABLE

14:00 – 16h30 › **PARALLEL SESSIONS 8**

**CHALCOGENIDE GLASSES** – MAUPERTUIS  
**MECHANICAL PROPERTIES 2** – LAMENNAIS 1&2  
**LASER INTERACTION** – LAMENNAIS 3  
**GLASS-CERAMICS 2** – LAMENNAIS 4&5

16:30 – 18h00 › **POSTER SESSION & COFFEE BREAK**  
*BOUVET & CHARCOT Rooms*

19:30 - 00:00 › **BANQUET**  
*Salle LE GRAND LARGE*

# THURSDAY 12<sup>th</sup> JULY - PM

14:00 – 16h30 › **PARALLEL SESSIONS 8**

	MAUPERTUIS	LAMENNAIS 1&2	LAMENNAIS 3	LAMENNAIS 4&5
	CHALCOGENIDE GLASSES	MECHANICAL PROPERTIES 2	LASER INTERACTION	GLASS-CERAMICS 2
14:00 – 14:15	L. ZHANG	C. ROUNTREE	B. POUHELLEC	K. THIEME
14:15 – 14:30		T. TO		P. GLATZ
14:30 – 14:45	A. PIARRISTEGUY	Z. ROUSE	Y. BELLOUARD	C. PATZIG
14:45 – 15:00	A. ZEIDLER	C. FUSCO		A. ZANDONA
15:00 – 15:15	R. ZAITER	P. KIEFER	S. FEDOTOV	O. DYMSHITS
15:15 – 15:30	M. CHAZOT	J. MORICEAU	T. GUERINEAU	A.C. RIMBACH
15:30 – 15:45	S. HOSOKAWA	N. WILES	J. TIAN	R. AL-MUKADAM
15:45 – 16:00	A. NOVIKOVA	I. GUVEN	E. VERDIER	J. ROCHERULLE
16:00 – 16:15	M. DUSSAUZE	T. LACONDEMINE	M. POULAIN	M.R. CICCONI
16:15 – 16:30	K. RAMESH		L. KOUNDE	M. MONTAZERIAN



**CHALCOGENIDE GLASSES***Session Chair: Jean-Luc ADAM**Room: MAUPERTUIS*

MAUPERTUIS

- 14:00 › **Invited: Long Zhang**, *Shanghai Institute of Optical and Fine Mechanics, Chinese Academy of Science*  
Recent development of materials for IR applications
- 14:30 › **Andrea Piarristeguy**, *Institut Charles Gerhardt Montpellier*  
Local vibrational and mechanical characterization of Ag conducting chalcogenide glasses
- 14:45 › **Anita Zeidler**, *University of Bath*  
Structure of Ge-Se glasses
- 15:00 › **Rayan Zaiter**, *Laboratoire de Physico-Chimie de l'Atmosphère*  
Transport and structural properties of silver bromide doped chalcogenide glasses
- 15:15 › **Matthieu Chazot**, *Université de Bordeaux*  
Fiber drawing region investigation and structural characterization of Ge-S-I chalcogenide glasses
- 15:30 › **Shinya Hosokawa**, *Kumamoto University*  
Local- and intermediate-range structures of room-temperature superionic Ag-GeSe<sub>3</sub> glasses
- 15:45 › **Anna Novikova**, *Verres et céramiques, Diafir*  
Infrared optics of chalcogenide glasses made by mechanical alloying and sintering
- 16:00 › **Marc Dussauze**, *Institut des Sciences Moléculaires*  
Structure of Telluride Glasses: a Theoretical and Spectroscopic Investigation
- 16:15 › **Karuppannan Ramesh**, *Department of Physics, Indian Institute of Science*  
Local structure and glass formation in Al<sub>20</sub>Te<sub>80</sub> glass

## MECHANICAL PROPERTIES 2

*Session Chair: Tanguy ROUXEL*

*Room: LAMENNAIS 1&2*

LAMENNAIS 1&2

- 14:00 › **Cindy Rountree**, *Service de physique de l'état condensé*  
SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O Glasses: Understanding how microscale changes alter macroscale fracture properties
- 14:15 › **Theany To**, *Glass & Mechanics Dept., Inst. of Physics, Univ. Rennes 1*  
The Single-Edge Pre-cracked Beam (SEPB) method to assess the fracture toughness, the fracture energy and the stress corrosion cracking of glass
- 14:30 › **Zachary Rouse**, *Cornell University, Dept. of Mater. Science and Engineering*  
Effect of humidity and included OH during indentation of silica glass
- 14:45 › **Claudio Fusco**, *Matériaux, ingénierie et sciences de Villeurbanne*  
On the role of amorphous overlays on the mechanical properties of Ni nanoparticles under compression
- 15:00 › **Philippe Kiefer**, *Clausthal University of Technology*  
Statistical analysis of subcritical crack growth in water bearing soda-lime silicate glasses
- 15:15 › **Julien Moriceau**, *Dept. of Glass Mechanics, IPR, University of Rennes 1*  
Synthesis by SPS of new glass matrix composite with functional properties - toward self-healing glass
- 15:30 › **Nicole Wiles**, *Cornell University*  
Ex-situ Raman Investigation of Indentations in Vitreous Silica
- 15:45 › **Ibrahim Guven**, *Virginia Commonwealth University*  
Erosion of Glass Substrates due to Microparticles
- 16:00 › **Tanguy Lacondémine**, *Univ. of Rennes 1, IPR, Dept of Glass Mechanics*  
In-situ observation of the formation of indentation cracks in glass by means of synchrotron X-ray tomography

## LASER INTERACTION

*Session Chair: Thierry CARDINAL*

*Room: LAMENNAIS 3*

LAMENNAIS 3

- 14:00 › **Invited: Bertrand Pommellec**, *Inst. de Chimie Moléculaire et des Matériaux d'Orsay*  
Femtosecond laser induced structural transformations in transparent oxide glasses
- 14:30 › **Invited: Yves Bellouard**, *Ecole Polytechnique Fédérale de Lausanne*  
Femtosecond laser three-dimensional exposure of silica substrate in the non-ablative regime : from laser-induced modifications to applications
- 14:45 › **Sergey Fedotov**, *D. Mendeleev Univ. of Chemical Technology of Russia*  
Femtosecond laser-written nanogratings in alkali silicate glasses
- 15:00 › **Théo Guerineau**, *Institut de Chimie de la Matière Condensée de Bordeaux*  
The impact of the silver-containing phosphate glass composition on femtosecond laser induced optical properties
- 15:30 › **Jing Tian**, *Institut de Chimie Moléculaire et des Matériaux d'Orsay*  
Polarization dependence of femtosecond laser induced circular birefringence in silica glass
- 15:45 › **Emma Verdier**, *ALPhANOV*  
3D Glass Decoration by Nonlinear Absorption of Ultrafast Lasers
- 16:00 › **Marcel Poulain**, *Verres et Céramiques, Univ. Rennes 1, Le Verre Fluore*  
Low loss fluoride optical fibers: properties and application
- 16:15 › **Ludovic Kounde**, *Inst. de Recherche et des Procédés d'Application du Laser*  
Glass and silicon welding by femtosecond laser: set up improvement through modeling

## GLASS-CERAMICS 2

*Session Chair: Joachim DEUBENER*

*Room: LAMENNAIS 4&5*

LAMENNAIS 4&5

- 14:00 › **Katrin Thieme**, *Otto Schott Institute of Materials Research, Jena University*  
On the search for appropriate nucleating agents in BaO-SrO-ZnO-SiO<sub>2</sub> glasses
- 14:15 › **Pauline Glatz**, *Corning European Technology Center, UCCS, IMPMC*  
Role of phosphorous in the nucleation of alkali aluminosilicate glass-ceramics
- 14:30 › **Christian Patzig**, *Fraunhofer Inst. for Microstructure of Materials and Systems*  
Nucleation and Crystallization in LAS Glass Ceramics: Recent Advances in Understanding Fundamentals Based on Nanostructure Diagnostics
- 14:45 › **Alessio Zandona**, *Inst. Non-Metallic Materials, Clausthal Univ. of Technology*  
Crystallization and ordering process in stoichiometric cordierite glass-ceramics with TiO<sub>2</sub> as nucleating agent
- 15:00 › **Olga Dymshits**, *Research and Technological Institute of Optical Materials Science Vavilov State Optical Institute*  
Structural transformations and optical properties of glass-ceramics based on ZnO, β- and α- Zn<sub>2</sub>SiO<sub>4</sub> nanocrystals and doped with Er<sub>2</sub>O<sub>3</sub> and Yb<sub>2</sub>O<sub>3</sub>
- 15:15 › **A. Charlotte Rimbach**, *Faculty of Electrical Engineering, South Westphalia University of Applied Sciences*  
Controlled crystallization in luminescent lithium borate glass for LED applications
- 15:30 › **Raschid Al- Mukadam**, *Institute of Non-Metallic Materials; Clausthal University of Technology*  
Nucleation kinetics of lithium disilicate glasses undercooled at various speeds
- 15:45 › **Jean Rocherullé**, *University of Rennes*  
Crystallization pathways and some properties of lithium disilicate oxynitride glasses
- 16:00 › **Maria Rita Cicconi**, *Friedrich-Alexander Universität*  
Nucleation and crystallization of lithium silicate glass-ceramics: understanding of crack initiation
- 16:15 › **Maziar Montazerian**, *Dept of Materials Engineering (DEMa), CeRTEV, Federal University of São Carlos (UFSCar), São Carlos*  
Past, present, and future of bioactive glass-ceramics

## TIMETABLE

08:30 – 10h30 › **PARALLEL SESSIONS 9**

**FIBERS 1** – MAUPERTUIS

**STRUCTURE 6** – LAMENNAIS 1&2

**OPTOELECTRONICS AND OPTICAL PROPERTIES 2** – LAMENNAIS 3

**TELLURITE** – LAMENNAIS 4&5

**THERMODYNAMICS** – VAUBAN

**USTV Ph-D AWARD** – MAUPERTUIS

10:30 - 11:00 › **COFFEE BREAK**

*Salle LE GRAND LARGE*

11:00 – 12h15 › **PARALLEL SESSIONS 10**

**FIBERS 2** – MAUPERTUIS

**STRUCTURE 7** – LAMENNAIS 1&2

**FURNACE AND ELABORATION 3** – LAMENNAIS 3

**PROPERTIES 3** – LAMENNAIS 4&5

12:15 - 12:30 › **CLOSING CEREMONY**

*MAUPERTUIS*

# FRIDAY 13<sup>th</sup> JULY

08:30 – 10h30 › **PARALLEL SESSIONS 9**

	MAUPERTUIS	LAMENNAIS 1&2	LAMENNAIS 3	LAMENNAIS 4&5	VAUBAN
	FIBERS 1	STRUCTURE 6	OPTOELECTRONICS AND OPTICAL PROPERTIES 2	TELLURITE	THERMODYNAMICS
8:30 – 8:45	USTV Ph-D AWARD	J. DREWITT	H. FNEICH	P. THOMAS	O. GEDEON
8:45 – 9:00			A. VEBER		S. CONTE
9:00 – 9:15	T. CARDINAL	M. FICHEUX	L. PETIT	A. KHANNA	A. TAKADA
9:15 – 9:30		J. SCHNEIDER	L. BOROICA	T. KUBIENA	M.A. RAMOS
9:30 – 9:45	L. LUO	J. CHOI	J. ZHANG	N. GEDIKOGLU	A. SAITTER
9:45 – 10:00	V. SHIRYAEV	J. MARCIAL	J. WANG	E. KAMITSOS	E. CHETCHETKINA
10:00 – 10:15	S. DANTO	M. MAHFOUDHI	H. LI	M. WILDING	S. LINNENKUGEL
10:15 – 10:30	P. FROIDEVAUX	B. MOULTON	M. VERMILLAC	J. DE CLERMONT	J. PETROVIC

## USTV Ph-D AWARD

*Session Chair: Daniel NEUVILLE, President of USTV and ESG*  
*Room: MAUPERTUIS*

- 08:30 › **Alexandre Barnini**,  
 Fabrication and characterization of new ytterbium-doped silica glasses compositions using a plasma method (SPCVD) for laser fiber applications



## FIBERS 1

*Session Chair: Bertrand POUMELLEC*  
*Room: MAUPERTUIS*

- 09:00 › **Invited: Thierry Cardinal**, ICMCB  
 Design of oxide glass composition for laser structuring and fiber manufacturing
- 09:30 › **Lida Luo**, Donghua University  
 Preparation and characterization of high strength glass fiber from fly ash
- 09:45 › **Vladimir Shiryaev**, *Inst. of Chemistry of High-Purity Substances of the Russian Academy of Sciences*  
 Recent advances in development of high-purity chalcogenide glasses for mid-IR fiber optics
- 10:00 › **Sylvain Danto**, *Institut de Chimie de la Matière Condensée de Bordeaux*  
 Intermediate-Tg glasses for multi-materials fibers
- 10:15 › **Paul Froidevaux**, *Laboratoire Interdisciplinaire Carnot de Bourgogne*  
 Two octave mid-IR supercontinuum generation using tellurite step-index fibers

## STRUCTURE 6

*Session Chair: Bernard HEHLEN*

*Room: LAMENNAIS 1&2*

- 08:30 › **Invited: James Drewitt**, *University of Bristol*  
Structure of aluminate liquids and glasses under extreme conditions
- 09:00 › **Maxime Fichoux**, *IMPMC, Surface du Verre et Interfaces*  
Structure and phase separation investigation of Zr containing Na<sub>2</sub>O-CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> glass
- 09:15 › **José Schneider**, *Instituto de Física de São Carlos, Universidade de São Paulo*  
Ca and Sr Bonding in Mixed Phosphate Glasses
- 09:30 › **JoonSung Choi**, *Yonsei University*  
Role of basicity and Al<sub>2</sub>O<sub>3</sub> on the NBO/T in calcium aluminosilicate melts
- 09:45 › **Jose Marcial**, *Washington State University*  
Glass structure – crystallization relationships through EPSR modelling of synchrotron X-ray total scattering data of Na, Li, Fe, and B, substituted aluminosilicate glasses
- 10:00 › **Mohamed Mahfoudhi**, *Laboratoire des Solides Irradiés*  
Europium environment modification by Electron irradiation in metaphosphate and polyphosphate glasses: impact of electron energy
- 10:15 › **Benjamin Moulton**, *Univesidade Federal de Sao Carlos*  
Time-resolved structural evolution of supercooled barium disilicate liquid during in-situ crystallization



**OPTOELECTRONICS AND OPTICAL PROPERTIES 2***Session Chair: Marc DUSSAUZE**Room: LAMENNAIS 3*

LAMENNAIS 3

- 08:30 › **Hussein Fneich**, *Institut Charles Gerhardt Montpellier*  
Size and temperature effect on the photoluminescent properties of Europium-doped silica nanoparticles
- 08:45 › **Alexander Veber**, *Friedrich-Alexander Universität*  
Devitrification behavior of sol-gel derived ZrO<sub>2</sub>-SiO<sub>2</sub> rare-earth doped glass: correlation between structural and optical properties
- 09:00 › **Laeticia Petit**, *Tampere University of Technology*  
Up-converter phosphate glasses prepared using direct doping method
- 09:15 › **Lucica Boroica**, *Nat. Inst. for Laser, Plasma and Radiation Physics, Magurele*  
Cobalt oxide doped zinc-boron-phosphate glasses, preparation and properties
- 09:30 › **Jihong Zhang**, *State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology*  
Mutual Effect of Quantum Dots and Rare Earth Ions in glass Matrix
- 09:45 › **Jing Wang**, *Wuhan University of Technology*  
Photoluminescence from PbSe and Sr<sup>2+</sup>-doped PbSe quantum dots embedded in silicate glass
- 10:00 › **Hong Li**, *State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology*  
Preparation and application of phosphor-in-glass for Fabricating white LEDS
- 10:15 › **Manuel Vermillac**, *Institut de Physique de Nice*  
Elongation, break-up, dissolution and growth of nanoparticles during the fiber drawing of silica-based optical preforms

## TELLURITE

*Session Chair: Alex HANNON*

*Room: LAMENNAIS 4&5*

- 08:30 › **Invited: Philippe Thomas**, *Institut de Recherche sur les Céramiques*  
Elaboration, structure, nonlinear optical and lasing properties of tellurite based glasses and glass-ceramics
- 09:00 › **Atul Khanna**, *Guru Nanak Dev University*  
Structural studies of tellurite glass, antiglass and crystalline phases
- 09:15 › **Teo Kubiena**, *University of Nottingham*  
Developing Structure-Property Relationships in Optical Glasses to Optimize Functional Designs
- 09:30 › **Nuşik Gedikoğlu**, *Yildiz Technical University*  
Comparison of TeO<sub>2</sub> and Sb<sub>2</sub>O<sub>3</sub> as Heavy Metal Oxide Glass Formers
- 09:45 › **E. I. Kamitsos**, *Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation*  
Thermal, mechanical and structural properties of tellurite glasses
- 10:00 › **Martin Wilding**, *University College London*  
The formation of liquids, glasses and the anti-glass phase in the system Bi<sub>2</sub>O<sub>3</sub>-Nb<sub>2</sub>O<sub>5</sub>-TeO<sub>2</sub>
- 10:15 › **Jonathan de Clermont Gallerande**, *IRCER*  
Structural, mechanical and optical properties of glasses within the TeO<sub>2</sub>-TiO<sub>2</sub>-ZnO ternary system

**THERMODYNAMICS***Session Chair: Roberto MORETTI**Room: VAUBAN*

VAUBAN

- 08:30 › **Invited: Ondrej Gedeon**, *University of Chemistry and Technology*  
Origin of empirical Vogel temperature emerging from Molecular dynamics simulations
- 08:45 › **Sonia Conte**, *Nat. Res. Council – Inst. Sci. and Tech. of Ceramic Materials*  
High temperature viscosity of the vitreous phase into porcelain stoneware bodies
- 09:00 › **Akira Takada**, *Asahi Glass Company*  
New theoretical model for partition function and configurational entropy in non-equilibrium states
- 09:15 › **Miguel Angel Ramos**, *Laboratorio de Bajas Temperaturas, Departamento de Física de la Materia Condensada, Universidad Autónoma de Madrid*  
Low-temperature glassy anomalies in highly stable glasses
- 09:30 › **Allisson Saiter**, *Groupe de Physique des Matériaux*  
Segmental mobility at the glass transition in glass forming liquids: Comparison of two approaches
- 09:45 › **Elena Chechetkina**, *Inst. of General and Inorganic Chemistry of Russian Academy of Sciences*  
Is the glass-forming melt in equilibrium state?
- 10:00 › **Sebastian Linnenkugel**, *School of Engineering and Advanced Technology*  
Prediction of the glass transition temperature of sugar rich mixtures
- 10:15 › **Jelena Petrovic**, *Otto Schott Institute of Materials Research*  
Glass transition and fragility of polyionic glasses

# FRIDAY 13<sup>th</sup> JULY

11:00 – 12h15 › **PARALLEL SESSIONS 10**

	MAUPERTUIS	LAMENNAIS 1&2	LAMENNAIS 3	LAMENNAIS 4&5
	FIBERS 2	STRUCTURE 7	FURNACE AND ELABORATION 3	PROPERTIES 3
11:00 – 11:15	A. CASSEZ	O. ALDERMAN	Y. DOI	A. MITCHELL
11:15 – 11:30	G. DONG	L. HENNET	F. PIGEONNEAU	M. DUSSAUZE
11:30 – 11:45	L. YANG	L. KOUDELKA	M. EISENGA	A. LIPOVSKII
11:45 – 12:00	Q. WANG	E. DE CLERMONT	E. MUIJSENBERG	B. BOUTEILLE
12:00 – 12:15	C. STRUTYNSKI	K. BODIANG	W. BATTAGLIA	M. MIKA

**FIBERS 2***Session Chair: Bertrand POUMELLE**Room: MAUPERTUIS*

- 11:00 › **Andy Cassez**, *Univ. Lille, PhLAM Physique des Lasers Atomes et Molécules*  
All vapor phase ytterbium doped silica glass fabrication by outside vapor deposition combined to chelate flash vaporization
- 11:15 › **Guoping Dong**, *South China University of Technology*  
Nanocrystal-Doped Glass Ceramic Fibers: Novel Near/Mid-Infrared fiber laser materials
- 11:30 › **Luyun Yang**, *Wuhan National Laboratory for Optoelectronics-Huazhong University of Science and Technology*  
Porous silica glasses for rare earth ions heavily doped extralarge core fiber
- 11:45 › **Qingwei Wang**, *Donghua University*  
Effect of redox state of iron on properties of basalt fiber
- 12:00 › **Clément Strutynski**, *ICMCB*  
Development of highlydoped rare-earth phosphate glasses for NIR and SWIR fiber Laser sources

## STRUCTURE 7

*Session Chair: Georges CALAS*

*Room: LAMENNAIS 1&2*

- 11:00 › **Oliver Alderman**, *Materials Development, Inc., Argonne National Laboratory*  
Amorphous Ta<sub>2</sub>O<sub>5</sub> and its Relationship with the Liquid State
- 11:15 › **Louis Henet**, *CEMHTI*  
Structure and properties of strontium aluminosilicate melts
- 11:30 › **Ladislav Koudelka**, *University of Pardubice*  
Structure and properties of barium borophosphate glasses modified with molybdenum oxide
- 11:45 › **Emmanuelle de Clermont Gallerande**, *IMPMC*  
Oxygen environment in lithium borates and silicates: an experimental and theoretical study
- 12:00 › **Kadiali Bodiang**, *Unité de Catalyse et de Chimie du Solide*  
<sup>95</sup>Mo Solid State NMR: Structural study of molybdophosphate glasses

**FURNACE AND ELABORATION 3***Session Chair: Tetsuji YANO**Room: LAMENNAIS 3*

LAMENNAIS 3

- 11:00 › **Yoji Doi**, *Dept of Material Science and Engineering, Tokyo Institute of Technology, Production Technology Division, Asahi Glass Co., Ltd.*  
Viscosity of sodalime silicate glass raw materials during batch-to-melt conversion
- 11:15 › **Franck Pigeonneau**, *MINES ParisTech CEMEF*  
Thermoconvective instabilities of a non-uniform Joule-heated liquid enclosed in a rectangular cavity
- 11:30 › **Menno Eisenga**, *Glass Service B.V.*  
Advantages of ES III full automatic control of glass feeders
- 11:45 › **Erik Muijsenberg**, *Glass Service*  
Improve Glass Quality and Furnace Efficiency with advanced Simulation models
- 12:00 › **Walter Battaglia**, *Stazione Sperimentale del Vetro*  
Sulphur balance and Carryover measurements methodologies

# FRIDAY 13<sup>th</sup> JULY

## PROPERTIES 3

*Session Chair: Efstratios KAMITSOS*

*Room: LAMENNAIS 4&5*

LAMENNAIS 4&5

- 11:00 › **Alexandra Mitchell**, *Corning Research and Development Corporation*  
The Effect of Alkaline Earths on Fictive Temperature Dependent Glass Properties
- 11:15 › **Marc Dussauze**, *Institut des Sciences Moléculaires*  
Optical and chemical functionalities controlled at the micrometer scale in glassy materials by an imprinting thermo-electrical process.
- 11:30 › **Andrey Lipovskii**, *St. Petersburg Academic University, Peter the Great St. Petersburg Polytechnic University*  
Poled glasses: relaxation and surface relief formation
- 11:45 › **Barbara Bouteille**, *Physique et mécanique des milieux hétérogènes, Surface du Verre et Interfaces*  
Kinetics of phase separation in barium borosilicate glass thin films deposited by magnetron sputtering
- 12:00 › **Martin Mika**, *University of Chemistry and Technology Prague*  
Magneto-optic glass for fast infrared modulators







## LIST OF POSTERS

1	Study of Non-Crystalline Structure of Polymer Solid by Utilizing Motion of Impurity Ion <b><u>Yuichi Anada</u></b>
2	Surface and Volume Crystallization in a SrO-CaO-B <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub> glass <b><u>Aluisio Cabral</u></b> , Lais Silva, Alisson Rodrigues, Ana Rodrigues, Alicia Durán, Maria Pascual
3	Compositional effects on the rheology of glass particle suspensions <b><u>Rodrigo Cardoso dos Passos</u></b> , Hansjörg Bornhöft, Joachim Deubener
4	Voltammetry and oxygen activity in SnO <sub>2</sub> -doped alkali free aluminoborosilicate melts <b><u>Geunho Choi</u></b> , Kicheol Kim, Kidong Kim
5	Raman spectroscopy and structure of selected Ga <sub>2</sub> O <sub>3</sub> -CaO-P <sub>2</sub> O <sub>5</sub> glasses <b><u>Maria Chromcikova</u></b> , Jana Holubova, Jan Machacek, Zdenek Cernosek, Marek Liska
6	Tellurium oxide based glasses: establishing of nonlinear optical properties from ab-initio calculations Olivier Noguera, Eugene Roginskii, Mikhaïl Smirnov, <b><u>Maggy Colas</u></b> , Olivier Masson, Philippe Thomas
7	Structural characterization of thin film chalcogenide glasses used in ovonic threshold switches <b><u>Francesco D'Acapito</u></b> , Jean Raty, Antonin Verdy, Gabriele Navarro, Françoise Hippert, J Gaudin, M Bernard, Pierre Noé
8	Ag <sup>+</sup> and H <sup>+</sup> emission from sharp-edged glasses under non-vacuum atmosphere <b><u>Yusuke Daiko</u></b> , Kyohei Segawa, Sawao Honda, Yuji Iwamoto
9	Lithium Aluminosilicate Glass-Ceramics Nucleated by Rare-Earth Orthoniobates and Orthotantalates <b><u>Olga Dymshits</u></b> , Alexander Zhilin, Michail Shepilov, Svetlana Zapalova, Anastasia Bachina, Irina Alekseeva, Alexander Khubetsov, Pavel Loiko, Marina Tsenter, Anna Volokitina, Xavier Mateos, Alena Vilejshikova
10	The Effect of Nb-doping on thermochromic behavior of VO <sub>2</sub> -based thin films for energy-efficient windows Eren Doğan, Miray Celikbilek Ersundu, <b><u>Ali Ercin Ersundu</u></b>
11	Investigation of Tellurite Glasses for Radiation Applications Volkan Akilli, Orhan Kibrıslı, Miray Çelikbilek Ersundu, <b><u>Ali Ercin Ersundu</u></b>
12	Comparison on Chemical Tempering Behavior of Commercial Aluminosilicate and Soda Lime Silicate Glasses Ahmet Caner Kayaalp, Berkel Kayacan, Nahide Özben, İlkay Sökmen, Ali Ercin Ersundu, <b><u>Miray Celikbilek Ersundu</u></b>
13	The Effect of Glass Thickness on Chemical Tempering Efficiency Berkel Kayacan, Ahmet Caner Kayaalp, Nahide Özben, İlkay Sökmen, Ali Ercin Ersundu, <b><u>Miray Celikbilek Ersundu</u></b>
14	Surface morphology of AgGeSe thin films deposited by PLD <b><u>Juan Manuel Conde Garrido</u></b> , Joel Bobadilla, Josefina María Silveyra

15	Dissolution dynamics of AgGeSe chalcogenide glasses in basic aqueous solutions <i>Orietha Cuellar Rodrigues, A Romero, María Andrea Ureña, Josefina María Silveyra, <b>Juan Manuel Conde Garrido</b></i>
16	Electrical characterization of thin film chalcogenide glasses for gas sensors <i>Ana Escobar, Orietha Cuellar Rodrigues, María Andrea Ureña, Josefina María Silveyra, <b>Juan Manuel Conde Garrido</b></i>
17	Macroscopic and structural effects of electron irradiation on model glasses <i><b>Tadeas Gavenda</b>, Ondrej Gedeon, Karel Jurek</i>
18	New application for geopolymer materials: integration as matrix in Antennas <i><b>Ameni Gharzouni</b>, Houda Nadir, Edson Martinod, Noel Feix, Valérie Bertrand, Olivier Tantot, Michèle Lalande, Sylvie Rossignol</i>
19	Up-Conversion emission in Er-Yb doped transparent oxyfluoride nano-glass-ceramics <i><b>Giulio Gorni</b>, Rolindes Balda, Joaquín Fernández, J.J. Velazquez, Laura Pascual, Alicia Durán, María Jesús Pascual</i>
20	Thin film crystallization of Y and Er doped sol-gel derived hafnia <i><b>Inga Katharina Götz</b>, Gundula Hensch, Joachim Deubener</i>
21	How to determine the cooling rate of a blast furnace slag? <i><b>Daniel Hart</b>, Natalja Pronina, Hansjörg Bornhöft, Joachim Deubener</i>
22	Kinetics Study of Non isothermal crystallization in SeX chalcogenide glasses <i><b>Lamia Heireche</b>, Mohamed Heireche</i>
23	The influence of titanium on the structure and some properties of calcium and sodium zinc-phosphate glasses <i><b>Jana Holubova</b>, Zdeněk Černošek, Petr Hejda, Eva Černošková</i>
24	The effect of thermal annealing on structure relaxation and optical properties of Yb <sup>3+</sup> doped Al <sub>2</sub> O <sub>3</sub> -P <sub>2</sub> O <sub>5</sub> -SiO <sub>2</sub> glass <i><b>Lili Hu</b>, Chongyun Shao, Mengting Guo</i>
25	Scratch groove and ionic packing ratio of oxide glasses <i><b>Seiji Inaba</b>, Haruo Aizawa, Akio Koike</i>
26	Formation of Hierarchical Nanoporous Layer on glass of various compositions <i><b>Takumi Ito</b>, Erika Tabata, Keita Yasumoro, Takuya Fujima</i>
27	Characterization of deformation and cracking behavior of high Poisson's ratio oxide glasses with La <sub>2</sub> O <sub>3</sub> <i><b>Kacper Januchta</b>, Ruofu Sun, Liping Huang, Morten Smedskjaer</i>
28	Structure and properties of barium tungstate-phosphate glasses <i><b>Petr Kalenda</b>, Ladislav Koudelka, Petr Mošner, Lionel Montagne, Bertrand Revel</i>
29	Redox interaction between Fe and secondary multivalent elements in soda lime silicate glass melts <i><b>Sohee Kang</b>, Kicheol Kim, Kidong Kim</i>
30	Development of REE-doped chalcogenide fibers for active mid-IR optics <i><b>Ella Karaksina</b>, <b>Vladimir Shiryaev</b>, Tatyana Kotereva, Aleksander Velmuzhov, Maksim Sukhanov</i>

31	Mercury thiogermanate HgS-GeS <sub>2</sub> glasses: macroscopic, electric, and structural properties <b><u>Mohammad Kassem</u></b> , Rayan Zaiter, Eugène Bychkov
32	Immobilization of heavy metal oxides by sintering of mixture of LCD waste glass and MSW incinerator fly ash <b><u>Kicheol Kim</u></b> , Kidong Kim
33	Temperature and illumination dependent mass transport during the surface relief formation in As-S(Se) amorphous chalcogenides Sandor Molnar, Roland Bohdan, Viktor Takacs, Istvan Csarnovics, Yuri Kaganovsky, <b><u>Sandor Kokenyesi</u></b>
34	Features of the silver nanoparticles formation in the bulk and on the surface of the fluoride phosphate glasses. <b><u>Elena Kolobkova</u></b> , Nikolay Nikonorov
35	Research Tools and Methodology for Waste Vitrification Process Development <b><u>Virginie Labe</u></b> , Patrice Brun, Milène Delaunay, Jean-François Hollebecque, Alain Ledoux, Stéphane Lemonnier, Caroline Michel, Emilien Sauvage, Sophie Schuller, Armand Bonnetier
36	Role of Poisson's ratio mismatch on the crack path in glass matrix particulate composites <b><u>Tanguy Lacondémine</u></b> , Clément Roux-Langlois, Tanguy Rouxel
37	Reversible EPR signature of Self-Trapped Holes in fictive temperature-treated irradiated silica <b><u>Mathieu Lancry</u></b> , Nadège Ollier, Babu Hari Babu, Bertrand Pommellec
38	Fictive temperature approach: a valuable tool for silica glass photonics <b><u>Mathieu Lancry</u></b> , Nadège Ollier, Manon Heili, Bertrand Pommellec
39	Plasma-chemical etching of 2D-poled glasses Sergey Alexandrov, <b><u>Andrey Lipovskii</u></b> , Artem Osipov, Dmitry Tagantsev
40	Simulation of bubbles dynamics in beer tumblers Emilie Debout, Fabien Beaumont, <b><u>Ludovic Marquant</u></b> , Jean-Luc Harion, Guillaume Polidori, Yvan Garnier
41	Faraday rotator based on dysprosium ions-doped aluminophosphate glass <b><u>Elisa Mihail</u></b> , R. Stefan, B. A. Bava, B. A. Bava, L. Boroica, M. Valeanu, V. Kuncser, A. C. Galca, A. Beldiceanu
42	Understanding Nineteenth Century Glass Deterioration Through Artificial Accelerated Aging <b><u>Elizabeth Montagnino</u></b> , Isabelle Muller, Andrew Buechele, Stephanie Zaleski, Nikolaus Deems
43	Investigation of boson peak of densified silica glass by terahertz time-domain spectroscopy <b><u>Tatsuya Mori</u></b> , Koki Nakano, Yasuhiro Fujii, Suguru Kitani, Shinji Kohara, Norimasa Nishiyama, Atsunobu Masuno, Akitoshi Koreeda, Hitoshi Kawaji, Seiji Kojima
44	A catalogue of cation coordination polyhedra in glasses and disordered solids <b><u>Gavin Mountjoy</u></b> , Maha Rai
45	Probing the degree of polymerization in iron-bearing calcium silicate glasses: A view from high-resolution solid-state Nuclear Magnetic Resonance <b><u>Kwan Young Mun</u></b> , Hyo-Im Kim, Sung Keun Lee
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# AWARDS

# Fabrication and characterization of new ytterbium-doped silica glasses compositions using a plasma method (SPCVD) for laser fiber applications

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Ytterbium-doped silica optical fibers are widely used for high power laser applications for several years. These powers keep on increasing due to continuous improvements in optical fibers fabrication processes. The aim of this PhD is to synthesize ytterbium-doped silica optical fibers' cores using a plasma process named SPCVD. This method has been created in 1986 for telecommunications optical fibers synthesis, and we have adapted it to fit the fabrication of rare earth-doped large-mode-area optical fiber cores. We first present the development of ways of evaporating low vapor pressure reagents. All the synthesized optical fiber cores are silica-rich, and slightly doped with both aluminum, fluorine and ytterbium. Radial and longitudinal homogeneities are discussed, and we propose several options in order to improve them. Then, the glassy network structure of the fabricated cores and also the neighborhood and dispersal of Yb<sup>3+</sup> ion in the silicate network are studied. Thus, we used several spectroscopic studies: nuclear magnetic resonance enables to focus on non-zero nuclear spin nucleus (<sup>29</sup>Si, <sup>27</sup>Al, <sup>19</sup>F) whereas electronic paramagnetic resonance is used to probe the neighborhood and the dispersal of Yb<sup>3+</sup> ions. We also based our study on optical characterizations as absorption and luminescence of Yb<sup>3+</sup> ions. Finally, the fibers' cores we synthesized using the SPCVD process have been characterized in a laser cavity. We present the power conversion efficiency, the beam quality and the resistance to photodarkening of several ytterbium and fluorine-co-doped aluminosilicate cores.

**Keywords:** Fiber

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\*Speaker

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# Improving the damage resistance of oxide glasses from knowledge of their structural response to densification

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Increasing the hardness and crack resistance of oxide glasses is critical for the development of damage resistant and mechanically durable glasses for advanced applications. These properties can conventionally be measured using instrumented indentation (such as Vickers) that mimics the real-life damage for certain applications. Early indentation experiments have shown that oxide glasses exhibit pronounced tendency to densify under compressive load, in addition to elastic deformation and shear flow. The deformation mechanism affects the build-up of residual stress, and thus the driving force for cracking. Here, we discuss how knowledge of the deformation mechanism and the accompanying pressure/stress-induced structural transformations in the glassy network can be used to design crack resistant glasses. Our results show that high crack resistance can be associated with the ability of the glasses to self-adapt the connectivity of their network under compressive stress, which facilitates densification and thus aids in dissipation of the energy supplied during impact. We have used this knowledge in the design of highly crack resistant aluminoborate glasses. In addition to lowering the driving force for cracking, the glass' resistance to cracking should also be considered, which is likely related to the bond constraint density. High-temperature densification can be used to increase the latter, but typically results in less densification during indentation and thus an increased driving force for cracking. However, by carefully tailoring the glass structure, we show that it is possible to use high-temperature densification to improve hardness and crack resistance simultaneously by avoiding the pressure-induced decrease in densification contribution to deformation. Finally, we also show that the effect of pre-densification on hardness, crack resistance, and ion exchange strengthening characteristics depends on the utilized densification route (thermal vs. pressure). Overall the results suggest that understanding the structural response of oxide glasses to compression can be helpful for improving their damage resistance.

**Keywords:** Densification

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# PLENARY

# Transparent oxyfluoride nano-glass ceramics: Processing is the key

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Transparent oxyfluoride glass-ceramics (OxFGCs) have attracted great interest in the field of photonics since the pioneering work of Wang and Ohwaki. Alumina-silicate glass matrices are particularly suitable for their excellent mechanical, thermal and chemical properties compared to phosphate or fluoride glasses. On the other hand, fluoride crystals, especially those containing Ln<sup>3+</sup> ions, are especially good hosts for their low phonon energy and offer high solubility of Rare-Earth (RE) ions. The classical processing route to obtain transparent OxGFCs consists on a controlled crystallization of the precursor glass obtained by melt-quenching (MQ). Bulk materials and fibers have been obtained by this method although this processing route faces the problem of the high melting temperatures that cause a fluorine loss, limiting the final crystal content to less than 10 wt%.

On the other hand, the sol-gel process is a suitable alternative to prepare OxGFCs materials due to the low synthesis and sintering temperatures involved, thus allowing the preparation of novel compositions, especially as thin films, with higher crystal content up to 30 wt%.

In this work we will show the results, obtained in the last ten years, for bulk, optical fibers and thin films produced by MQ, sol-gel and fiberizing. In particular, the relationship between processing, structure and improved optical properties will be discussed focusing on the superior optical properties of these materials as compared to the precursor glasses.

**Keywords:** glass, ceramics, processing, sol, gel, optical properties, oxyfluorides

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\*Speaker

# Hybrid Glasses and Melts

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Hybrid Glasses have recently been discovered, derived from the newly emerging and versatile Metal Organic Framework Materials or MOFs. Several ways of producing Hybrid Glasses have been developed, so far, starting with low density Zeolitic Imidazolate Frameworks or ZIFs: melt-quenching, amorphization, ball-milling, and low temperature solution chemistry. These diverse methods raise issues currently fundamental to glass science: conventional melting, low temperature or decelerated melting, pressure-induced amorphization, polyamorphism and liquid-liquid phase transitions, perfect glasses, rheometry at supercooled temperatures, and glass forming ability (GFA) etc. There is also the question of porosity, as glasses incorporating a solvent moderator by can exhibit accessible internal areas comparable to crystalline ZIFs, whereas, for melt-quenched glasses, internal voids occupy far less capacity and are unconnected, and are similar to the distribution of Free Volume in oxide glasses. Structurally Hybrid Glasses, and the melts they can be derived from, align with the familiar Continuous Random Network, but with tetrahedral metals, like zinc and cobalt, replacing silicon or germanium for example, and organic linkers such as imidazolate groups, substituting for bridging oxygens. In contrast to conventional CRN glasses, though, metal nodes in Hybrid Glasses are floppy while linkers are stiff. Moreover, different combinations of linker strongly affect the viscosity at the melting point  $T_m$ , so that by increasing the linker rigidity the viscosity at  $T_m$  can be substantially increased, significantly reducing the supercooled range. As a result, GFA can be raised, and for selected Hybrid Glasses is currently superior to that for any other melt-quenched glass. Throughout this presentation the physical, structural and dynamic properties of Hybrid Glasses, and the liquids they are condensed from, will be emphasised, and future developments will be considered in this exciting new branch of glass science.

**Keywords:** hybrid glasses, glass forming ability, polyamorphism, porosity

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\*Speaker

# Control of metastable state of glass

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Glass is a special material featuring good homogeneity, variable composition, easy shaping and doping, owing to its meta-stable state and topological network structure. It is considered that the nature of glass and glass transition are among the most important problems in the field of condensed matter. However, no dramatic change of the glass properties can be realized by controlling fictive temperature of glass. We focus our research on the change and enhancement of the properties of glass by manipulation of the metastable nature of glasses. This strategy allows for precise control of the microstructure of glasses by using external fields e.g. light, temperature and pressure, and the development of novel and enhanced functionalities by controlling electronic band structure, defect state and nano- or microstructure of glass. In this talk, I will highlight our recent research developments on the design and control of the optical properties of glass through fast-cooling, crystallization and phase separation. We have demonstrated the realization of ultra-broadband near-infrared emission via control of valence state of Bi ion, ligand field around transition metal ions and energy transfer between two active ions for broadband optical amplification and tunable laser. I will also introduce our recent results on the printing of three-dimensional nano- or microstructures and multiple functions inside glasses by fs laser based on multiphoton absorption assisted control of excited state of dopants and nanostructures. These studies are not only helpful for understanding the nature of glass, but also valuable for the fabrication of optical devices.

**Keywords:** glass, metastable state, crystallization, laser

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\*Speaker

# Advances in infrared optics: novel materials towards next-generation components and devices

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Novel optical materials capable of advanced functionality across the infrared will enable optical designs that can offer light-weight or small footprint solutions in both planar and bulk optical systems. UCF's *Glass Processing and Characterization Laboratory (GPCL)* and our collaborators have been evaluating compositional design and processing strategies for both bulk and film solutions employing multi-component chalcogenide glasses (ChGs). These materials can be processed with broad compositional flexibility that allows tailoring of their transmission window, physical and optical properties, allowing them to be engineered for compatibility with other homogeneous amorphous or crystalline optical components or in the case of planar photonic applications, underlying substrates. Specific examples of this strategy demonstrated for solution-derived ChG layers for gradient refractive index (GRIN) and extended to applications as phase change materials (PCMs), poled ChGs with gradient compositional and surface reactivity behavior, nanocomposite bulk ChGs and glass ceramics, and metalens structures realized through direct laser manufacturing (DLM) of ChGs are discussed. Limitations and opportunities of these strategies within these applications, are reviewed.

**Keywords:** chalcogenide glasses, GRIN, glass ceramics, planar photonics

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# Moving to the Glass Age

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Based on the unique combination of transparency and formability, glass objects have been fabricated since prehistoric times. Over the centuries, glass has become a material of choice for distinctive architectural applications or selective containment of goods. All along the 20th century, a number of technological breakthroughs have propelled glass to being a common feature in everyone's daily environment. In the past 50 years more inventions and more fundamental understanding of the ultimate capabilities of that material have enabled further proliferation of unexpected applications, which are opening a new era, the Glass Age! Examples of such capabilities and applications will be mentioned in the presentation.

**Keywords:** Glass, future, applications

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\*Speaker

# Impact of structural ordering in supercooled liquids on glassy slow dynamics and glass-forming ability

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Dynamics of a liquid drastically slows down when approaching the glass transition. Despite a long history of research, its physical origin has remained elusive. We show evidence of intrinsic structure-dynamics correlation in glass-forming liquids [1-3]. We find that there exist two intrinsic characteristic lengths, the particle size and structural correlation length, which control dynamics in local and nonlocal manners, respectively, resulting in the emergence of the two key relaxation modes, fast beta and slow alpha processes [3]. The presence of such intrinsic structure-dynamics correlation strongly indicates a thermodynamic nature of glass transition. We also discuss the impact of structural ordering on crystal nucleation, or glass-forming ability [1,4-7]. The similarity between structural order formed in a supercooled liquid and the crystal structure is the key control factor of the ease of crystal nucleation: A liquid having stronger frustration against crystallization is more difficult to crystallize, or the better glass-former.

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**Keywords:** structural ordering, supercooled liquids, slow dynamics, glass, forming ability

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# Homogeneous Crystal Nucleation in Deeply Supercooled Glass-forming Liquids – Open Issues

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We summarize the classical nucleation theory (CNT) and discuss selected experimental tests and MD simulations that were performed since the fifties with metallic, polymer and inorganic glass-formers. Some oxide system show internal (homogeneous) nucleation rates in laboratory scales even without the addition of nucleating agents. We demonstrate that their nucleation rates show a rather remarkable pattern: i) the maximum values always occur at a temperature  $T^* \sim T_{g12}$  ( $T_{g12}$  = glass transition temperature). And, ii) for these substances, the structural order of the network modifier cations of the parent liquids is very similar to that of their isochemical crystal phases!

The CNT describes quite well the experimental nucleation rates with a fitted (2-parameter) temperature dependent surface energy,  $s(T)$ , for  $T > T^*$ , but there is always a substantial discrepancy for  $T < T^*$ . We investigate some reasonable possibilities to explain this break at  $T^*$ , for instance: can the diffusion coefficient that controls nucleation be replaced by the viscosity via the Stokes-Einstein equation; what is the effect of internal stresses in the nucleation rates at deep undercoolings? What is the role of dynamic heterogeneities that exist in the liquid? We also dwell on other unusual problems, such as the possibility to measure or estimate the average time for formation of the first crystalline nucleus.

We conclude by showing that, despite some yet unexplained phenomena and other shortcomings, the CNT has been successfully used for different purposes. For instance, to distinguish glasses that nucleate homogeneously from those which only show heterogeneous nucleation, to predict nucleation rates and induction times, to explain why some glasses, such as albite and B<sub>2</sub>O<sub>3</sub>, "never" crystallize, and for the development of novel or improved glass-ceramics with higher fracture strength and toughness or optical transparency.

**Keywords:** nucleation, crystal, surface energy, viscosity, crystallization, glass, ceramic

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# Understanding the atomistic origin of the ultra-rapid crystallization and radiation hardness of the phase-change non-volatile memory material, Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>, via *ab initio* molecular-dynamics simulations

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Non-volatile electronic computer memory has been provided up to now by Si CMOS floating-gate (FG) MOSFET ‘flash’ technology. However, its Moore’s Law technology roadmap, driven by feature down-sizing, is shortly to come to an end due to the tunnelling of electrons, trapped on the FG, through ever-thinner layers of dielectric, resulting in memory volatility. Thus, there is a pressing need for a new technology to replace Si CMOS flash memory. One such potential non-volatile memory technology is ‘phase-change random-access memory’ (PCRAM), based on materials such as Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> (GST), in which binary digital data are stored as a structural state of the material, viz. an electrically-resistive (semiconducting) amorphous/ glassy state and a conducting (‘metallic’) crystalline state. Reversible and ultra-rapid (~ ns) transitions between these two phases can be induced by the application of appropriate voltage pulses which cause Joule heating of the material. In this paper, we will describe recent density-functional-theory-based *ab initio* molecular-dynamics (AIMD) simulations carried out on phase transitions in GST in which the atomistic origin of the ultra-rapid crystallization is clarified via a careful analysis of changes in the local atomic coordination characterized in terms of the actual chemical bonding. In addition, we have performed the first AIMD simulations of ion implantation in GST, which reveal the origin of the resilience of this memory material to radiation.

**Keywords:** *ab initio* molecular dynamics, phase, change memory, Ge, Sb, Te, radiation hardness, crystallization

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\*Speaker

# Crystallization and phase separation in chalcogenide glasses

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Chalcogenide glasses are the counterparts of oxide glasses where the oxygen ion is replaced by a chalcogen (S<sup>2-</sup>, Se<sup>2-</sup>, Te<sup>2-</sup>). Because of the presence of chalcogen, more polarizable than oxygen, and the presence of a more active pair of free electrons, the chalcogenide glasses have very different properties than their oxide counterparts and therefore, found applications in specific domains, e.g optical components for the development of night vision devices or IR waveguides for environmental metrology, phase change materials for electric memory development or even, electrolytes for all-solid-state battery and ionic memory development,.

In many applications, total or partial crystallization of the material plays an important role. Indispensable in electrical and optical memories in which amorphous and crystalline phases are 0 and 1 bits of the operative part, the crystallization becomes an element of optimization in the case of optical components to improve the mechanical resistance of the material, or in the case of solid electrolytes to produce an electrochemically stable material and to improve the ion conductivity. On the other hand, the presence of phase separation allows the ultra-fast switching of ionic memories based upon Ag<sup>+</sup>-conductive chalcogenide films.

In all cases, investigation to identify a crystalline phase with optimal properties needs to be carried out first with outcomes like evidence of new unreported or metastable phases. Their stabilization in a glassy matrix is then another challenge. Recent work coupling the sensitivity of neutron thermodiffraction with the versatility of spark plasma sintering procedures helped in stabilizing a unique, either stable or metastable, phase in a glassy matrix and in producing glass-ceramics with improved thermoelectric properties in the system Cu-As-Te.

Similarly, investigation of phase separation and evaluation of derived morphology is required to control the glass properties and therefore, design optimized compositions for applications. Recent work in Ag-Ge-Se system coupling synthesis conditions and structural experiments such as small angle neutron-ray scattering and Raman will be used as an illustration.

**Keywords:** Chalcogenide, Glass, Crystallization, Phase separation

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\*Speaker

# BIOGLASSES 1

# Structure-dissolution relationships in bioactive phosphate glasses

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Degradation of phosphate glasses in aqueous environments is interesting for biomedical applications. However, in order to be able to design materials with tailored solubility, it is imperative to obtain meaningful dissolution kinetics data to better predict in vivo performance. In the present work, structural characterization via P-31 MAS NMR and thermal analysis was correlated with both static and dynamic dissolution profiles of the system  $45\text{P}_2\text{O}_5-x\text{CaO}-(55-x)\text{M}_2\text{O}$  (mol%;  $x$ : 25 to 40) with  $M = \text{Li, Na or K}$ , where the  $\text{CaO}:\text{Na}_2\text{O}$  ratio was varied while the phosphate content was maintained constant. Dissolution kinetics in Tris buffer (pH 7.4) were addressed through time-dependent P-31 solution NMR, pH and ICP-OES measurements. According to MAS NMR, all glasses were composed of pyrophosphate Q1 and metaphosphate Q2 species with chains from 8 to 9 phosphate groups in length. The glasses with the general composition  $45\text{P}_2\text{O}_5-x\text{CaO}-(1-x)\text{Na}_2\text{O}$  showed an increase in the P-31 shielding with increasing CaO content. This substitution also produced a systematic increase in the  $T_g$  and  $T_c$ . Such relationships were expected owing to the higher field strength of calcium compared to sodium. Dissolution experiments showed congruent dissolution with the rate of degradation decreasing with increasing CaO content and field strength of the alkali cation ( $\text{Li}^+ > \text{Na}^+ > \text{K}^+$ ). The relative dissolution ratio among the series of glasses was maintained in both static and dynamic conditions. However, the latter provided a better picture of pH changes at early times, showing the average result of two competing reactions, thus ion exchange and hydrolysis of polyphosphates, being the CaO content proportional to relative more acidic pH values. This was consistent with P-31 solution NMR findings, which showed that the presence of CaO, trapped in complexes, led to hydrolytic degradation of long-chain phosphates into orthophosphate and trimetaphosphate.

**Keywords:** phosphate glasses, kinetics, dynamic dissolution, static dissolution, P31 MAS NMR, P31 NMR, pH, ICP OES, field strength, ion exchange, hydrolysis

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# Interaction of glass-ceramic scaffold with simulated body fluid buffered by BES

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Simulated body fluid (SBF) buffered by TRIS is the standard solution (ISO23317) for the evaluation of apatite-forming ability of biomaterials used in *in vitro* test. TRIS buffer speeds up the glass-ceramic dissolution and thus gives the false positive results of an experiment. This work is concerned on the interaction of glass-ceramic scaffolds (Bioglass® derived) with SBF buffered by BES (the other buffer from the Good's buffers family). The *in vitro* test was arranged as "static-dynamic" with daily changed (refreshed) SBF solutions. The pH and Si, Ca and P concentration changes in the SBF leachant were analysed by AAS and UV-VIS. Material was characterized by SEM/EDS, XRD, XRF and BET before and after *in vitro* test. We found that scaffold dissolution was less significant in SBF+BES than in SBF+TRIS (due to Ca ions releasing) and consequently the hydroxyapatite (HAp) growth rate was slower in SBF+BES. Based on these results we can conclude, that the BES affects the glass-ceramic scaffold dissolution less compared with TRIS buffer.

**Keywords:** glass ceramic scaffold, SBF, in vitro test, hydroxyapatite, buffer BES

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\*Speaker

# In vitro and in vivo correlations of silicate –based bioactive glasses

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Over the years, the understanding of the interactions of bioactive glass with biological processes has steadily increased. From the glass technology point of view, the capability of the bioactive glasses to stimulate and support tissue regeneration depends on their poor chemical durability. Fundamentally, the release of inorganic ions from the bioactive glass is decisive for its tissue regenerative capability. Traditionally, the ability of a particular glass composition to form a hydroxyapatite surface layer in a solution mimicking the human extracellular fluids is used to prove its bioactivity. The hydroxyapatite layer provides a chemical bonding between the glass and the biological apatite in bone tissue. Today we know that the ions dissolving from the glass have an essential function: when released at controlled concentrations, they stimulate the cellular processes and thus enhance the tissue regeneration. Accordingly, increasing research efforts are paid to tailor glasses, which release inorganic ions known to enhance not only bone but also soft tissue regeneration. In vivo studies are used to demonstrate for example the bonding of the bioactive glass to tissue, the thickness of the reaction layers formed at the glass surface, or the quality of the new tissue after various implantation times. In contrast, the observations from long-term clinical follow-up studies of implanted bioactive glasses are rare. In this presentation, the in vitro ion dissolution kinetics and the hydroxyapatite layer formation are correlated with the in vivo layer formation at several bioactive glasses. The goal is to enhance the understanding of the in vitro dissolution kinetics on the in vivo bioactivity of the glass. Finally, the in vitro, in vivo and clinical results of one composition, the bioactive glass S53P4, are discussed.

**Keywords:** bioactive glass, dissolution kinetics, in vitro, in vivo

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\*Speaker

# Glassy foam from cullet for biomaterials applications, comparison with 46S6 glass

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Materials for bone substitution applications currently include bioactive glasses that are capable of bonding to bone tissue. 46S6 bioglass is a reference material that is able to develop a biologically active hydroxy-carbonate apatite (HCA) layer on their surface when soaked in body fluid. Cellular glasses are commonly studied to copy the porous structure of natural bones. The aim of this work is to study the feasibility to build a 3D macroporous glassy materials using a common silicate soda-lime cullet glass (~75SiO<sub>2</sub>-15Na<sub>2</sub>O-10CaO wt%) doped with different content of P<sub>2</sub>O<sub>5</sub> and to evaluate its biocompatibility with the 46S6 "standard" bioglass (46 SiO<sub>2</sub> - 24 Na<sub>2</sub>O - 24 CaO- 6P<sub>2</sub>O<sub>5</sub> wt%).

The foamy glasses are produced by using crushed clear cullet and calcium carbonate as foaming agent and by a thermal treatment of the mixture around 850°C. The route explored to incorporate P<sub>2</sub>O<sub>5</sub> in the final cellular material is achieved by the use of NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (MAP) or (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> (DAP) as dopant precursors during the scaffold synthesis. The ratio Ca:P for the P<sub>2</sub>O<sub>5</sub> doped cullet based samples can be tuned from 5 to 1. Prepared foam materials and 46S6 samples were crushed and sieved under 40 micrometres particles for toxicity study. Human osteoblast cells Saos-2 and human endothelial cells EAhy926 were used for viability assays with two incubation duration 24 and 72h. Encouraging first results concerning cullet based powders for viability assays will be complemented with synthetic body fluid (SBF) study for HCA growth verification on the foam bulk samples.

**Keywords:** foam glass, cullet, biomaterials, cytotoxicity

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\*Speaker



# Development of Lanthanide glass-reinforced Hydroxyapatite composites: MG63 Cells behaviour and Antimicrobial response

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Human skeletal bone loss and infections are major health concerns in the XXI century, with significant socio-economic implications. It is estimated, that each year around 700,000 deaths worldwide result from antimicrobial resistance. Unless action is taken, this is projected to rise to 10 million deaths each year by 2050, with the added impact of a cumulative \$100 trillion of economic output at risk due to the rise of drug-resistant infections [1]. Hence, it is necessary to develop alternative antibacterial agents for healthcare. Lanthanide ions (Ln<sup>3+</sup>), also known as Rare-Earths [2] are a group of elements from lanthanum to lutetium (Z=57 to 71) and including scandium (Z=21) and Yttrium (Z=39). Lanthanides have been previously shown to display an effective antibacterial activity, and to further modulate bone metabolism, broadly due to their affinity to calcium interaction sites [3]. Inclusion of Ln<sup>3+</sup> ion containing glasses into hydroxyapatite (HA) is expected to influence the biological response of composites by modulating the cell behaviour and simultaneously displaying an effective antibacterial activity. Previously, the authors developed work on lanthanide materials for luminescence, anti-infective and bone regenerative applications [4]. In the present work, Lanthanide-doped boro-silicate host glasses have been developed which were incorporated in the HA matrix. The developed composites were characterized *in vitro*, using human osteoblastic cell populations - for cytocompatibility assays, and *S. aureus* – the most relevant bacteria for bone tissue infection, for antibacterial efficacy evaluation. The results obtained suggested that lanthanide glass-reinforced HA composites presented enhanced osteoblastic cell response and antibacterial activity, as comparing with control samples - the two key features contributing to an improved biological outcome following bone graft implantation. **Acknowledgement:** The authors (SHN and AS) would like to thank the European Union’s Horizon 2020 research and Innovation programme under the Marie Skłodowska-Curie in grant agreement No. 753636. **References:** [1] [http://www.jpiaamr.eu/wp-content/uploads/2014/12/AMR-Review-Paper-Tackling-a-crisis-for-the-health-and-wealth-of-nations\\_1-2.pdf](http://www.jpiaamr.eu/wp-content/uploads/2014/12/AMR-Review-Paper-Tackling-a-crisis-for-the-health-and-wealth-of-nations_1-2.pdf). [2] Handbook on the ‘Physics and Chemistry of Rare Earths’, eds. K. A. Gschneidner, Jr & L. Eyring, Elsevier, USA, vol. 25,1998.[3] S.P. Fricker, Chem. Soc. Rev., 2006; 35(6)524. [4] N.S.Hussain, et.al, Adv. Mater. Lett., 2016; 7(9)702; & J. Mater. Chem. B, 2014; 2(35)5872.

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**Keywords:** Lanthanide glass, MG63 cells, Antimicrobial

# Fluoride Fiber Lasers Sources for Medical Applications

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Fiber lasers are increasingly used in various fields: industrial, environment, biomedical, defense... Their main advantages over classical lasers are their power, their efficiency and reliability. Until now they are based on silica fibers, and they are operating in limited spectral range, mostly in the near infrared.

While laser emission is usually confined in a narrow bandwidth, supercontinuum sources are now available to operate in a broad spectral range, typically between 400 and 2400 nm.

Fluoride glass fibers are opening new prospects with the development of fiber lasers at 2.9  $\mu\text{m}$  with output power in excess of 30 W in CW operation [1]. Experimental lasers have been reported at 2.3  $\mu\text{m}$  and 3.55  $\mu\text{m}$ . Fiber lasers emitting beyond 4  $\mu\text{m}$  are now considered.

Mid-IR supercontinuum sources based on fluoride fibers are now available. Their emission extends to 4 to 5  $\mu\text{m}$ , typically from 0.8 up to 4.8  $\mu\text{m}$ , with more than 1 W average output power.

YAG:Er laser at 2.94  $\mu\text{m}$  is used in dentistry and laser surgery. Optical fibers make easier beam handling. This is the case for ZBLAN fibers that withstand 1.6 J pulses at 2.94  $\mu\text{m}$ . This wavelength corresponds to the maximum absorption coefficient of water, which makes it an excellent laser for surgical cutting. In these conditions, laser ablation does not induce heating of underlying tissues. It is expected that fiber laser will replace YAG:Er in various cases. In addition to compactness and reliability, its unique beam quality ensures higher precision and lower required power, as shown by preliminary experiments.

Medical diagnosis may be achieved by absorption/reflection spectroscopy. Limits arise from the intensity of the illuminating source. By comparison to standard components, infrared supercontinuum sources are brighter by several orders of magnitude. This could lead to a breakthrough diagnostic technology that replicates measurements made with synchrotron beam. A first field of application relates to skin cancer. In vivo experiments could be investigated using optical fiber probes.

V. Fortin, M. Bernier, S. T. Bah, et R. Vallée, *Opt. Lett.*, 40, 2882 (2015).

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\*Speaker

**Keywords:** Laser Surgery, Diagnosis, Mid IR lasers

# Atomic-level clustering in fluorinated phosphate-based glass

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Phosphate-based glasses (PBG) have wide application as biomaterials because they dissolve when implanted into the body, with a composition-dependent dissolution rate that varies over several orders of magnitude. They can be synthesised containing different substances or materials, making them useful for controlled delivery of therapeutically relevant substances. In order to optimise PBGs for these applications, it is vital to understand the dependence of their dissolution rate on the glass composition and structure.

Over the past few years, computer simulation, typically molecular dynamics (MD) simulations, has pioneered our understanding of phosphate glass structure [1], particularly identifying the structural motifs which affect the glass dissolution rate when implanted [2]. Much work has been concentrated on the effects of cation inclusion, but, in this talk, we will discuss recent results on the inclusion of fluorine into PBG for, e.g., dental applications.

In fluorinated *silicate* glasses, local-scale atomic clustering leads to structural inhomogeneity within the glass [3], and there is evidence for [4] and against [5] this in fluorinated phosphate glasses. By developing an accurate polarizable potential which represents the interatomic forces in fluorinated PBG, we propose the existence of significant structural inhomogeneities, which are likely to reduce its bioactivity.

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**Keywords:** phosphate glass, bioactivity, fluorine, dissolution, molecular dynamics

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\*Speaker

# **BIOGLASSES 2**

# Bioactive Glasses: Controlling Dissolution & Ion Release via Modifier Ionic Radius

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The most famous glasses used as implant materials are undoubtedly bioactive (phospho-) silicate glasses. Invented by Larry Hench in the late 1960's, they have been in continuous clinical use for over 30 years now. These bioactive glasses undergo surface reactions and degradation when implanted, resulting in formation of a mineralised surface layer of biomimetic apatite. This surface layer allows for formation of a strong interfacial bond between glass and both hard and soft body tissue. In addition, as the amorphous structure of glass is less dependent on a specific stoichiometry than crystals are, it allows for the incorporation of a wide range of ions of potentially therapeutic benefits. These ions can be released during the bioactive glass degradation process to perform their therapeutic action. If glass is to be used as a biomaterial to regenerate tissue, it therefore needs to react with aqueous solutions, release ions and degrade over time. The "network connectivity" or polymerisation of the silicate network has usually been described as the key structural parameter to control bioactive glass degradation, ion release and bioactivity. Here it is shown that the types of modifiers used, and particularly their ionic radii, can have a pronounced effect on the degradation behaviour, too. This effect is particularly pronounced when using different alkali metal cations (lithium, sodium or potassium) where an increase in ionic radius of the modifier ion results in faster ion release and vice versa. Interestingly, this effect appears in mixed alkali bioactive glass compositions as well, rather than the expected mixed alkali effect.

**Keywords:** Bioactive Glass, Degradation, Structure

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\*Speaker

# Influence of Strontium Substitution for Calcium on the Apatite Formation Ability of Chloride-Containing Bioactive Glasses

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Chloride-containing bioactive glasses (BGs) were found to be highly degradable and form apatite rapidly, therefore, they are useful for medical and dental applications. Strontium is an attractive component to be incorporated into BGs and is known to up-regulate osteoblasts and down-regulate osteoclasts. The Sr<sup>2+</sup> cation is slightly larger than the Ca<sup>2+</sup> cation, the substitution of strontium for calcium results in an expansion of the glass network and a faster glass dissolution that might lead to a faster apatite formation. However, recently, it was shown that strontium substitution for calcium in fluoride-free BG inhibited the formation of apatite when immersed in Tris buffer. The objective of this work is to investigate the influence of strontium substitution for calcium on the apatite forming of chloride-containing BGs.

A series of chloride-containing BGs were produced by progressively substituting strontium oxide for calcium oxide. Glass thermal properties were characterized by differential scanning calorimetry. A chloride ion select electrode was used to measure the retention of chloride in the initial compositions. The apatite formation capability on dissolution of the glasses in Tris buffer was followed by X-ray Diffraction, Fourier Transform Infrared and Nuclear Magnetic Resonance spectroscopy. Dissolution studies were followed by the ion release measurements.

It was found that all the studied glasses partially crystallized to chlorapatite-like phases. The chloride content measurements reveal that most of chloride (around 70%) was retained in the studied Q2 type silicate glasses. The results of the in vitro studies show that strontium substitution for calcium suppresses apatite formation in chloride-containing BGs. This is probably a result of strontium not being able to substitute completely for calcium in octacalcium phosphate, which is a precursor phase for hydroxycarbonated apatite formation. Strontium retards the formation of octacalcium phosphate therefore hindering the formation of an apatite-like phase.

**Keywords:** bioactive glasses, chloride containing, apatite, strontium substitution, highly degradable

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\*Speaker



# Structure and Dissolution Behaviour of Multifunctional Borophosphate Bioactive Glasses

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Glass has become a widely used and extensively studied biomaterial for bone regeneration, soft tissue repair and dental applications. The chemical durability requirements well known for bone growth are relaxed for wound-healing applications, where glass dissolution is essential for efficacy. We have explored the structure and dissolution properties of a series of low-durability borophosphate glasses doped with ions thought to have therapeutic properties, such as silver for antibacterial effects, and zinc for angiogenesis and enhanced nerve regeneration. Glass network formers boron and phosphorus disintegrate to aid in the expression of matrix protein and the vascularization process, respectively. Multinuclear magnetic resonance (NMR) spectroscopy of the glasses before and after dissolution confirms congruent dissolution in most compositions, as implied by leachate analysis, and reveals the formation of secondary crystalline phases at the highest boron concentrations. Morphological alterations are visualized using scanning-electron microscopy. The dissolution behaviour is correlated with structural features such as cation coordination number and connectivity, as measured by NMR spectroscopy.

**Keywords:** NMR, borate, phosphate, biomaterials, dissolution

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\*Speaker

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# Albumin and fibronectin attachment on silicate and phosphate bioactive glasses

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Phosphate glasses within the composition 50P2O5-20CaO-20SrO-10Na2O (Sr50) react in biological media and form a dicalcium phosphate di-hydrate layer at their surface. Cell test was performed on these glasses using two cell types: human gingival fibroblasts and human adipose stem cells. While the fibroblasts attached and proliferated at the glass surface (at a slower rate than on typical bioactive glasses), the stem cells only proliferated near the glass. Therefore, the dissolution by-products were appropriate for the proliferation of cells but the glass surface does not act as a good substrate for cell adhesion. However, cells, in-vivo, do not interact with the surface of the biomaterial but rather with a dynamic protein (mono)layer adsorbed at the implant surface. Therefore, to understand the cell attachment and enhance the glass's ability to promote cell adhesion, their surface chemistry was studied. Understanding the glass surface chemistry can allow for developing suitable surface modifications, which will enable superior protein adsorption. In this context, the glass Sr50 as well as Sr50 doped with Cu, Ag and Fe (to tailor the dissolution rate) were studied. The glasses were washed using basic, neutral and acid buffer solutions before silanization. Two types of proteins (albumin and fibronectin) were deposited at the sample surface. The impact of surface treatment on the glass surface chemistry was studied with contact angle measurement, FTIR and zeta-potential. The protein adsorption was assessed by fluorescence microscopy. All tests were also conducted on silicate bioactive glasses, used as reference. Washing improved protein adsorption. And while the acidic wash was best suited to the adsorption of albumin, basic wash was optimum for the adsorption of fibronectin. The silanization further increased the protein adsorption. The impact of surface modification on cell attachment was studied using fibroblasts cultured for 24h and imaged with an integrated live imaging system.

**Keywords:** bioactive glass, phosphate glass, protein adhesion, cell adhesion

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\*Speaker

# Effect of substitution amount of magnesium and zinc on dissolution behaviour and thermal properties of Bioglass 45S5

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This study investigates the effect of Mg or Zn for Ca substitution (2.5, 5, 7.5, 10, 15, 25, 50, 75 and 100%) on thermal and dissolution properties of Bioglass 45S5 (46.1 SiO<sub>2</sub>-2.6 P<sub>2</sub>O<sub>5</sub>-26.9 CaO-24.3 Na<sub>2</sub>O; mol%). Glasses were prepared by a melt-quench route, and their thermal properties were characterised by dilatometry and DSC. Glass transition temperature (T<sub>g</sub>) showed a decrease with Mg or Zn for Ca substitution up to 75 %. Surprisingly, complete substitution of Mg or Zn for Ca led to a rise of T<sub>g</sub>. Owing to higher field strengths of Mg and Zn compared to Ca an increase in T<sub>g</sub> is expected, whereas the results suggested a mixed cation effect. Crystallisation temperature increased with increasing substitution, resulting in an increased processing window of partially substituted Bioglass and improved glass formation. To study the ion release behaviour, glass powder was immersed in tris(hydroxymethyl)aminomethane (Tris) buffer solution for up to 3 days. FTIR spectra of treated glass powders showed that only glasses with low Mg substitution (up to 25 %) or very low Zn substitution (2.5%) formed crystalline hydroxyapatite. The spectra of glasses with higher Mg substitution showed broad bands indicating amorphous apatite formation, while those of glasses with higher Zn substitution no characteristic hydroxyapatite bands were found. Comparing both glass series revealed that thermal properties were affected by Mg and Zn substitution in a similar way, whereas the dissolution behaviour differed significantly, despite similarities in ionic radius and size of Mg and Zn ions.

**Keywords:** Bioglass, Magnesium, Zinc, dissolution properties, thermal properties

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# **BIOGLASSES 3**

# Structure-bioactivity relationships of phosphate-based glass from computer modelling

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Phosphate-based glasses (PBG) have wide application as biomaterials because they dissolve when implanted into the body, with a composition-dependent dissolution rate that varies over several orders of magnitude. They can be synthesised containing different substances or materials, making them useful for controlled delivery of therapeutically relevant substances. In order to optimise PBGs for these applications, it is vital to understand the dependence of their dissolution rate on the glass composition and structure.

Over the past few years, computer modelling, typically molecular dynamics (MD) simulations, has pioneered our understanding of phosphate glass structure [1], particularly identifying the structural motifs which control the glass dissolution rate [2], such as the bonding of network modifying atoms to phosphate chains. MD simulations allow us to understand the ways in which therapeutic substances affect the glass structure and dissolution properties, which are often difficult to elucidate experimentally.

In this presentation, we outline results from our investigations into the structures of PBG doped with various cations, and the ways in which these cations affect the glass structure and dissolution properties. The ultimate aim is to be able to tailor the dissolution rate to a specific application and we will explain our progress toward this goal, making appropriate connections to experimental results.

J. K. Christie, R. I. Ainsworth, S. E. Ruiz Hernandez, N. H. de Leeuw, *J. Mater. Chem. B* 5, 5297 (2017)

J. K. Christie, R. I. Ainsworth, D. Di Tommaso, N. H. de Leeuw, *J. Phys. Chem. B* 117, 10652 (2013)

**Keywords:** phosphate glass, bioactivity, dissolution, molecular dynamics

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\*Speaker

# Applications of bioactive glasses for glass ionomer cements

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Glass ionomer cements (GICs) are materials traditionally used in dentistry for filling and luting purposes. However, applications extend to their use for bone applications owing to advantages such as a low exothermic reaction when setting and ability to bond to bone. Dental GICs are formed by a neutralisation reaction between a fluoro aluminosilicate glass and an acid such as poly (acrylic acid) (PAA). This reaction occurs when the glass is degraded by the acid, allowing the release of ions such as calcium and aluminium that crosslink with the carboxylate (COO-) groups from the acid, resulting in a matrix of polyacrylate-based salts and embedded glass particles. The final composite is biocompatible; however, their surface is relatively inert owing to the reduced degradation of the glass after the cement is set, which is translated into a low release of ionic species of biological interest for the formation of a bioactive layer as a precursor of bone formation. By contrast, bioactive glasses based on the SiO<sub>2</sub>-Na<sub>2</sub>O-CaO-P<sub>2</sub>O<sub>5</sub> system described by Hench, are known for their osteoinductive and osteoconductive properties derived from the ability of the glass to degrade and release silicon, calcium and phosphate ions. In addition, other ions that function as network modifiers (e.g. Sr<sup>2+</sup>) can be substituted in the glass structure and released when the glass is exposed to a media such as simulated body fluid (SBF). Therefore, the use of bioactive glasses has been of special interest as an additive of GICs, since their degradability have the potential to improve the formation of a calcium phosphate layer on their surface, as previously described by Yli Urpo *et al.* (2005). Here, we present results of bioactive glass-based GICs including their setting time, chemistry and mechanical properties. FTIR-ATR was used to characterise the setting of cements through the change of the characteristic bands over time.

## References

Yli-Urpo H., Lassila, L, N'arhi, T & Vallittu, P. 2005. Compressive strength and surface characterization of glass ionomer cements modified by particles of bioactive glass. *Dental Materials.*, 21, 201-209.

**Keywords:** GICs, bioactive glass, setting time, mechanical properties, FTIR, ATR

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\*Speaker

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# Structure Property Relationships in OxyHalide Bioactive Glasses

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Bioactive glasses were invented by Larry Hench. These glasses degrade in body fluids releasing Ca<sup>2+</sup>, PO<sub>4</sub><sup>3-</sup> ions and form an "apatite like phase" similar to bone and tooth mineral. They are used as bone substitutes, for treating periodontal disease and for re-mineralizing toothpastes such as Sensodyne® Repair and Protect for treating dentine hypersensitivity.

Composition-structure-property relationships in Bioactive Glasses will be discussed with an emphasis on the importance of glass network connectivity. The structural role of phosphate, soda and halogens including fluorine and chlorine in bioactive glasses will be reviewed and discussed in relation to their influence on physical properties; glass transition temperature, hardness, density and refractive index. In addition the dissolution behavior and phases formed upon immersion will be discussed.

It will then be shown how this understanding can be used to design glasses with different hardness values for air abrasives, fluoride releasing re-mineralizing hypersensitivity toothpastes, bioactive glass based dental fillings and adhesives.

A specific focus of the talk will be the development of BioMinF® toothpaste based on a fluoride containing bioactive glass launched by BioMin Technologies Ltd [www.biomin.co.uk](http://www.biomin.co.uk)

**Keywords:** Bioactive Glass Fluoride Chloride

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\*Speaker

# Amorphous Borosilicate Bioactive Glass Scaffolds Processing and In-Vitro Dissolution

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Sintering of commercially available bioactive glasses particles, such as 45S5 and S53P4, leads to porous scaffolds partially to fully crystallized with low mechanical properties. Crystallization is known to reduced, or even suppress in some cases, the material's bioactivity. Recently, Borosilicate bioactive glasses have emerged as a class of glasses highly interesting for tissue engineering applications. They have enhanced thermal properties, and faster conversion to hydroxyapatite (HA) in physiological conditions compared to the traditional silica-based bioactive glasses. Borosilicate glasses, that can be sintered into porous scaffold without adverse crystallization, have even been developed. One drawback of the developed glasses lies in their reduce cell attachment and proliferation when compared to typical silicate bioactive glasses. Here, we report on the processing of 3D porous scaffolds using Mg and Sr-containing borosilicate bioactive glasses. These glasses exhibit cell attachment and proliferation similar or superior to the typical silicate bioactive glasses. Scaffolds were produced using 3D printing and the porogen burn-off technique. All the scaffolds produced were amorphous in nature. Porosity was greater than 60-70% with interconnected pores larger than 200  $\mu\text{m}$  in average. The Mg-containing glass have higher sintering ability as evidenced by the increased mechanical properties and further confirmed by  $\mu\text{CT}$ . Immersion of the scaffolds in simulated body fluids suggested that the scaffolds prepared by robocasting reacts at a slightly higher rate than those obtained using the porogen burn-off method. ICP-OES and FTIR was used to quantify the glass dissolution and probe the change in the glass structure. Presence of Sr and/or Mg led to a slower glass reactivity. However, the presence of Sr induced precipitation of a Sr-substituted hydroxyapatite layer at the scaffolds surface. The change in compressive strength, as a function of immersion time, were also measured for all processed scaffolds.

**Keywords:** Bioactive glass, Borosilicate, Scaffolds, Sr, HA

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\*Speaker



# Setting process of glass ionomer cements studied by dielectric spectroscopy

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Glass ionomer cements (GICs) belong to the class of restorative dental materials with a long and extensive usage. These materials consist of an aluminofluorosilicate glass powder and an aqueous polyacrylic acid and the cement formation arises from the acid–base reaction between components. Over the past decade, a significant effort has been undertaken to develop a hybrid material composed of the glass ionomer and an additional component, resins for example, to obtain the material with superior mechanical and esthetical properties. In such resin-modified glass ionomer (RM-GI), the setting process involves an acid–base reaction and polymerization (light and/or chemically activated). The key point in designing an advanced dental material with desired properties is a thorough understanding of the setting reaction. In this study, the setting process in the commercial GIC (Fuji IX Fast) and RM-GI (Fuji II LC) was investigated by dielectric spectroscopy and digital laser interferometry. The changes in the real and imaginary parts of the dielectric permittivity as well as dielectric loss tangent with time for Fuji IX Fast show several distinct regions which can be related to the different stages of the acid–base reaction. Interestingly, the first stage that lasts for approximately 12 minutes terminates with a sharp decrease in dielectric parameters which is most probably related to the instantaneous (micro)fracturing of the sample due to a rapid build–up of the shrinkage stress. On the contrary, evolution of the dielectric properties during the setting of Fuji II LC indicates fast light-activated polymerization in the initial stage (less than a minute) followed by the slow gradual change. This results from the competing nature of the acid–base reaction and light-activated polymerization. In general, these results demonstrate that the dielectric spectroscopy is a sensitive tool for monitoring the complex changes during the setting process in dental materials.

**Keywords:** dental materials, glass ionomer cements, setting reaction, dielectric spectroscopy

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# CHALCOGENIDE GLASSES

# Fiber drawing region investigation and structural characterization of Ge-S-I chalcocalide glasses

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In the aim to produce new multimaterial fibers, we investigate Ge-S-I glass properties as they present a wide transparency from the visible to the infrared as well as good chemical and thermal stability which is needed for fiber production. Ge-S-I glass samples with 5, 10 and 15% of iodine and a concentration of germanium varying between 25 and 35% were produced and their physical properties such as T<sub>g</sub>, density, visible and infrared light absorption were investigated [1]. From this study, we were able to show the impact of iodine as modifier with the observation of important change in T<sub>g</sub> and Band-gap. We established that these change follow the (GeS<sub>2</sub>)<sub>X</sub>-(GeI<sub>4</sub>)<sub>1-X</sub> composition line and we proposed an equation of composition that take into account the effect of iodine on the glass properties. According to these results we conduct a study of their drawing ability using the preform-to-fiber drawing technic. This enabled us to draw a fiber drawing region in the Ge-S-I ternary diagram. We then carried out a structural analysis on the samples. A novel approach [2] based on a simultaneous desumation of IR and polarized Raman spectra (RS-VV and RS-HV) has been applied on Ge-S-I chalcocalide glasses. By a careful analysis of the multipolar activities between 180 and 280 cm<sup>-1</sup> and a comparison of these results with DFT calculation made on Ge-S-I clusters, we proposed a new attributions of the bands in this region. Four peaks between 230 and 280 cm<sup>-1</sup>, were assigned to symmetric and anti-symmetric GeI<sub>2</sub> vibrations in corner-sharing and edge-sharing tetrahedral, while two normal modes at 190 and 210 cm<sup>-1</sup> were attributed to I<sub>2</sub> in a molecular form, trap in the glass network. This permit us to underline a correlation between the structure and the physical properties of Ge-S-I glasses.

**Keywords:** Chalcocalide glasses, Raman spectroscopy, Strucural characterization

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\*Speaker

# Structure of Telluride Glasses: a Theoretical and Spectroscopic Investigation

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The central goal of our project is to rationalize the substituent effect on the glass structure and physical properties of a new generation of far-infrared transmitting telluride materials. Indeed the research area is nowadays receiving an increased attention because of the various potential photonic-related application, like monitoring, night vision, and CO<sub>2</sub> greenhouse effect monitoring<sup>1</sup>. Due to the lack of long-range order in glasses, structural characterization is always a challenge. Spectroscopic techniques probing the local environment of selected atoms, such as solid-state NMR, is a well-known approach to understand the structural and physical properties of new families of glasses. Another way to get structural and dynamical insights of our materials are the use of structural characterization by IR/Raman vibrational spectroscopies. In this study, an accurate structural characterization of ternary glasses in the systems Ga-Ge-Te and Ge-Te-Se is presented. The NMR study has been carried out using quite unusual nucleus like <sup>73</sup>Ge, <sup>77</sup>Se, <sup>125</sup>Te and <sup>69/71</sup>Ga. For instance, the <sup>73</sup>Ge nucleus, which is a very low-gamma nucleus with a large quadrupolar moment, needs to be probed using a high magnetic field spectrometer. Besides, results of vibrational spectroscopies will be shown for the two families of telluride glasses, a careful assignment of vibrational modes is proposed thanks to DFT calculations implemented using the Gaussian software.

**Keywords:** telluride glasses, NMR, infrared, Raman, DFT calculation

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\*Speaker

# Local- and intermediate-range structures of room-temperature superionic Ag-GeSe3 glasses

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Recently, much attention has been paid for investigating superionic conductors, which can be used as solid electrolytes for solid-state batteries. Superionic glasses with a high ionic conductivity of 10<sup>-6</sup>-10<sup>-2</sup> S/cm are promising materials for such applications. It is well-known that superionic behavior in Ag containing chalcogenide glasses is observed at room temperature, such as for Ag-GeSe3 alloys, in contrast to high temperatures needed in crystalline superionic conductors.

To investigate the ion conduction mechanism in Ag ion conducting glasses Ag $x$ (GeSe3) $1-x$  with  $x = 0.15$  [1], 0.28, 0.33 and 0.50 [2] from the local structural point of view, we carried out anomalous x-ray scattering (AXS) experiments near the x-ray energies close to the Ge, Se, and Ag  $K$  absorption edges. Details of the experiment and analysis are given elsewhere [3]. This method can provide insight into the structural properties enabling the effect of superionic conductivity for compositions with  $x > 0.30$  in the amorphous phase. The experimental results were analyzed with reverse Monte Carlo (RMC) modeling, providing the partial structure factors and the corresponding partial pair-distribution functions. Evidence is found for a high level of intermediate range order for low silver concentrations, whereas the superionic conducting phase formed at high silver concentrations is characterized by cluster-like configurations of Ag atoms on a nanometer scale.

In the presentation, we will show full sets of partial structural information obtained in combination with Ge, Se, and Ag  $K$  edge AXS data and RMC modeling, and explain the structural information on the ion conduction mechanism in Ag $x$ (GeSe3) $1-x$  glasses by also citing the previous works [1-3].

J. R. Stellhorn et al., Z. Phys. Chem. **230**, 369 (2016).

J. R. Stellhorn et al., J. Non-Cryst. Solids **431**, 68 (2016).

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†Speaker

S. Hosokawa et al., Phys. Rev. B **84**, 014201 (2011).

**Keywords:** Chalcogenide glasses, Local structures, Room temperature superionic conductors

# Infrared optics of chalcogenide glasses made by mechanical alloying and sintering

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Needs in infrared lenses are rising together with the demand in infrared cameras. Chalcogenide glasses are good candidates in order to provide infrared lenses with good resolution at low cost. Sensitive to oxygen, they are synthesized under vacuum, in a sealed silica tube. Non re-usable and expensive, the silica tube accounts for 30% of the final product price. Also, silica has a low thermal conductivity that lessens the quenching rate and thus the size of the lenses and the variety of compositions that can be obtained at large dimensions.

To avoid these limitations, a new process has been developed: it combines mechanical milling and SPS sintering. Mechanical milling allows production of large varieties of glass compositions without any use of silica. The mechanical energy brought to the starting elements (Ge, Ga...) leads to their reaction and the formation of glass powder. The obtained powder is then sintered by SPS. By this process, lenses of desired geometry and a low surface roughness are achieved. The present work took interest in two glasses: Ge<sub>28</sub>Sb<sub>12</sub>Se<sub>60</sub> and 80GeSe<sub>2</sub>-20Ga<sub>2</sub>Se<sub>3</sub>. The first one is a commercial glass (IG5, Optir3, AMTIR-3). It has been used in order to test the feasibility of the technique. The second one is an interesting and unique composition discovered in 2008. Indeed, it can undergo controlled crystallization in order to form glass-ceramics and so improve the mechanical properties of the final product. This type of composition is usually inappropriate for industrial production. Using silica tubes, only 10mm diameter pellets can be obtained. Higher diameter tube generates an important crystallization that is characterized by a tremendous decrease in transmission.

This simple and innovative process is really promising for the shaping of chalcogenide glasses and production of lenses by molding.

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**Keywords:** Infrared, optics, lens, sintering

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\*Speaker

# Local vibrational and mechanical characterization of Ag conducting chalcogenide glasses

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Chalcogenide glasses exhibit remarkable properties, which could be used in the development of electrical memory susceptible to replace the current flash memories. During the last decades, a strong interest has been focused on superionic Ag-Ge-Se glasses for their high ionic conductivity, a property that could be used to develop ionic Conductive-Bridging Random Access Memories (CB-RAM).

Bulk Ag-Ge-Se glasses have already been widely studied for their electrical, structural and thermal properties. In particular it was shown that the conductivity of phase separated  $\text{Ag}_x(\text{Ge}_{0.25}\text{Se}_{0.75})_{100-x}$  glasses increases suddenly by seven to eight orders of magnitude at 7-10 at.%Ag. The percolation of the Ag-rich phase was at the origin of this sudden jump in conductivity.

Despite a convergence on the inhomogeneous nature of these glasses, some questions remain open such as the composition of the Ag-rich and Ag-poor phases, size and shape of the different phases. These questions has hardly been treated in literature to date.

In this talk, investigations on bulk  $\text{Ag}_x(\text{Ge}_{0.25}\text{Se}_{0.75})_{100-x}$  glasses will be performed focusing on the inhomogeneous nature of the glasses. Macroscopic and local studies of vibrational and mechanical properties will conduct using Raman (mapping) spectroscopy, Vickers microhardness and Contact Resonance Atomic Force Microscopy (CR-AFM). For the glass containing 10 at. % in Ag, Raman mapping will give evidence of a phase separation for through continuous interpenetrating phases in the spinodal decomposition process. Combined mechanical characterizations will indicate that the microhardness and rigidity modulus decrease with the silver content in the glass. At nanoscale level, CR-AFM measurements will highlight a modulation of the rigidity with Ag content. The structural origin of these changes will be confirmed using

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\*Speaker



Raman mapping evidencing modifications in the tetrahedral network between two phases. The results could suggest a different Ge/Se ratio in Ag-poor and Ag-rich phases.

**Keywords:** Chalcogenide glasses, Raman mapping, mechanical properties, Contact Resonance Atomic Force Microscopy

# Local structure and glass formation in Al<sub>20</sub>Te<sub>80</sub> glass

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Chalcogenide glasses are known for their wide range of application in many areas. Properties of chalcogenide glasses can be altered to a larger extent by the addition of metal atoms. In these glasses metal atoms are normally found to be in higher coordination state. For example, Al atoms are reported to be in 4- and 6- fold coordination in Al-Te and Al doped As-Te glasses. But recent reports on Al-Te glasses show 5- fold coordination for Al along with 4- and 6- fold coordination states. Correspondingly the electrical properties particularly, the electrical switching is found to be completely different. We believe that there should be a favourable preparation condition at which the 5- fold coordinated Al may form. In this study <sup>27</sup>Al Magic Angle Spinning (MAS) NMR measurements have been carried out to understand the origin of 5- fold coordinated Al in Al<sub>20</sub>Te<sub>80</sub> glass.

Two series of glasses have been prepared by melt quenching method: (i) quenching of the melt from different temperatures (700 oC, 800 oC and 900 oC) (ii) quenching of the melt from different pressures (atmospheric pressure, 10<sup>-2</sup> Torr, 10<sup>-4</sup> Torr, 10<sup>-5</sup> Torr and 10<sup>-6</sup> Torr). The glasses quenched from different temperatures do not show any variation in 5- fold coordinated Al whereas the glasses prepared from different pressures show systematic changes in 5- fold coordinated Al. This study indicates that to form Al-Te glass a minimum pressure of 10<sup>-4</sup> Torr is needed. The samples prepared from pressures > 10<sup>-4</sup> Torr show only 4 and 6 coordinated Al while the glasses formed from pressures ≤ 10<sup>-5</sup> showed the appearance of 5- fold coordinated Al.

**Keywords:** Chalcogenide glasses, MAS, NMR, Melt quenching, Glass formation, Network connectivity

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\*Speaker

# Transport and structural properties of silver bromide doped chalcogenide glasses

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Silver-halide doped glasses which show high Ag+ **ionic conductivity** at room temperature are suitable materials for the sensors' development. They are also suitable model materials to investigate the structural origin of conductivity changes in fast ionic conducting glasses. To this end, the quasi-binary AgBr-As<sub>2</sub>S<sub>3</sub> glass system has been synthesized and characterized. X-ray diffraction (XRD) shows that the glass-forming range for the (AgBr)<sub>x</sub>(As<sub>2</sub>S<sub>3</sub>)<sub>1-x</sub> compositions varies between  $0.0 \leq x \leq 0.5$ . The glass transition and crystallization temperatures ( $T_g$  and  $T_x$ ), density ( $d$ ), and the total conductivity ( $\sigma$ ) have been measured for all the samples ( $0.0 \leq x \leq 0.6$ ). The ionic conductivity increases by 13 orders of magnitude with increasing the Ag atomic concentration ([Ag]<sub>max</sub> = 18.75 at.%) and two distinctly ion transport regimes, above the percolation threshold at  $x_c$ , are distinguished. Glass-phase separation occurs over a wide range of Ag content, i.e.  $7.3 \leq [Ag] \leq 18.75$  at.% and is confirmed by both thermal and SEM studies. Raman spectroscopy, high-energy X-ray diffraction and neutron diffraction experiments have been carried out to elucidate the structural aspects at both short- and intermediate-range order. The results suggest that the dominant structural entities in **AgBr-poor** glasses ( $x \leq 0.1-0.2$ ) are isolated edge-sharing **ES-Ag<sub>2</sub>Br<sub>2</sub>S<sub>4</sub>/2 dimers** distributed more or less randomly in the corner-sharing **CS-As<sub>2</sub>S<sub>3</sub>/2** host network. Meanwhile, for the **AgBr-rich** glasses ( $0.2 < x \leq 0.4$ ), the silver structural entities are formed by **tetrahedral** chains (AgBr<sub>2</sub>/2S<sub>2</sub>/2)<sub>n</sub>. Further increase of the AgBr content, thus for the **high-AgBr rich** glasses ( $x > 0.4$ ), new **AgBr<sub>3</sub>/3S<sub>1</sub>/2** mixed tetrahedra appear giving rise either to 2D layers or 3D sub-network.

**Keywords:** Chalcohalide glasses, Electrical properties, Raman spectroscopy, High energy X-ray diffraction, Neutron diffraction

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\*Speaker

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# Structure of Ge-Se glasses

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Chalcogenide glasses (those containing S, Se or Te) can be formed over a wide compositional range, and feature networks that are built from a rich variety of structural motifs that include homopolar bonds and edge sharing tetrahedral units. It is therefore a formidable challenge to solve the structure of these materials by diffraction methods, especially when the chemical species in a given material have similar neutron scattering lengths or x-ray form factors. In this talk, I will present new results on the structure of Ge-Se based glasses as obtained by using the method of neutron diffraction with isotope substitution. I will show how the technique can be used to gain site-specific information on the coordination environments of the chemical species over multiple length scales, thus providing essential information on the glass structure. I will show how advances in neutron diffraction now make it possible to measure the full set of partial structure factors for an enhanced range of glassy materials. The results are compared to those obtained from first-principles molecular dynamics simulations. Future challenges for experiment and simulation are discussed.

**Keywords:** Chalcogenide glasses, Neutron diffraction, partial structure factors, glass structure

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\*Speaker

# Recent development of materials for IR applications

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Infrared windows and optics are widely used in low temperature imaging, night vision, ranging and surveying, remote sensing applications and free space optical communication. Important bands for imaging are the spectral regions that cover the wave-length range from 0.4 to 12  $\mu\text{m}$ . Unlike the visible applications, the range of materials for infrared applications is much more limited and their cost increases rapidly with increased performance. The windows and domes of middle-IR (MIR) far-IR (FIR) sensors on missiles and aircraft often become the key point of failure for systems because of their interaction with the harsh environment. These windows must provide maximum transmission of signal with negligible absorption, withstanding the thermal shock, electromagnetic interference (EMI), radar latent, and abrasion from raindrops and sand particles. The window must also be isotropic, easily moldable in large and complex shapes and available at low cost. Large numbers of programs (e.g. used in aircraft and HEL systems) require flat (or dome) windows with sizes larger than 500 mm diameter, which puts additional limitations on the available materials. It's still a great challenge to fabricate the IR- transparent materials with high-properties and large size. In this talk, the recent progress to face the above challenge was demonstrated and reviewed, especially which were done in our group. The prospect of the infrared materials toward cutting-edge applications was also discussed in this talk.

**Keywords:** Infrared materials

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# DURABILITY, DISSOLUTION & CORROSION

# Topological control on glasses' dissolution kinetics

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Understanding and predicting the dissolution rate of silicate glasses is of primary importance for various applications, including bioactive glasses and borosilicate wasteforms. However, the mechanism of silicates' dissolution-and its rate-limiting step-remains poorly understood. In particular, present models linking the composition and structure of silicate glasses to their dissolution rate in a given solvent have remained largely empirical thus far. Here, based on vertical scanning interferometry (VSI) experiments and molecular dynamics (MD) simulations, we study the dissolution of a large variety of silicate glasses under various pH conditions. From a detailed analysis of the simulated structures, we demonstrate that the kinetics of the dissolution is controlled by the topology of the atomic network. We propose a new topological model of silicates' corrosion, which is shown to offer realistic predictions of dissolution rates and activation energies for a wide selection range of silicate glasses and crystals.

**Keywords:** Dissolution, Topological constraint theory, Molecular Dynamics

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# Formation of Hierarchical Nanoporous Layer etched on a silicate glass

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Hierarchically porous materials, with pores of which size changes under certain regularity, are gathering much attention because of its various functionalities. A drug container in a drug delivery system (DDS), metal adsorbent from polluted water and so on. are expectedly realized by the structures. Silica-based materials with such a hierarchical porous structure have reportedly been fabricated by using particular templates so far.

We have developed a new hierarchically nanoporous layer (HNL) formed on a silicate glass surface by a simple etching process in an alkaline solution.[1] A three-dimensionally continuous porous structure like a sponge was clearly observed by SEM micrography. The porous size gradually decreases from the apparent surface to the interface of the porous layer and bulk substrate. That is, a hierarchically porous structure was spontaneously formed by the simple etching process other than previously developed ones by template methods. The temperature and time dependence of the HNL formation indicated some activation energy for this phenomenon.

The HNL glasses exhibits lower optical reflectivity all over the visible light range than untreated glass and super-hydrophilic property that remains its water contact angle around 5 degree for more than 100 days. The long-life superhydrophilicity realizes practically useful anti-fouling and anti-fogging functionalities. We will discuss the properties and mechanism of the functionalities. 1T. Fujima, E. Futakuchi, T. Tomita, Y. Orai and T. Sunaoshi, Langmuir 30 (2014), 14494.

**Keywords:** porous, etching, superhydrophilicity, antifogging, antifouling, antireflection(AR)

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# Glass durability under elevated pH conditions

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It is expected that vitrified nuclear waste will ultimately be disposed in an underground repository, where eventually groundwater will penetrate the multi-barrier system and interact with the glass. Under some repository scenarios this water may have an elevated pH due to the presence of significant cementitious material. Results from studies on a range of model glass compositions, including the international simple glass (ISG), and glasses that are representative of potential vitreous wasteforms, as well as basaltic glass used as a natural analogue, will be reported. These studies have included structural characterisation and durability measurements in both KOH and Ca(OH)<sub>2</sub> solutions. The presence of calcium has a significant effect on performance as it leads to the formation of calcium silicate hydrate (CSH) gels which appear to limit the rapid dissolution that is otherwise seen in high pH conditions when calcium is not present. Distinct mechanistic differences were seen according to glass composition, with more rapid dissolution being seen for compositions that contain significant amounts of Al<sub>2</sub>O<sub>3</sub> and/ or MgO than for compositions which do not. The phase evolution in the alteration layer was also significantly different between the different glasses studied. The implications of these compositional differences for the use of simplified glass compositions and natural analogues, especially ISG, as models for full waste loaded glasses will be discussed.

**Keywords:** Nuclear waste vitrification, glass durability

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\*Speaker

# Evaluation and mechanisms of a surface treatment based on zinc salts to slow down atmospheric alteration

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In the flat glass industry, zinc salts are sometimes used to protect glasses from atmospheric alteration during their transport and storage. A zinc salts based treatment could be an interesting complement to the control of the environment performed by museums to slow down the processes of alteration of ancient glass. The current research is focused on this potentiality. The protective action of zinc salts is investigated by the mean of ageing experiments (temperature and humidity control) on relevant ancient glass composition replica.

Our results put in evidence that treated glass plates develop a significantly thinner hydrated layer thickness than the untreated one at 80°C or 40°C (85% RH). Furthermore, zinc salts treatment modifies the nature of salts on glass surface. Different Zn(II) species are identified on the glass surface prior or after the ageing and their distribution is tracked by Tof-SIMS. Notably, the study of the Zn(II) speciation on glass surface by Grazing Incidence X-Ray Absorption Spectroscopy at SOLEIL synchrotron shows the incorporation of Zn(II) into the silicate network with the ageing.

Based on these results, several hypotheses on the protective action of Zn(II) against glass atmospheric alteration are formulated and discussed : (i) Surface acidification, (ii) Weakening of the hydrophilic character of the surface by diminishing the surface charge, (iii) Formation of a passivating zinc-hydroxy-silicate layer, (iv) Very low solubility of this layer.

**Keywords:** Atmospheric alteration, surface chemistry

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\*Speaker

# RE<sub>2</sub>O<sub>3</sub> dissolution kinetics and mechanisms in CMAS silicate melts: influence of the rare-earth

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Fine particles of sand, dust or volcanic ashes ingested by aircraft engines are well-known to damage Thermal Barrier Coatings (TBC, ZrO<sub>2</sub>-8wt. %Y<sub>2</sub>O<sub>3</sub>). In service, these particles deposit on hot TBC surface ( $\geq 1200^\circ\text{C}$ ) as molten silicate and infiltrate porous microstructure of coating. They are mainly constituted of CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (CMAS) in variable proportions and also contain metallic oxides. Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> TBC has shown efficiency to mitigate synthetic CMAS infiltration due to its reactivity with CMAS. Indeed, the dissolution reaction leads to rapid formation of a sealing-layer in the topcoat mainly constituted of crystalline Ca<sub>2</sub>Gd<sub>8</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub> apatite. However, this phase is not always stable in contact with CMAS and many rare-earth silicates may compete with apatite crystallization. Several rare-earth oxides RE<sub>2</sub>O<sub>3</sub> can be considered to replace yttria in ZrO<sub>2</sub>-based TBC but little is known on reaction kinetics and thermodynamics involving RE<sub>2</sub>O<sub>3</sub> and multi-component CMAS system.

In this study, a simplified CMAS was selected with eutectic (1170°C) 65SiO<sub>2</sub>-26CaO-9Al<sub>2</sub>O<sub>3</sub> (mol. %) composition. Investigation on RE<sub>2</sub>O<sub>3</sub> (RE = Nd, Sm, Gd, Dy and Yb) dissolution mechanism in CAS-melt was then performed at 1200°C. For this, CAS-glass beads containing dispersed RE<sub>2</sub>O<sub>3</sub> solid powder in adequate amount to reach oversaturation were elaborated. Beads were then annealed in air for several durations and quenched. SEM observations coupled with XRD analysis gave information about dissolution/precipitation sequences and phase equilibria. The evolution of RE content dissolved in CAS over time and chemical evolution of CAS-melt was measured by EPMA.

Reaction mechanism in CAS of RE<sub>2</sub>O<sub>3</sub> was identified to be incongruent dissolution leading to precipitation of different RE-rich silicates. Dissolution of Nd<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub> and Dy<sub>2</sub>O<sub>3</sub> in CAS results in formation of apatite, and then precipitation of cyclosilicate. Disilicate Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> was also obtained in Yb<sub>2</sub>O<sub>3</sub> bead-sample. The silicate precipitations induced significant variations of local CAS composition resulting in CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> anorthite formation. The RE<sub>2</sub>O<sub>3</sub> basicity has a direct influence on silicates solubility limits in CAS and on reaction kinetics.

**Keywords:** Molten silicates, Rare earth oxides, Dissolution, Precipitation

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\*Speaker

# Corrosion of sodium silicate glasses: the influence of concentration effects

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Sodium water glass can be produced by dissolving sodium silicate glasses at elevated temperatures. To contribute to the understanding of the dissolution process, studies on sodium silicate glasses having the composition  $\text{Na}_2\text{O} \times x\text{SiO}_2$  ( $x = 2.0, 2.5$  and  $3.3$ ) were performed. The glasses were dissolved in different neutral to alkaline corrosion media ( $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}$  containing different concentrations of dissolved  $\text{SiO}_2$ , concentration series of sodium water glasses having nearly identical molar  $\text{SiO}_2:\text{Na}_2\text{O}$  ratios with  $\text{SiO}_2$  contents up to 27 wt. %) at moderate to elevated temperatures in static as well as dynamic corrosion tests. Dynamic corrosion tests were only applicable as long as the viscosity of the leachants were low enough for pumping them through the corrosion containers. Depending on leachant composition and resulting pH, reaction layers were observed and investigated. Some kinds of saturation effects were observed in dynamic corrosion tests with silica enriched  $\text{H}_2\text{O}$  as leachant. Static as well as some dynamic corrosion test results with diluted sodium water glasses as leachant depend on glass composition. For  $\text{Na}_2\text{O} \times 2\text{SiO}_2$  the corrosion rates declined with increasing water glass concentration, whereas for  $\text{Na}_2\text{O} \times 3.3\text{SiO}_2$  the corrosion rate increased with increasing water glass concentration. To test this behavior an intermediate composition  $\text{Na}_2\text{O} \times 2.5\text{SiO}_2$  was tested. Here, corrosion rates first increase and then decline with water glass concentration. An explanation of these concentration dependencies on the basis of leachate pH and reaction layer formation will be discussed.

**Keywords:** sodium silicate, chemical durability, glass corrosion

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\*Speaker

# DYNAMICS, EXCITATIONS & RELAXATION

# Stretched exponential relaxation of glasses and origin of the mixed alkali effect

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Despite the dramatic increase in their viscosity as temperature decreases, some glasses are known to feature room-temperature relaxation. However, the structural origin of this phenomenon-known as the "thermometer effect"-remains unclear. Here, based on accelerated molecular dynamics simulations of alkali silicate glasses, we show that both enthalpy and volume follow some stretched exponential decay functions upon relaxation. However, we observe a bifurcation in their stretching exponents, with  $\beta = 3/5$  and  $3/7$  for enthalpy and volume relaxation, respectively-in agreement with Phillips' topological diffusion-trap model. Based on these results, we demonstrate that the thermometer effect is a manifestation of the mixed alkali effect. We show that relaxation is driven by the existence of stressed local structural instabilities in mixed alkali glasses. This driving force is found to be at a maximum when the concentrations of each alkali atom equal each other, which arises from a balance between the concentration of each alkali atom and the magnitude of the local stress that they experience.

**Keywords:** Molecular dynamics, relaxation, mixed alkali effect

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# Impact of structural water on sub-T<sub>g</sub> relaxations in glass

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Structural relaxation at temperatures below glass transition provides the basis for aging and fatigue phenomena of glasses. Different water species are discussed to contribute to sub-T<sub>g</sub> relaxation. Their dynamics are found to be decoupled from the cooperative rearrangements of the glassy network (alpha-relaxation) and the local motions of diffusional transport of ionic species (gamma-relaxation). Using mechanical spectroscopy, two types of new relaxations peaks (beta-relaxations) are evident in hydrous soda-lime silicate and hydrous sodium borosilicate glasses, which are assigned to the contributions of OH-groups and H<sub>2</sub>O molecules. Projected characteristic times at ambient temperatures of water-induced internal friction are ca. 10<sup>1</sup> seconds for beta(H<sub>2</sub>O) and ca. 10<sup>3</sup> seconds for beta(OH). In general, beta-relaxations are assumed to involve stress accommodating rearrangements that are located at non-bridging oxygen (NBO) containing silicon tetrahedra, but in case of the faster beta(H<sub>2</sub>O)-relaxation, the discussion also addresses possible jumps of H<sub>2</sub>O molecules between network cavities besides a hopping mechanism of protons between H<sub>2</sub>O and NBO.

**Keywords:** Relaxation, Water species, Mechanical spectroscopy

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\*Speaker

# Phonon excitations in an anisotropic metaphosphate glass

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Usually, inorganic glasses are structurally and elastically isotropic unlike organic glasses, and thus, an azimuthal angle dependence of momentum transfer in scattering experiments is totally meaningless. However, Inaba et al. [1] recently found that  $(\text{Li}_2\text{O})_{12.5}(\text{Na}_2\text{O})_{12.5}(\text{K}_2\text{O})_{12.5}(\text{Cs}_2\text{O})_{12.5}(\text{P}_2\text{O}_5)_{50}$  metaphosphate glass shows an entropic shrinkage by heating beyond its glass transition temperature,  $T_g$ . The experimental findings are as follows. The glass rod was stretched at a temperature higher than  $T_g$  and cooled down to room temperature. When it was again heated up to a temperature higher than  $T_g$ , the rod was shrunk automatically and endothermically in the longitudinal direction by a large value of about 35%, while it was expanded in the lateral direction so as to keep the total volume of the rod. They measured several anisotropic properties, such as birefringence, polarized Raman spectra, x-ray diffraction [1], and elastic constants [2], and discussed the origin of such an interesting anisotropic behavior of this glass in the sense of microscopic structure.

To clarify the mechanism of the entropic shrinkage for this metaphosphate glass, an anisotropy of the microscopic elastic properties is a key knowledge. For this, inelastic x-ray scattering (IXS) is very powerful since the small size of the x-ray beam matches the diameter of the sample rod of sub mm. We have carried out high-resolution IXS measurements at BL35XU of the SPring-8 by changing the sample rod directions, perpendicular and parallel to the x-ray scattering plane. The obtained IXS signals exhibit at least two phonon excitation modes, and those with the rod direction perpendicular to the x-ray polarization are slightly larger than those with parallel. The further data analyses are now in progress.

S. Inaba et al., *Nature Mater.* 14, 312 (2015).

J. Endo et al., *J. Am. Ceram. Soc.* 98, 2767 (2015).

**Keywords:** Metaphosphate glass, Phonon dynamics, Synchrotron radiation

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\*Speaker



# Investigation of boson peak and fracton in protein lysozyme by terahertz time-domain spectroscopy

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Terahertz time-domain spectroscopy and low-frequency Raman scattering have been performed on protein hen egg white lysozyme to investigate the boson peak (BP) and fracton dynamics. The BP dynamics is a universal feature in the glassy states and the fracton dynamics is a universal feature of polymer glass materials. In the  $\alpha(\nu)/2$  plot of the infrared spectrum, where  $\alpha(\nu)$  is absorption coefficient, the boson peak of lysozyme was detected at about 0.58 THz at room temperature. In Raman spectrum, the BP was observed at about 0.82 THz at room temperature from Raman susceptibility divided frequency. Neither the imaginary part of complex dielectric constant nor Raman susceptibility shows absorption peak around their BP frequencies. In the frequency region above the BP, the fracton behavior has been observed both in the infrared and Raman spectrum of lysozyme. The fracton region has a frequency range from 0.58 THz to 3.3 THz in the infrared spectrum, and 0.82 THz to 2.6 THz in the case of Raman spectrum.

**Keywords:** Boson peak, fractal dynamics, terahertz time domain spectroscopy, protein

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# Modeling viscoelasticity and energy dissipation in Silica in the THz regime

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The attenuation of sound waves in glasses is still poorly understood, partly because the underlying mechanism strongly depends on the frequency of the incident wave and on the ratio between its wavelength and the characteristic length scales of the glasses. Here, we investigate energy dissipation in oxide glasses using atomic-scale simulations. We employ Molecular Dynamics (MD) to measure energy dissipation using simulated mechanical spectroscopy in the GHz and THz regimes in a model SiO<sub>2</sub> glass. We find that the computed dissipation compares favorably with existing experimental data. We also show that when the forcing frequency lies within the frequency range of the main band of normal modes of the system, dissipation is harmonic. We develop an exact analytical expression of the energy dissipation in the harmonic approximation, which allows to study the contribution of individual vibration modes to the overall dissipation. We show that dissipation arises mainly from the non-affine bending of Si-O-Si bonds triggered by the applied affine deformation. Moreover, this expression, valid both below and above the Ioffe-Regel (IR) crossover, extends the domain of application of the usual treatment of sound attenuation in glasses based on fitting the dynamical structure factor with damped harmonic oscillators, which is valid only below the IR limit.

Reference:

Damart T., Tanguy A., Rodney D. ‘Theory of harmonic dissipation in glasses’ *Physical Review B* **95** (2017) 054203.

**Keywords:** energy dissipation, atomistic modeling, harmonic dynamics

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\*Speaker

# Secondary relaxations in ultrastable glasses and their connection with structural relaxation

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Secondary relaxations persistent in the glassy state below  $T_g$  are remarkably relevant due to their connection to several properties of the glass. There are different types of secondary relaxations and not all of them are important for the same reason. One of the main concerns is to identify which of those secondary relaxations are relevant for their connection to the structural relaxation. Glass aging is often studied to understand this issue, but it is often insufficient, since it is a slow and inefficient process to explore the energy landscape. The so-called ultrastable glasses, formed by physical vapour deposition at proper growth conditions, exhibit density and enthalpy levels comparable to those ordinary glasses aged for thousands or millions of years, and permit to analyse the evolution of secondary processes in cases where aging does not provide any information. Here, we present a recent study on the secondary relaxations of several ultrastable glassy materials to identify different types of relaxations and its relationship with the structural relaxation. We show the existence of two clearly differentiated groups of relaxations: those which are slower in the ultrastable state and those which are faster, with respect to the ordinary unaged glass. For the first group, we find an unprecedented connection between secondary and structural relaxations in the ultrastable glass in exactly the same manner as in the ordinary glass, manifested through different properties, such as thermodynamic state or devitrification temperature at variable pressure. Furthermore, we propose a model based on density heterogeneities to distinguish between those relaxation which are connected to the structural relaxation and those which are originated from the particular microstructure of the material.

**Keywords:** Secondary relaxation, ultrastable glasses, physical vapour deposition, dielectric spectroscopy, organic glasses.

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# FIBERS 1

# Design of oxide glass composition for laser structuring and fiber manufacturing

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Direct Laser Writing (DLW) using IR femtosecond laser is offering new opportunity for fabrication of advanced components and devices by mixing both top down and bottom up material processing approaches. Oxide glass are of particular interest due to their intrinsic high transparency in the visible and the near infrared range. Laser structuring allows controlling different scales at once. Indeed, the control of micro- and nano-structures for photonics using laser/material interaction is challenging and relies on the control of the local electron/hole trapping, phase separation and diffusion processes.

One of the interest of glass is the possibility of modifying and adapting the material composition. Femtosecond laser structuring applied to silver-containing tailored glass allows creating a variety of photo-induced species or nanoparticles depending on the laser parameters but also the material glass composition. Unique three-dimensional optical structures with linear and nonlinear optical properties exhibiting dimensions below the diffraction limit becomes accessible [1, 2, 3].

Pristine glass structures has an important impact on the photo-induced modifications. Introduction of rare earth in glass has been investigated in order to take advantage of the silver ions reactivity toward femtosecond laser exposure. The fabrication of photosensitive silver-containing glass fibers has been developed [4]. Correlations have been established between fiber architectures, materials chemistry and photonics properties.

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\*Speaker

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**Keywords:** phosphate, photosensitivity, fiber, laser writing

# Intermediate-Tg glasses for multi-materials fibers

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Research on multimaterial multifunctional fibers flourished in the recent years, proposing an ever growing set of materials suitable for co-drawing as well as of fiber functionalities. So far however advances relied mostly on high-Tg silica-based materials ( $T_g > 1000$  °C) due to the technological interest of silica, and on low-Tg chalcogenide glasses ( $T_g < 250$  °C) that were deployed for integration in multimaterial glass/polymer/metal fibers.

Here we will review recent progresses in the feasibility of fabricating multimaterial fibers using glasses with intermediate Tg. The presentation focuses on phosphate glasses ( $T_g \sim 350$ - $450$  °C) and on tellurite glasses ( $T_g \sim 250$ - $300$  °C). Firstly, we report on the drawing of photosensitive silver-containing phosphate glass ribbon fibers. We demonstrate that luminescence properties of the native glass are preserved after shaping. Furthermore, we establish that the unique fiber's flat geometry allows for the direct, accurate Laser writing of complex luminescent silver clusters patterns and wave-guiding functionalities within the glass matrix.

Alternatively, we explore tellurite-based fibers. Here, bringing together the merits of these materials with fiber optic technology, we report on the direct drawing of tellurite-based core-clad dual-electrodes composite fibers. The rheological and optical properties of the selected glasses allow both to regulate the metallic melting flow and to manage the refractive index core/clad waveguide profile. We demonstrate the electrical continuity of the electrodes over meters of fiber. We believe the drawing of architectures merging electrical and optical features in a unique elongated wave-guiding structure will enable to develop new in-fiber sensing functionalities based on hybrid electric/optic nonlinear effects.

Great challenges lie ahead when it comes to mastering the implementation of intermediate-Tg oxide glasses within multimaterial fibers, but great opportunities lie ahead too, as it would give access to a whole new range of materials properties, and hence of functionalities, in linear/nonlinear optics, photonics, electro-optics or sensing.

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\*Speaker

**Keywords:** Phosphates, Tellurites, Glasses, Fibers



# Two octave mid-IR supercontinuum generation using tellurite step-index fibers

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The interest in the development of broadband supercontinuum (SC) fibered laser sources in the mid-infrared (MIR) never cease to increase in the last decade because of its potential in various fields of application such as spectroscopy, defense, medical science and others. Silica was first investigated for such system but tellurite glasses quickly become a more suitable alternative because of their 1-6  $\mu\text{m}$  transparency window, high nonlinear optical properties (10 times that of silica) and moderate dispersion (bulk ZDW around 2  $\mu\text{m}$ ). Microstructured optical fibers (MOF) are good waveguides to generate large supercontinuum but exhibit some ageing issues which leads to a decreasing efficiency in SC generation over time. To avoid this problem, high numerical aperture step-index fibers are an alternative. We report here a study on the drawing of a step-index fibers using a pair of tellurite with a refractive index difference of 0.138 at 1550 nm. Fibers with large core (40  $\mu\text{m}$ ) and small cores (between 3 and 5  $\mu\text{m}$ ) are drawn. The background losses for large-core step-index fibers are around 1 dB/m between 1 and 3  $\mu\text{m}$ . The chromatic dispersion of the small core fibers as a function of core diameter is discussed, and numerical simulations based on the generalized nonlinear Schrödinger equation are performed to explore supercontinuum generation in these fibers. Fibers exhibiting a flat dispersion with two ZDWs are then experimentally tested. The pumping of this fibers with an OPO near their ZDW allow the generation of a supercontinuum in the infrared with a good agreement between numerical simulations and experimental results. Different parameters such as pump wavelength, fiber length and the core size influence on the SC generation were investigated. The maximum extension we managed to obtain starts around 1  $\mu\text{m}$  and exceeds 5  $\mu\text{m}$ , covering the IR fingerprint patterns of various molecules.

**Keywords:** Tellurite glasses, Supercontinuum generation, nonlinear optics

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\*Speaker

# Recent advances in development of high-purity chalcogenide glasses for mid-IR fiber optics

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Chalcogenide glasses due to their optical and physico-chemical properties are promising materials for production of optical fibers for the mid-infrared range. The report gives the current status on preparation and investigation of high-purity chalcogenide glasses and fibers, as well as the ways for improvement of their optical properties and functional characteristics for passive and active mid-IR photonics. The methods for preparation of high-purity chalcogenide glasses of various systems, such as As-S, As-Se, Ge-As-Se, Ge-Se-I, Ga(In)-Ge-As(Sb)-Se, Ge-As-Se-Te and Ge-Te-X (X=I, Ga, Se or AgI), including glasses doped with rare-earth elements, have been developed [1,2]. To synthesize the high-purity glass samples, the multi-stage methods included the chemical distillation purification of glass and components, vacuum loading of components, as well as the chemical vapor transport reaction technique have been applied. The optical transmittance of the produced glasses, their structure, physico-chemical, optical linear and non-linear properties and the content of limiting impurities were determined. The prepared glass samples have ultra-low content of limiting impurities (in ppmwt): oxygen - < 0.1, carbon - < 0.5, hydrogen - < 0.02, silicon - < 0.1, transition metals - < 0.05. The main directions of investigations and technological developments for improvement of operational characteristics of chalcogenide glass fibers are considered. Using the "rod-in-tube" and "double crucible" drawing methods, the multimode and single-mode optical fibers were prepared; their optical and mechanical properties were investigated. Minimum optical losses in multimode As-S, As-Se, Ge-As-Se and As-Se-Te glass fibers in the mid-IR range were within 12-100 dB/km depending on composition. Minimum optical losses in REE-doped glass fibers were 400-500 dB/km [3]. The obtained optical chalcogenide fibers were tested for photonics applications.

This work was supported by the Russian Science Foundation (Grant No. 16-13-10251).

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**Keywords:** chalcogenide glasses, purification, impurities, fibers, optical loss, properties

# Preparation and characterization of high strength glass fiber from fly ash

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Glass fiber was made with different content of fly ash (25%, 35%, 45%) with silica, magnesia and calcium oxide. The influence of fly ash content on the glass drawing process and the properties of glass fiber were investigated. The results show that there is no crystallization occurring during the preparation process of fly ash glass fiber. The temperature needed for normal drawing increased with the increase of fly ash content, and the drawing flow rate decreased with the increase of fly ash content at the same temperature. The higher the fly ash content, the higher the tensile strength. Fly ash fiber acid resistance is superior to alkali resistance. The higher the content of fly ash, the acid resistance is better and the alkali resistance is worse.

**Keywords:** glass fiber, flyash, tensile strength, chemical stability

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## **FIBERS 2**

# All vapor phase ytterbium doped silica glass fabrication by outside vapor deposition combined to chelate flash vaporization

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The fabrication of fiber lasers requires the synthesis of high purity silica-based matrix doped with optically active ions. This glass material will then be used as core of an optical fiber with suited geometry. Yb<sup>3+</sup>-doped fibers are among the most widespread for high power applications based on large mode area (LMA) fibers because this ion possesses a simple energy level configuration and can be incorporated at high concentration levels into the silica network.

The historical way to realize such active glass is based on modified chemical vapor deposition (MCVD) and solution doping technique. Although this method allows reaching high concentration levels, some limitations remain such as radial inhomogeneity (concentration and refractive index) and small glass volume accessible. The use of vapor-phase approach based on chelates as Yb<sup>3+</sup> ions source has partly solved this problem and has contributed to the latest advances on LMA fibers designed for high-power applications.

Nevertheless, for the fabrication of very large mode area fibers, even larger glass volumes are needed. To overcome this limitation, we have developed an all vapor-phase approach based on the outside vapor deposition (OVD) combined to chelate flash vaporization. The flame hydrolysis of chlorides and chelates precursors permits to reach relatively high Yb<sup>3+</sup> concentration (0.6 wt.%) and to tune the optical properties of the glass by the incorporation of doping elements such as aluminum, germanium and phosphorus as well as fluorine. The resulting centimeter-sized glasses can be drawn into several meters of millimeter-sized active material used for the fabrication of micro-structured fibers. The chemical composition of these rods has been analyzed, together with the refractive index profiles and the optical properties of fibers. Low optical losses of 20 dB/km are reported at 1200 nm. Photodarkening experiments and laser efficiency measurement of fiber lasers obtained from these materials will be presented.

**Keywords:** outside vapor deposition, lasers, fibers and waveguides, rare earth in glass, absorption, silica, flash vaporization

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# Nanocrystal-Doped Glass Ceramic Fibers: Novel Near/Mid-Infrared fiber laser materials

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Fiber amplifiers and tunable fiber lasers working in near (NIR, 1.0~1.7 $\mu$ m) and middle infrared (MIR, 2~5 $\mu$ m) regions are being extensively investigated owing to their various potential applications in optical telecommunication, environmental monitoring, remote sensing and so forth.[1,2] PbS quantum dot (QD) doped glass fiber with tunable broadband NIR emission and rare-earth-ion (such as Er<sup>3+</sup>) doped glass ceramic fiber with enhanced MIR emission are well suitable for the above-described applications. Importantly, novel "melt-in-tube" method is developed to solve the key bottleneck problem of uncontrollable rapid growth of QDs or nanocrystals existing in traditional fiber-drawing technique.[3,4] Furthermore, thermal and optical properties between fiber core and cladding glass are well matched, which ensure that the structure of the precursor fiber is well preserved during the fiber-drawing process. The excellent spectroscopic characteristics and well-preserved structure suggest that the obtained glass fiber may be a promising material for fiber amplifiers and tunable fiber lasers.

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**Keywords:** Glass Ceramic Fibers, Nanocrystal, Near/Mid, Infrared Emission

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# Development of highly-doped rare-earth phosphate glasses for NIR and SWIR fiber Laser sources

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When compared to classical Laser systems, fiber Lasers are compact, robust devices allowing, due to their geometry, efficient thermal management and high-power generation. Because of the greatly advanced silica fibers fabrication process (purification, thermal drawing, etc...), most of fiber Laser developments were carried out on SiO<sub>2</sub>-based materials (technological improvement in pump, fiber design and fabrication techniques). Yet it appears that silica-based materials are not in many cases the most suitable candidates for the challenge that remain to be solved. Indeed, SiO<sub>2</sub> glasses offer low solubility for most of luminescent materials such as rare-earth or transition ions and are also very prone to photo-darkening effects. For this reason, the development of new type of glass fibers for lasing applications is of primary importance. In this work, we report on the fabrication of highly-doped rare-earth phosphate glasses for fiber Lasers applications. Phosphate glasses possess the highest rare-earth ions solubility as well as good chemical durability, excellent optical properties, good fiber-shaping ability and high threshold versus photo-modification processes. As a first step, zinc-phosphate host matrices doped with Neodymium were explored. Investigations concerning the optimal Nd<sup>3+</sup> ions concentration were carried out through emission luminescence and lifetime measurements of the manufactured glasses. Step-index fibers were then fabricated based on the developed glasses. Great efforts were put to reduce impurity as well as glass inhomogeneity-based optical losses. Different precursors

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and varying synthesis conditions were explored. Gain measurement were conducted. Finally the investigation was extended to Ytterbium and Erbium ions doping.

**Keywords:** Phosphate, Glasses, Fibers

# Porous silica glasses for rare earth ions heavily doped extra-large core fiber

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Rare-earth doped fiber lasers have important applications in high-speed optical communication, industrial processing, medical treatment, military defense and other fields due to their low pumping threshold power, high conversion efficiency, excellent heat dissipation, wide tunable range, high coupling efficiency and compact structure. However, there are some problems to be solved in fiber lasers. The biggest barrier is from the nonlinear effects such as stimulated Brillouin scattering(SBS), stimulated Raman scattering(SRS) and self phase modulation(SPM). In recent years, in order to solve these problems, researchers all around the world have carried out a great deal of study from fiber structure and gain media, and found that the large mode area short fiber can effectively suppress nonlinear effects in fiber and reduce the influence of ambient acoustic noise.

For the gain medium, in order to overcome the disadvantage of reducing the optical fiber power caused by shortening the optical fiber length, the doping concentration of the fiber must be increased.

Herein, we developed 3D nanoporous silica rods based on glass phase-separation technology to solve these requirements. Benefiting from uniformly distributed nanoscale pores, nanoporous silica glass exhibits remarkable performance in its doping level, refractive index controlling, core diameter, and optical homogeneity. These properties make nanoporous silica glasses very suitable as a fiber-core material and greatly distinguished from other fiber materials. We prepared a series of Yb<sup>3+</sup> heavily doped extra-large-core double cladding silica fibers based on nanoporous silica glass. The diameter of a typical extra-large-core fiber can reach to over 80  $\mu\text{m}$  with a negligible refractive index fluctuation. The fiber exhibits an excellent laser performance with a slope efficiency of 78% for 302 W laser emission at 1080 nm in a 55 cm length fiber. This study will make nanoporous silica glasses shining out new energy in fiber materials and will boost the advancement of high-power fiber lasers.

**Keywords:** nanoporous silica glass, active fiber, fiber laser, large mode area

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\*Speaker

# Effect of redox state of iron on properties of basalt fiber

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Basalt fiber with high strength, good temperature resistance and chemical resistance and other properties, are widely used in reinforced concrete and other composite materials. Basalt fiber was manufactured with natural basalt rock from China, and measured by XRD, SEM, XRF, fiber strength tester and visible spectrophotometer. The concentration of two different valence iron oxide were changed though adding oxidation agents or reduction agents in the condition of keeping the same total iron concentration. the influence of the redox state of iron on mechanical property of basalt fiber was studied. The result show, the tensile strength of fiber was increasing respectively by 30.56% when the redox state of iron dropping to 0.26. While the index rise to 0.80, the strength was decreased by 10.42%. It is inferred that ferric oxide is beneficial to improve basalt fiber performance as a network form.

**Keywords:** Basalt fiber, Redox state of iron, Tensile strength, Glass network

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# **FURNACE AND ELABORATION 1**

# Improving batch caking and melting properties by using calcined lime. An industrial experience

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Energy consumption is one of the biggest concerns in the glass industry, as it is one of the highest costs of the company, the main part being used for melting. These figures have always led glass industry to the search of new energy reducing alternatives, in technologies, raw materials and batch preparation methods.

Alternative raw materials for reducing energy consumption are already well known among glass technologists: glassy materials like slags, flux materials like lithium oxide, calcined materials like calcined lime or dolomite... All of them have been more or less widely tested on an industrial scale.

Calcined lime and dolomite have been largely proposed to container glass industry since long, but its use has always been limited due to the high cost of these materials, that can be hardly compensated by the melting benefits, being restricted to higher value-added glass products like fiberglass or enamels. In addition, many problems have been reported related to the manageability of these calcined products due to their high hygroscopicity, like dust, batch segregation, etc.

Batch caking or clogging is another problem that can occur in low cullet batches due to the sodium carbonate/moisture ratio. In factories producing high tonnage of glass with low cullet content and high moisture sands, batch caking can generate big problems in the batch plant conveyors and silos and in the furnace chargers, that, if they are not quickly solved, can prevent feeding the furnace and drive to a reduction of glass level.

Two years ago, Vidrala saw the opportunity of using calcined lime to solve the batch caking problems affecting one of its plants in Spain producing flint glass; in the meantime, it appeared to be also a good chance to verify the melting improving properties of this material. This presentation will show the industrial experience when testing the calcined lime and the results obtained on energy consumption, melting rate and batch caking behaviour.

**Keywords:** energy consumption, energy reducing alternatives, calcined lime, batch caking, batch clogging, melting.

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# Transition to CO<sub>2</sub> neutral glass furnaces: technological options and challenges

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The worldwide transition to durable energy resources will have major consequences for the glass manufacturing industry. The objective of this paper is to highlight the technological opportunities for CO<sub>2</sub> neutral melting of glass, including: flexible hybrid (green gas-electric) melters, full electric melters and application of low carbon combustion processes by power-to-gas conversion. The current status, advantages and challenges of these various technological solutions will be discussed. Moreover, the required knowledge development in view of designing new CO<sub>2</sub> neutral glass melter concepts will be outlined.

**Keywords:** glass melting furnaces CO<sub>2</sub> neutral

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# Platinum equipment for manufacturing of high quality glasses

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**Precious metals have vital roles in glass industry. HERAEUS is a leader in this technology.**

As for a metal, the glass must be melted then transported before to be moulded, shaped. Melting glass and transport are done inside furnaces and feeders made out of refractory oxides parts subjected to corrosion by liquid glass. The glass composition is then modified and charged of refractory oxide particles; this leads to 2 main things:

- many discards on final glass articles.
- The refractories age very quickly, resulting to rebuild the furnaces very often.

Productivity efficiency and high quality oblige the glassmakers to install "corrosion barriers" over parts subjected to corrosion damages; despite the development of better ceramics.

Platinum devices remain today the best solutions against the corrosion by molten glasses.

The Platinum systems for the manufacturing of specialized technical glasses are made up of a large variety of components. Each Platinum component requires different choice of materials.

The increased severity of the running conditions has needed the perfecting of materials: The **Platinum DPH** material has proved it in hardly conditions due to its higher strength and temperature resistance.

More than ten years ago, the company Heraeus and the University of Applied Sciences Jena developed a new ODS-Platinum materials with the aim of overcoming disadvantages of other ODS-platinum materials. These are the **Platinum DPH materials**. They have excellent properties, including good weldability and ductility. These materials are being used very successfully in industry, especially in glass melting equipment for high temperatures.

The ductile **DPH materials** compensate thermal expansion which occurs in use without being damaged. Other parts like stirrers need high torsional rigidity, then **DPH-A material** (a new type of DPH) is the perfect candidate for this application.

A solution of each applications, Heraeus people are there to find the best material you need for your application.

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\*Speaker

**Keywords:** Platinum, Rhodium, high temperatures, high strenght, funaces, crucibles, reinforced material



# Interaction of Gas Phase and Glass during Melting Process

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Glass melting and vitrification processes are accompanied by the evolution of a large amount of gases that exceed several times the volume of the resulting melt. During early stadium of the process, gases produced by chemical reactions form primary foam, the formation and collapse of which control the glass production rate via its effect on heat transfer to the reacting batch. Experimental methods of Evolved Gas Analysis and High Temperature Observation of reacting batch were used to identify and evaluate crucial chemical reactions. Heterogeneous bubble nucleation during production of commercial glasses is one of the negative factors affecting both technology and final product properties. We made the extensive research of bubble nucleation in soda-lime-silica glass melts containing sulphur compounds at variable redox state of glass. The phenomenon was studied quantitatively by a method of High Temperature Observation to determine the temperature at which the bubbles were nucleated on a platinum wire immersed in the melt. The intensity of bubble nucleation in the form of the number of nucleated bubbles and the volume of released gas versus time were also measured and described by theoretical equations. The fining action of sulphates at reducing conditions started at temperatures between 1200 and 1300°C. In addition, extensive nucleation of bubbles took place at relatively low temperatures. The nucleation of bubbles in variously reduced glasses has been observed at temperatures lower than 1300°C and further decreased with decreased redox state. The foaming and bubble nucleation on the level of the molten glass were observed in glasses containing sulphate when the water vapour partial pressure in the atmosphere exceeded 50 kPa. Reduced glasses show the nucleation also at a lower partial pressure of water vapour.

**Keywords:** Bubble, Foam, Nucleation, Glass melt

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\*Speaker

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# Nucleated bubbles in glass former liquids undergoing coalescence and growth

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2D spatial distributions and growths of nucleated bubbles during the remelting of glass samples forming by float process are experimentally investigated. To follow the bubble population undergoing coalescence, the temporal behavior of the Voronoï tessellation built by the bubble positions are monitored. During coalescence, the Voronoï cell areas are fitted by a single parameter Gamma distribution.

Numerical time simulation of population of bubbles undergoing coalescence shows an exponential increase of the parameter associated to the Gamma distribution with the fraction of coalesced bubbles in agreement with experimental observation. An initial density of nuclei is then estimated; direct observation would require an extremely high space resolution.

The bubble number density is two orders of magnitude larger on the side which was in contact with tin bath than on the other side in contact with atmosphere. Moreover, bubbles grow faster on tin side. From a thermodynamic and mass transfer models, we prove that tin reduces the glass former liquid which leads to an increase of dissolved sulfur explaining the more abundant bubble population and the enhanced growth rate on tin side.

**Keywords:** remelting, cullet, bubble nucleation, growth, redox reactions

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\*Speaker

# SSV's integrated approach for the assessment of quality and reliability of refractory materials

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In a Globalized World where low-cost suppliers of limited renown have entered the market of refractory materials for glass furnaces with products having very aggressive pricing, but "uncertain" performance level, the chance of striking a profitable deal today might be counterbalanced tomorrow by the risk of encountering service life issues, ranging from questionable glass quality to early catastrophic failure.

In order to avoid to fall prey either of conservative prejudice or of blind trust, Stazione Sperimentale del Vetro has developed an integrated approach to support glass producers in making a technically grounded choice of refractories suppliers for their furnace rebuilds.

The process consists of three main steps: first a reference performance benchmark is created on the basis of experimental characterisations of well known materials, having demonstrated good performances during past furnace campaigns.

Second, a detailed sampling and analytical plan, tailored for each specific furnace zone, is put in place to compare the key performances of various products of different suppliers, both among themselves, for the identification of the best candidate, and with the reference benchmark.

In particular, depending on the furnace zone, static or dynamic corrosion tests at various temperatures, exudation tests, alkali vapour resistance tests, blistering tests, etc are performed in SSV laboratories.

Third, the reliability of the suppliers, especially in the case of AZS materials, is assessed through an in depth audit of their production facilities, performed by experts of fused cast AZS science and technology.

In particular, the main parameters investigated during the audit are: installed technologies, production capabilities, technical proficiency and know-how, process control, quality management system, traceability, logistics, etc.

This integrated approach provides the glassmaker not only a wealth of information for the choice of refractories supplier, but also allows to assess an estimate of the future defect generation potential by furnace blocks.

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\*Speaker

**Keywords:** Glass melting furnaces, Refractories, AZS, Quality, Performance, Audit

# **FURNACE AND ELABORATION 2**

# In-situ Measurement of Reactions in a Glass-Forming Batch by Neutron Diffraction

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The effects of batch particle sizes on reaction behavior were studied in a sodium aluminosilicate glass-forming batch using neutron diffraction. The phase reactions were measured in-situ during heating to 1500 °C. Diffraction data was collected using VULCAN, the Engineering Diffractometer at the Spallation Neutron Source at Oak Ridge National Laboratory. The batch reaction kinetics were represented well by an nth order reaction model. The measured batch reaction path was compared to one predicted by a new model using a pseudo-equilibrium approach.

**Keywords:** glass, batch, diffraction, reaction kinetics

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# Development of low melting glasses as durable transparent enamel colors for the manufacture of decorated glass panels

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Today glass is broadly used in modern architecture. For applications indoor it is possible to produce decor glass by using enamel colors and glass painting techniques without any problems. However, this is more limited for applications outdoor. Humidity and environmental pollution attack the surface of the coating and damage it strongly. There are only few colors on the market which are resistant towards acids and bases until now. Additionally, most of those colors are opaque. In order to extend the color palette, chemically resistant colored glasses are being developed which are transparent, relatively low melting and intensively toned even in thin coat thickness. To achieve such ambitious aim, many parameters have to match which act in complex manner. Metal oxides were used to color the glasses. A lead-free glass composition was developed to avoid an exposition of heavy metals to the environment. The glasses were characterized, in particular in terms of their thermal properties, their crystallization and corrosion behavior as well as their chemical and environmental durability. Different practical applications will be shown.

**Keywords:** low melting glass, glass enamel, decoration, architecture, corrosion, chemical durability, environmental stability

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\*Speaker

# Behavior of a molten magnesium-aluminosilicate at elevated potentials

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Molten oxides represent a new medium to carry out electrolysis at very high temperature, typically above 1450°C. In molten state, electrochemical decomposition of refractory oxides can be studied by application of an electrical potential between electrodes.

An experimental device capable to perform this technique was designed in ArcelorMittal, allowing stable electrochemical measurements and the quantification of oxygen gas, produced by the faradaic reactions. In this study a magnesium aluminosilicate composition with varying iron oxide contents was put under an electrical tension of up to 6 V. To interpret the acquired charge transfer an ohmic drop correction was performed using the cell geometry and the molten oxide's electrical conductivity.

The presented results illustrate the electrochemical response of the molten glass to the applied electrical potential in dependence of iron oxide concentration. The corrected measurements show a diffusional mass transfer limitation in correlation with the varying iron oxide content. Further increase of the applied voltage then led to the decomposition of the aluminosilicate into oxygen gas, a liquid Fe-Si-Al alloy and a solid MgAl<sub>2</sub>O<sub>4</sub> spinel. The latter was formed due to the depletion of Fe- and Si- ions from the melt in the vicinity of the cathode. Ongoing application of the electrical potential finally resulted in the passivation of the electrode by the spinel phase and the termination of charge transfer.

**Keywords:** Molten oxide electrolysis, Molten silicates, Crystallization phenomena, Metal extraction, Electrochemistry

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\*Speaker



# High-temperature X-ray CT approach to the vitrification reactions of glass raw materials

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Vitrification process of raw materials is known to influence much on the melt behavior in glass melting tank and finally the quality of glass products. In-situ analysis has great benefit to understand physical and chemical behaviors of material on heating, and we are able to use various such techniques at the present owing to the development of basic technologies.

High-temperature X-ray Computed Tomography (CT) is one of them, and a powerful tool to provide us macroscopic status and alteration of materials. Especially, quantitative 3 dimensional datasets inform us the shape and volume of target materials. Our group has developed and used high-temperature X-ray CT instrument to understand the vitirification process of glass raw materials; industry glass batches and nuclear radioactive wastes. Batch blanket or cold cap are the places where the glass melts are formed. Reactions of materials produce new solid, liquid and gas phases, and determine the structural changes. Transportation of materials and thermal energy limit the reaction speeds, and total energy and cost consumed in melting. From X-ray CT analyses, we can know details of materials alteration on heating, and understand the effects of structure there on thermal insulating, vitirification speed, etc.

In this presentation, high-temperature X-ray CT analyses on soda-lime glass batch and nuclear radioactive wastes are reviewed, and a new detailed research result on the reaction phenomena of industry glass raw materials are focused, especially to understand the formulation of 1st liquid phase in raw materials.

**Keywords:** High temperature Xray CT, vitirification, glass batch, nuclear radioactive waste

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# **FURNACE AND ELABORATION 3**

# Sulphur balance and Carryover measurements methodologies

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Batch carryover is a well known phenomenon occurring in the glass furnace during the melting processes. It is mainly due to entrainment of solid particulates into the waste stream as it passes over the batch cover area (fine sand, lime and dolomite decrepitation, fine cullet and dust) and the condensation of the volatilized compounds from the exposed glass surface (sodium, calcium, magnesium, etc.).

The most important carryover effect is the deposition of materials in the regenerators with increase risk of plugging of the checkers and lifetime reduction of the refractory materials due to corrosion.

Furthermore aspects like glass type, glass oxidation state, capability of glass to absorb SO<sub>3</sub>, overall furnace functioning conditions and sulphur amount in the fuel are important in choosing the quantity of sulphate in batch composition. However the computation of sulphur oxides mass flows (Sulphur Balance) relative to glass furnaces, especially when filter dust is recycled, gives crucial information, which could be useful for different management purposes.

In spite of the method for determining the sulfur balance is well defined, unfortunately there are no uniquely defined methodologies to assess the carryover in a glass furnace.

In the first part of the presentation will be taken into consideration an empirical procedure to assess the sulphur balance. In the second part of the presentation will be compared two methods of sampling and analysis to investigate the amount of carryover in a glass furnace. The first method is based on a cooled suction probe connected with a series of impingers; the gas is withdrawn and the dust particles and condensed compounds adsorbed in a water solution. The second method whereas requires an alumina tube and a basket filter holder. The applicability and reliability of the methods will be assessed and discussed.

**Keywords:** Sulphur balance, Carryover

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\*Speaker

# Viscosity of soda-lime silicate glass raw materials during batch-to-melt conversion

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The viscosity of an industrial glass batch during conversion to molten glass within the temperature from 1050°C to 1300°C was measured at the shear rate of 0.02 s<sup>-1</sup> to access the effects of grain size and briquetting on glass batch melting. Based on the mass fraction of undissolved sand ( $x_s$ ), determined using x-ray diffraction analysis of quenched batches samples, and the gas phase fraction ( $p$ ), obtained from the volumetric measurements, we established the relationship  $\ln(\eta_b/\eta_m) = a_0 + b_s x_s + a_p p$ , where  $\eta_m$  the transition melt viscosity,  $a_0$  is the melt homogeneity coefficient,  $b_s$  is the coefficient for undissolved sand, and  $a_p$  is the coefficient for bubbles. The resulting coefficients of  $b_s$  and  $a_p$  were 8.756 and 0.658, respectively. The results indicated that undissolved silica sand strongly influenced on the viscosity. Due to the effect, finer raw materials and briquetting resulted in a lower viscosity during conversion. The result suggested that finer raw materials and briquettes are expected to enhance the melting rate of the batch blanket in an industrial melting furnace due to decrease of viscosity during conversion.

**Keywords:** Glass raw materials, viscosity, briquettes, particle size, melting kinetics

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# Advantages of ES III full automatic control of glass feeders

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This paper presents the advantages of ES III Advanced Process Control for glass feeders. Purpose of the feeder is to deliver a homogeneous gob of glass to the production machines. To achieve this the ES III system sets up all firing and cooling zones along the entire feeder within one integral Model-base Predictive Controller (MPC). The operator no longer has to specify temperatures in the individual conditioning zones. For ES III it is enough to specify just the final production temperature for the glass article at the feeder delivery, either in the spout or at a (multiple) triple thermo-element ('9-grid'). ES III sets the firing and cooling in the feeder as optimal as possible in order to minimize the risk for re-boil in the glass and to minimize the overall mixing pressure of the feeder burners, thus saving energy for heating the feeder. The ES III system can be continuously used 24/7, also during the job changes. After the job change the ES III system stabilizes the feeder temperatures as fast as possible so the new production can start with minimal delay and minimal production losses.

**Keywords:** Advanced Control, Glass Furnace and Feeder, Glass Conditioning, Energy Saving, Process Optimization

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\*Speaker

# Improve Glass Quality and Furnace Efficiency with advanced Simulation models

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Mathematical modeling of glass furnaces started around 1965. Such simulation models can reliably predict a glass melting furnace behavior and then help to improve its design, productivity and energy efficiency. The paper will show some the added value from new models with whom we can predict actual glass quality at a given furnace efficiency. What kind of melting efficiency can I expect from this new furnace? Mathematical models are a very good tool to help to select the best option, but they are not (yet) able to say exactly how many bubbles per kilogram of glass you will get. This is not only limited by the accuracy of the models, but also due to the fact that we cannot know now, how many bubbles per square meter per time unit will be nucleated. The good news is that if we assume a certain bubble source and a certain amount of nucleated bubbles, then "Yes," the model can help us to select the best furnace. This can be done by first calculating the temperature and velocity in the glass melt. Then the redox and gas distribution dissolved in the melt as well. For the model, we need to start the bubbles from an origin within the furnace and trace them. During the path of these bubbles travelling through the furnace, the gases can diffuse into and out of the bubble. In this presentation, we want to show recent developments and examples. Glass quality and furnace efficiency are calculated together for the optimal furnace operation.

**Keywords:** Glass Furnace Melting Optimisation, bubbles, defects, quality

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\*Speaker

# Thermoconvective instabilities of a non uniform Joule-heated liquid enclosed in a rectangular cavity

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The heating by Joule dissipation is employed in glass industry mainly for production of potentially volatile, polluting glasses, high added-value products and also for wool insulation. In this work, a numerical study is focused on a simplified model to mimic an electric glass furnace. Our investigation is limited to a two-dimensional enclosure with an aspect ratio equal to two. The energetic source is due to Joule dissipation produced by an electric potential applied with two electrodes corresponding of a fraction of the vertical walls.

The system of conservative equations of mass, momentum, energy and electric potential is solved with a finite element method. Three parameters are involved in the problem: the Rayleigh number  $Ra$ , the Prandtl number  $Pr$  and the electrode length  $Le$  normalized by the enclosure height.

The numerical method has been validated in a case where electrodes have the same length as the vertical walls leading to a uniform source term. The cutting of the electrodes from the bottom leads to a disappearance of the threshold of convection. At moderate Rayleigh number, the flow structure is mainly composed by a left clockwise rotation cell and a right anticlockwise rotation cell.

Numerical simulations have been achieved for a specific  $Le = 2/3$  with  $Ra \in [1; 10^5]$  and  $Pr \in [1; 10^3]$ . Four kinds of flow solutions are established characterized by a two-cell symmetric steady-state structure with down-flow in the middle of the cavity for the first one. A first instability occurs for which a critical Rayleigh number depends strongly on the Prandtl number when  $Pr < 3$ . The flow structure becomes asymmetric with only one steady-state cell. A second instability occurs above a second critical Rayleigh number quasi-constant when  $Pr > 10$ . The flow above the second critical Rayleigh number becomes periodic in time. When  $Pr < 3$ , a fourth steady-state solution is established when the  $Ra$  is larger than the second critical value characterized by a steady-state structure with up-flow in the middle of the cavity.

**Keywords:** electric furnace, natural convection, instabilities, numerical simulation

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\*Speaker

# GLASS-CERAMICS 1



# Novel Glass-ceramics from Glass Powders and Reactive Silicone Binders

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The processing of sintered glass-ceramics, i.e. material from the sintering of fine glass particles, with concurrent crystallization, is often conditioned by the debinding step. Typical carbonaceous polymeric binders, namely subjected to complete decomposition upon firing, may determine some defects in the final glass-ceramic directly, by causing some gas evolution continuing even at an advanced state of densification, or indirectly, by offering poor adhesion between particles (so that ‘green’ compact may be easily damaged). The present investigation is aimed at exploring a novel concept, based on the adoption of silicone polymers, providing an abundant ceramic residue after firing. Some glasses (belonging to the CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> and CaO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> systems), normally yielding useful glass-ceramics by heat treatment, were reproduced in form of ‘silica-defective’ variants, featuring a SiO<sub>2</sub> content, in the overall formulation, reduced up to 15 wt%. The overall silica content was recovered by mixing powders of the new glasses with silicone binders: upon firing in air, the interaction between glass powders and polymer-derived silica led to glass-ceramics with the same assemblage than those formed by the reference glasses. The new approach has been successfully applied to the manufacturing of glass-ceramic joints for SOFCs as well as of glass-ceramic scaffolds for tissue engineering

**Keywords:** glass, ceramics, additive manufacturing, silicones

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\*Speaker

# Crystallization of physical properties of aluminate glasses

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Aluminate glasses represent a suitable host matrix for optically active dopants. They are transparent in UV, vis and NIR, have lower phonon energies in comparison to common silicate glasses, and can accommodate higher concentrations of optically active dopants in comparison to their single- or polycrystalline counterparts of similar composition, such as yttrium- or ytterbium aluminium garnets, or the respective rare earth aluminate perovskites. The luminescence intensity and wavelength can be tuned by deliberate change of chemical environment of activators, either through tailoring chemical composition of the host matrix, or by changing the coordination sphere of the activator through controlled crystallization of the system. They can be also used as precursor powders for preparation of polycrystalline materials with various types of microstructures (e.g. submicrometre-sized polycrystalline materials, materials with eutectic microstructures etc.) In all three cases, detailed knowledge on mechanism and crystallization kinetics of host glass is required. Thermal and crystallization behaviour of various aluminate glasses prepared in the form of microspheres by flame synthesis from powder precursors obtained by the Pechini method was therefore studied by DSC, SEM-EDS, XRD and high temperature XRD. Fundamental thermal characteristics of glass microspheres with various compositions in the systems Al<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>-La<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>-Yb<sub>2</sub>O<sub>3</sub>, both undoped, and doped with up to 5 mol % of optically active elements (Ce, Er, Eu, Mn) were determined. The DSC data were analysed with the use of the Johnson-Mehl-Avrami-Kolmogorov (JMAK) model. In some cases the raw data were mathematically deconvoluted into two peaks representing two overlapping thermal effects. These were examined by the nucleation – growth Johnson – Mehl – Avrami model, autocatalytic Sestak – Berggren model and by Malek  $z(\alpha)$  and  $y(\alpha)$  functions. The influence of glass composition on crystallization characteristics and kinetic parameters was evaluated and discussed.

**Keywords:** Crystallization, aluminate glasses

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# Glasses containing halide perovskite nanocrystals and their potential applications

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Cesium lead halide nanocrystals have attracted much attention due to their particular optoelectronic properties. Stability of those perovskite nanocrystals synthesized through wet chemistry hinders the practical applications due to the sensitivity to moisture, oxygen and UV light. To overcome these problems, perovskite quantum dots are synthesized in glasses through melt-quenching and subsequent thermal annealing. Perovskite nanocrystals with tunable size, tunable composition, and tunable emission range can be achieved through adjusting thermal annealing conditions, light irradiation conditions, and ion-exchange. Perovskite nanocrystals thus formed in the glass have photoluminescence efficiency as high as 70% and strong stability against water, UV light, and temperature. Potential applications of these glasses embedded with perovskite nanocrystals towards spectral conversions will be discussed.

**Keywords:** Perovskite nanocrystals, Spectral conversion, LSC, LEDs

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\*Speaker

# Electrical transport in Li<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub>-GeO<sub>2</sub> glass-ceramics

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Mixed glass former system with the composition 40Li<sub>2</sub>O-(60-x)P<sub>2</sub>O<sub>5</sub>- xGeO<sub>2</sub>, x = 0-25 mol% was chosen for the investigation of the effect of induced crystallization on electrical properties. Gradual addition of GeO<sub>2</sub> units into phosphate chains causes a depolymerisation which leads to facilitated Li<sup>+</sup> ions mobility. Therefore, our interest was to investigate how various steps of crystallization influence the electrical transport in these glasses. Electrical properties of glass-ceramics have been studied using impedance spectroscopy and correlated with the results of structural analysis. Heat-treated glasses have been characterized by XRD, MAS NMR and SEM. With increasing GeO<sub>2</sub> content from single to multi crystalline phase glass-ceramics were formed. For GeO<sub>2</sub>-free glass-ceramic a slight increase in the electrical conductivity was evidenced whereas a conductivity decrease for glass-ceramics containing up to 20 mol% of GeO<sub>2</sub> is related to the reduction of number of Li<sup>+</sup> ions in residual glass matrix since the LiPO<sub>3</sub> crystalline phase was formed. The crystallization in the glass-ceramics with higher GeO<sub>2</sub> content causes an increase in the electrical conductivity due to formation of crystallites with well-defined shapes, which pronounces easy conduction pathways for Li<sup>+</sup> ions transport within crystalline grains and along crystalline grain boundaries. The contribution of grains and grain boundaries to the total electrical transport in these polycrystalline glass-ceramics is discussed in detail.

**Keywords:** Germanate glasses, Electrical properties, Glass ceramics

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# Phase separation and crystallization strategies to enhance the luminescence of silver and rare earth doped multi-phase glass and glass-ceramics

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Sub-nanometer noble metal quantum-clusters, such as [Agm]<sup>n+</sup>, are emerging as an attractive luminescent specie to develop new types of biosensor applications, optoelectronic devices, chemical sensing and optical recording media. However, metal nanoclusters tend to aggregate irreversibly so as to reduce the surface energy. An organic or inorganic scaffold is thus indispensably to be employed as stabilizing ligands to [Agm]<sup>n+</sup>. The reported maximum PL QY of organically stabilized [Agm]<sup>n+</sup> is 64 %, while that of inorganically stabilized has been up to 96.7%. It is easy to form mono-dispersed and heavily-doped [Agm]<sup>n+</sup> active quantum clusters in some inorganic glass due to the stabilization role of network tetrahedra, such as [BO<sub>4</sub>], [AlO<sub>4</sub>] and [ZnO<sub>4</sub>].

Trivalent rare earth ions (Ln<sup>3+</sup>) are also typical luminescent centers, but 4f-4f transition dominated PL of rare earths are usually parity-forbidden and suffer from their weak absorption and low efficient emission. On the contrary, [Agm]<sup>n+</sup> possess parity-allowed molecule-like PL transition with broad band width and high QYs. Mutually, codoping [Agm]<sup>n+</sup> and rare earths in an identical glass host should be a good strategy to mutually reinforce the spectroscopic performance of materials. However, energy transfers (ETs) between [Agm]<sup>n+</sup> and Ln<sup>3+</sup> will lead to a significant PL quenching. We thus propose to suppress such ET processes by means of typical behaviors of inorganic glass, which are phase separation and crystallization.

Here we prepared a series of glass-ceramics simultaneously containing [Agm]<sup>n+</sup>-enriched borate nano-glassy-phases, Ln<sup>3+</sup>-doped fluoride nano-crystalline phases, and residual silicate glass phases. On the one hand, the borate glass phase separation and fluoride nano-crystals are well isolated by the residual silicate glass phase. There is no mutual interference between [Agm]<sup>n+</sup> and Ln<sup>3+</sup>, ETs are well suppressed and QYs are greatly enhanced. The enhancement of QYs are as high as about 2 times than the precursor glasses. On the other hand, aggregation degree and charge quantity of [Agm]<sup>n+</sup> in the glasses could be well controlled to tailor the PL band via solubility and charge compensation strategies. It is further interpreted through a TDDFT simulation with B3LYP and LANL2DZ basis sets.

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\*Speaker

**Keywords:** [Agm]<sup>n+</sup> quantum cluster, Rare earth, Glass ceramics, Luminescence, phase separation, crystallization

# Influence of crystalline phases on optical characteristics of a glass-ceramic in the visible range

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Since 1958, opal glasses have been one of Arc France most popular produced products. Such compounds are obtained by melting a mixture of precursors through a cold-top furnace at approximately 1500 °C. Then, from a casting at about 1100 °C, forming machines give the shape to the glass articles that are subsequently quenched in air to achieve specific properties. The resulting ceramic glasses are characterized by a milky white color and exhibit a remarkable mechanical resistance. These opal glasses consist of a glassy matrix built upon silicon dioxide network containing crystalline fluoride phases (about 10 wt%). As reported in the literature, the presence of such well crystallized compounds causes the glass opalization (1,2). Few parameters such as refractive index, concentration, size and dispersion of the colorless crystalline particles strongly impact the overall color rendering. The desired control of all these parameters during the manufacturing process can be intricate but the impact of the aforementioned variables can be modelled via the 4-Flux method (3,4). Then, transmitted and reflected, diffuse and specular fluxes can be calculated and the impact of each of these parameters determined. The color of these ceramic glasses will be discussed based on this model through the correlation between simulation and observation. The role of the crystalline part nature will be specially highlighted.

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\*Speaker

**Keywords:** opal glass, opalization, optical properties, crystalline particles, transmission, reflexion, light, scattering



# Residual stresses in Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-ZnO-SiO<sub>2</sub> partially crystallizing glass-enamel

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Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-ZnO-SiO<sub>2</sub> partially crystallizing glass-enamel is used as a protective and decorative coating in various applications, such as glassware, automotive and architectural glass. Technical requirements for such enamel coatings are low glass transition temperature with excellent chemical durability and compatible thermal expansion coefficient.

The main drawback of this glass-ceramic system is their weakening effect on the mechanical strength of the glass substrate. One of the main root causes of this weakening are the internal residual stresses arising upon cooling. These internal residual stresses are induced by the thermal and elastic mismatch between the different crystalline and amorphous phases. Therefore, the degree of crystallization influences the thermo-mechanical properties of the glass-ceramic. Investigation of the microstructure evolution at different sintering temperatures can provide insight into the state of internal residual stresses of the microstructure at different sintering temperatures.

In this work, the formation of Bi<sub>4</sub>(SiO<sub>4</sub>)<sub>3</sub> and Zn<sub>2</sub>SiO<sub>4</sub> crystal structures with different temperature profiles have been investigated by X-Ray Diffraction. The crystallinity ratio was quantitatively determined by implementing the external standard method while the crystalline phases were quantified using Rietveld refinement method. Additionally, the crystal diameter and volume fractions of crystallized materials were assessed with the aid of SEM cross-section images and EDX analysis.

Finally, internal residual stresses are measured using focused ion beam ring core milling and digital image correlation (FIB-DIC). The internal residual stresses are then correlated with the microstructure and compared to calculated theoretical residual stresses.

An optimization of the enamel internal residual stresses by modifying the microstructure enables to reduce the weakening effect on the mechanical strength of the glass substrate, while fulfilling the technical requirements of the product.

**Keywords:** Residual stress, Glass enamel, Glass ceramic

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# GLASS-CERAMICS 2

# Nucleation kinetics of lithium disilicate glasses undercooled at various speeds

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The so-called statistical approach is used to analyze the nucleation kinetics of a stoichiometric lithium disilicate melts when cooled from above the melting temperature ( $T_m$ ) at various speeds. In this method, information is gained on the Poisson distributed lag-time of nucleation and the unique shape of the crystallization exotherm from  $> 200$  repetitive cooling runs of the same liquid volume at shallow undercoolings. Using a novel setup comprising of a water-cooled HT-DSC, the upper limit of the cooling speed in the temperature range from  $T_m+50$  K to  $T_m-150$  K was increased by a factor of four as compared to standard gas-cooled DSC devices, which enables us now to analyze cooling speeds of three magnitudes of order. For cooling at high speed bimodal distributed lag-times are evident which can be explained by a change in the nucleation mechanism or by nucleation at two different nucleation sites.

**Keywords:** Nucleation kinetics, LS2, DSC, statistical approach

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# Nucleation and crystallization of lithium silicate glass-ceramics: understanding of crack initiation

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Glass-ceramics are polycrystalline materials produced by controlled crystallization of glasses, and their properties are strongly dependent on the crystallization rate. The control of both composition and (micro-)structural arrangements (e.g. crystal size, shape, and orientation) has led to several applications for these materials, such as kitchenware, dental applications, optical device, bioactive implants, etc... Li-disilicate (LS2) glass-ceramics show great potential, especially for dentistry applications, because of the good aesthetic, high fracture resistance and bonding durability. Lately, it has been demonstrated that crystallite orientation in LS2 glass-ceramics significantly affects crack resistance.

In this study, LS2 glass-ceramics were synthesized starting from a non-stoichiometric glass. The coefficient of thermal expansion and elastic constants of the parent glass were determined experimentally, while the influence of different nucleating/crystallization temperatures and times on crystalline phases, crystal morphology, and mechanical properties were evaluated for the glass-ceramic materials. Indeed, it was verified both by Raman and XRPD the different crystalline phases occurring depending on temperatures and dwell times, and moreover, by SEM images the crystal morphology and crystallite volume fractions for various phases were estimated for residual thermal stress calculations.

Theoretical models were used to estimate the mechanical properties, and the data were compared to the mechanical properties experimentally obtained on different commercial samples, typically used for dental prosthesis applications.

**Keywords:** lithium disilicate, microstructure, mechanical properties, dental prosthesis

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# Structural transformations and optical properties of glass-ceramics based on ZnO, $\beta$ - and $\alpha$ -Zn<sub>2</sub>SiO<sub>4</sub> nanocrystals and doped with Er<sub>2</sub>O<sub>3</sub> and Yb<sub>2</sub>O<sub>3</sub>

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Structural transformations in potassium-zinc-aluminosilicate glass codoped with Er<sub>2</sub>O<sub>3</sub> and Yb<sub>2</sub>O<sub>3</sub> and subjected to heat-treatments in the temperature range from 680 to 1300 °C were studied by differential scanning calorimetry (DSC), X-ray diffraction analysis (XRD), transmission electron microscopy (TEM) and Raman spectroscopy. It was demonstrated that the structure of initial glasses depends on the concentration of the doping ions. The initial inhomogeneous glass contains either a small amount of ZnO nanocrystals of ~10 nm in size located in the phase separated regions, or an amorphous phase is RE-enriched. Transparent glass-ceramics based on nanosized ZnO crystals are prepared by heat-treatments in the temperature range of 700 – 800 °C. At elevated temperatures, in addition to ZnO nanosized crystals,  $\beta$ - and  $\alpha$ -Zn<sub>2</sub>SiO<sub>4</sub> (willemite), crystals precipitate and the material loses transparency. Crystallization of potassium aluminosilicates, leucite, KAlSi<sub>2</sub>O<sub>6</sub>, from the surface and calsilite, KAlSiO<sub>4</sub> from the bulk is observed. Absorption and luminescence properties of the initial glass and GCs based on ZnO,  $\beta$ - and  $\alpha$ -Zn<sub>2</sub>SiO<sub>4</sub> (willemite) and RE silicate nanocrystals are reported. Strong near-IR absorption at the wavelengths longer than ~1  $\mu$ m was detected. The effect of the RE<sup>3+</sup> ions on the appearance of this absorption is discussed; the possible reason is the formation of free charge carriers. Electron absorption and luminescence are assigned to certain crystals formation. In glass-ceramics, rare-earth (RE) ions are located in the residual glass phase until the heat-treatment temperature of 1200-1300 °C, when the crystals of RE<sub>2</sub>SiO<sub>5</sub> are formed, which results in a pronounced enhancement and structuring of the Er<sup>3+</sup> luminescence bands. This work was partly supported by the RFBR (Grant 16-03-01130). P.L. acknowledges financial support from the Government of the Russian Federation (Grant 074-U01) through ITMO Post-Doctoral Fellowship scheme.

**Keywords:** glass, ceramics, zinc oxide, willemite, X, ray diffraction, Raman spectroscopy, low,

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frequency Raman spectroscopy, luminescence

# Role of phosphorous in the nucleation of alkali aluminosilicate glass-ceramics

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Alkali aluminosilicate glass-ceramics have been extensively studied and industrially produced due to their low thermal expansion, high transparency and excellent thermal shock resistance. Bulk crystallization is a crucial step that can be controlled by employing various additives. P2O5 added to aluminosilicate glasses has been shown to be effective for bulk crystallization of some crystalline phases. It is thus a crucial issue to understand the role of phosphorus as a function of composition (alkali nature, alumina content). We have thus investigated the changes in the P environment occurring during the first steps of nucleation and growth of crystalline phases. Glasses of the systems Li2O-Al2O3-SiO2 and Na2O-Al2O3-SiO2 having different Al2O3/R2O ratios (R=Li,Na) and different P2O5 contents (0, 1 and 3 mol%) were prepared by melt quenching. DSC thermal analysis and XRD were performed to determine the crystallization profile of the glasses, and SEM and TEM allowed microstructure observation. The study of the environment around the phosphorous in the glass and its evolution with temperature has been done ex-situ by 31P MAS-NMR and correlation techniques such as 31P/27Al D-HMQC (Dipolar Hetero-nuclear Multiple-Quantum Coherence). We have evidenced different crystallization behaviors depending upon the Al2O3/R2O ratio. These behaviors have been related to different local environment of the phosphorus in the as-cast glasses. In particular, our study emphasizes the importance of POAl complexes in aluminosilicate glasses.

**Keywords:** Glass, ceramics, nucleating agent, glass structure, P2O5, NMR spectroscopy

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# Past, present, and future of bioactive glass-ceramics

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In 1969, Prof. Larry Hench discovered the first man-made material which forms a chemical bond with bone and initiated a whole new field of bioactive glasses and glass-ceramics. Later on, other bioactive glass-ceramics, such as Cerabone®<sup>®</sup>, Bioverit®<sup>®</sup>, and Biosilicate®<sup>®</sup> were developed and commercialized. Currently, there is an intense search for novel compositions and microstructural design of these materials. Additionally, the fracture toughness of these glass-ceramics (1-2 MPa.m<sup>1/2</sup>) is still in the lower range compared to cortical bone (2-12 MPa.m<sup>1/2</sup>). Bioactive glass-ceramics have been considered for low and medium load-bearing conditions, but their toughness (to K<sub>IC</sub> > 3 MPa.m<sup>1/2</sup>) and bioactivity should be promoted. 3D porous and mesoporous glass-ceramics for incorporation of biofactors, drugs, and cells are also promising for biomimetic regeneration of the complex structures of bone and teeth. Another potential application is hyperthermia treatment of cancer using magnetic bioactive glass-ceramics, and several other relevant examples could be given. Due to their inherent bioactivity and improved mechanical properties, bioactive glass-ceramics continue to be key candidates in the quest for adequate bone substitutes and scaffolds. There are clear signs that alone or in combination with other materials, such as polymers, these materials will find a wealth of applications for bone therapy in our aging population.

**Keywords:** Glass, ceramic, Bioactivity, Mechanical Properties, Biomedical

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\*Speaker



# Nucleation and Crystallization in LAS Glass Ceramics: Recent Advances in Understanding Fundamentals Based on Nanostructure Diagnostics

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From the base glass system Li<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (LAS), glass ceramics with low- or zero thermal expansion can be derived. They are of highest economic interest, especially because of their very good resistance to thermal shock, and are widely used for manifold commercial products, such as cooktop panels or large telescope mirrors.

Although the synthesis of such materials is state-of-the-art since decades, the fundamental principles of nucleation and crystallization of these LAS glasses are still not fully unraveled.

Based on techniques such as analytical transmission electron microscopy including energy-dispersive X-ray spectroscopy, X-ray diffraction and X-Ray absorption spectroscopy, we present new insights on the role of the nucleation agents ZrO<sub>2</sub>, TiO<sub>2</sub>, and the – usually applied - combination of both, on the course of crystallization within LAS glasses. The analyses of samples from different stages of annealing time at a fixed annealing temperature enabled the study of the temporal course of nucleation and crystallization within the LAS base glass. Coordination changes of the nucleation agents are monitored and interpreted, as well as nano- and microstructural changes within the LAS glass during the crystallization process - from the amorphous glass over the formation of first phase-separation droplets, to the precipitation of nanocrystals of the nucleation phases and, finally, to the subsequent growth of the aspired LAS crystals.

Furthermore, effects of a batch simplification on the crystallization behavior and microstructure formation in LAS glasses with ZrO<sub>2</sub> as nucleation agent will be shown and discussed.

**Keywords:** LAS, nucleation, crystallization, TEM, XAS

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# Controlled crystallization in luminescent lithium borate glass for LED applications

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The majority of white light emitting diodes (LEDs) is based on a blue light emitting diode with a yellow phosphor on top. The phosphor powder, which converts a part of the blue light from the LED into yellow light, is usually embedded in an organic polymer and directly coated onto the LED chip. Heat-induced degradation of the polymer-based encapsulate, however, results in an efficiency decrease and colour temperature change. Here, luminescent lanthanide-doped borate glasses and glass ceramics represent a promising alternative as frequency-converter. The borate glass system provides high transparency in the visible spectral range, good lanthanide ion solubility, and high mechanical stability. Lithium borate glasses optically activated with the lanthanide ions terbium (Tb<sup>3+</sup>) and europium (Eu<sup>3+</sup>) show a bright luminescence therein with quantum efficiency values of approx. 60 % (486 nm excitation) and 90 % (396 nm excitation), respectively. However, since the absorption coefficient of the lanthanide ions is low, only a small amount of the excitation light is absorbed resulting in a poor conversion efficiency. To increase the optical absorption by prolonging the optical pathway through multiple scattering within the glass, the as-made luminescent borate glasses are processed to glass ceramics in a subsequent annealing step. The focus of this work is on the analysis of the crystallization process in lithium-borate glass and the conversion from glass to glass ceramic. With in situ x-ray diffraction (XRD) the crystal growth for different annealing protocols is monitored. In addition, the influence of the grown crystallites on the optical parameters is investigated by optical spectroscopy and quantum efficiency (QE) measurements.

**Keywords:** luminescent borate glass, crystallization, in situ XRD, light yield, light distribution

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# Crystallization pathways and some properties of lithium disilicate oxynitride glasses

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Lithium silicates have been used as model glasses for scientific and technological studies of glass-ceramics because they easily crystallize in the interiors, even without the addition of any nucleating agent. On the other hand, partial replacement of oxygens with nitrogens affects most properties of oxide glasses, but its effect on the crystallization kinetics of the glasses has been poorly documented. In this work, we report, for the first time, on the crystallization kinetics of nitrated lithium silicate glasses. The oxynitride glasses were prepared by partial substitution of oxygen by nitrogen, up to 6 at.% N/(N+O), by melt-quenching the liquid under N<sub>2</sub> atmosphere inside a glove box. As expected, the density, microhardness, and Young's modulus of the glasses improved with increasing nitrogen content. Higher values of glass transition and crystallization peak temperatures were also obtained with an increase in the nitrogen content. Rietveld refinement analysis after adequate thermal treatment revealed that addition of nitrogen led to increasingly higher contents of lithium metasilicate at the expense of the (expected) lithium disilicate crystal phase. Crystallization kinetic parameters such as the activation energy and Avrami index were calculated using Ozawa's equations. These two parameters also increased with increasing nitrogen content, whereas the crystal growth rates decreased with increasing nitrogen content. The above-described changes in the properties of the oxynitride glasses are straightforwardly explained by the increase in the connectivity of the glass network, which results in enhancement of the atomic packing density owing to partial substitution of two-coordinated oxygens by three-coordinated nitrogens.

**Keywords:** Crystallization, oxynitride glasses

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\*Speaker

# On the search for appropriate nucleating agents in BaO-SrO-ZnO-SiO<sub>2</sub> glasses

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Recently, a new crystalline phase with the formula Ba<sub>1-x</sub>Sr<sub>x</sub>Zn<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> was found which shows a very low or even negative thermal expansion behavior. However, since this phase shows a pronounced contraction in the direction of the crystallographic b-axis while it expands in a- and c-direction, the thermal expansion is highly anisotropic.

In BaO-SrO-ZnO-SiO<sub>2</sub> glasses, this solid solution phase can be precipitated in high concentrations. However, these glasses normally tend to surface crystallization and due to the strong anisotropy of the coefficient of thermal expansion of this phase, the obtained glass-ceramics often show micro cracking limiting the preparation of larger samples. In order to overcome the as mentioned difficulties, the crystallization mechanism has to be switched to bulk crystallization by the use of appropriate nucleating agents and a high number density of volume crystals has to be precipitated.

This paper describes the effect of different additives such as P<sub>2</sub>O<sub>5</sub>, SnO<sub>2</sub>, or CeO<sub>2</sub> on the crystallization behavior and their ability as nucleating agent was studied. Phase formation and microstructure of the glass-ceramics were investigated using thermal analyses, X-ray diffraction, as well as scanning electron microscopy. Moreover, the thermal expansion behavior obtained from dilatometry was correlated with the microstructure. The appearance of micro cracks can be attributed to certain crystallographic directions using electron backscatter diffraction.

**Keywords:** Glass ceramics, nucleation, thermal expansion, microstructure

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# Crystallization and ordering process in stoichiometric cordierite glass-ceramics with TiO<sub>2</sub> as nucleating agent

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Glass samples of stoichiometric cordierite composition, increasingly doped with TiO<sub>2</sub> as nucleating agent, were ceramized up to 1300°C and analysed to highlight differences in their crystalline evolution. Employed analytical methods included (HT)-XRD, DSC, Raman spectroscopy and SEM. The specimens displayed a gradual transition to effective bulk crystallization with increasing TiO<sub>2</sub>-doping, manifested by earlier and sharper formation of HQss. The further phase transformation into indialite equally appeared to be influenced by TiO<sub>2</sub>-content and to be closely related to the compositional and structural evolution of the seed formers, Mg-Al-titanate and rutile. Furthermore, the indialite-cordierite ordering process was investigated by computation of Miyashiro's index[1] and Raman splitting at various temperatures: remarkable differences in ordering were spotted between surface and bulk of the samples, again hypothesized to be connected to the stability of Ti-bearing phases.

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**Keywords:** glass, ceramics, indialite, cordierite, rutile, XRD, Raman, surface, bulk

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# GLASS TECHNOLOGY AND CURRENT TRENDS

# Release from glass production process and regulation constraints : what to expect

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Beside glass properties, glass industry is also challenged on the process used to produce glass articles. Constraints are focusing on chemical used and worker protection but also on releases from glass plants.

Main releases from our activities are NOx, Sox, dust and greenhouse gases.

I propose to present main releases evolution from our sector in France and the main expectation from our authorities regarding releases from our activity.

**Keywords:** Glass production, Regulation constraints

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# Chemical Agents Exposure in the Glass Industry: assessment and main issues

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The chemical agents workplace assessment and evaluation in the glass industry is one of the activities that SSV currently carries out: the aim is to investigate the exposure of the workers to the main chemical agents, assess the related risk and define possible corrective actions.

The risk of exposure is mainly related to the type of raw materials used in the production, the type of process applied, the type of protection system adopted and finally the type of classification available for the specific substance. Such risk assessment is an important step and requires a deep knowledge of the process workflow and relate activities.

The main chemical agents that need to be analysed are: respirable crystalline silica (sand); hydrochloride acid and MBTC (hot end); Polycyclic Aromatic Hydrocarbons (forming), Soluble Nickel (mould soldering), Refractory Ceramic Fibres (insulation), etc. To assess the risk of exposure of these chemicals different methodologies can be used: such methods are not always the same and can change countries by countries.

The introduction of the REACH Regulation is still increasing the framework complexity; in fact the risk assessment has not only to abide by the CAD (Chemical Agent Directive) and CMD (Carcinogenic Mutagen Directive), but also the Exposure Scenarios defined by the supplier for the specific application.

The aim of the presentation is to provide an overview of the main pollutants present in the workplace of the glass industry and the relative methodologies applicable for their characterizations. Specific cases will be discussed, such as Respirable Crystalline Silica, MTBE, soluble nickel. Finally an investigation of the main problem link to the Exposure Scenario under the REACH Regulation will be analyzed.

**Keywords:** glass

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# CO2 laser processing of fused silica surfaces for high power laser applications

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CO2 laser processing of silica is used in many scientific and industrial applications, such as micromachining to produce optical components, processing of optical fibers, polishing of micro-optical components, production of free form optics, generation of holographic structures.... The 10.6- $\mu\text{m}$  irradiation by CO2 laser, is particularly adapted for fused silica because the energy is effectively absorbed within a few microns of the surface. Thermal effects subsequent to absorption induce heating of the material, temperature gradients, decrease of viscosity, viscous flow, evaporation and potentially material ablation. Such physical effects, if well controlled, can be used for micro-machining, polishing, annealing or other thermal treatments of the surface. The laser silica interaction process can however generate some detrimental effects for applications such as debris, thermo-mechanical residual stress, birefringence, reduced mechanical resistance, surface profile modifications due to viscous flow, densification... Therefore the laser material interaction has to be well controlled and understood for efficient process developments. In this communication we report on our work on the application of CO2 laser processing of fused silica optics for high power applications. Particularly, the targeted application is the improvement of the laser damage resistance to UV nanosecond pulses, in the context of the Laser MegaJoule project. Such processes include micro-shaping, surface smoothing, laser-based annealing and defect removal. In this presentation we will describe the experimental system and processing methods, as the characterization techniques that have been developed to measure the surface profile of treated fused silica optics and the residual birefringence related to thermomechanical stresses. We will also discuss about the development of a comprehensive thermo-mechanical numerical model, based on finite-element method, to simulate the laser material interaction and its effect on fused silica.

**Keywords:** fused silica, laser applications, optical properties, laser interaction, birefringence, thermal treatments

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\*Speaker

# ”Transparent Intelligence” for Sustainable Development

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Transparent materials are essential in everyone’s life. They enable daylight to reach the interior of buildings, thereby contributing to both our physical and mental well-being; they are the primary component for communication via optical fibers and a key component in electronic devices such as protective cover and/or dielectric material; and they enable clean energy production through solar panels or algae reactors by acting as protective and light transmitting barriers. Adding functions to transparent materials in an intelligent way creates further opportunities to use and enhance the beneficial impacts of transparency. The concept *Transparent Intelligence* covers transparent materials and products with integral intelligent functions – passive, active or interactive. By using Transparent Intelligence it is possible to embrace many of the societal challenges that we are facing today. The concept can be divided into five broad industrial sectors: Built Environment, Information and Communication Technologies (ICT), Solar Energy, Mobility, and Materials. A perspective on how Transparent Intelligence can improve the sustainable development of our world will be presented, using examples of electrochromic windows for energy-efficient buildings, photocatalytic coatings for improved indoor air quality, transparent conductive coatings for antennas, bandpass filters for mobile phone indoor coverage, UV down-converting components for efficient solar energy, hygienic surfaces for infection mitigation on electronic devices, printed electronics for sustainable glass packaging, and IR-reflecting coatings for fire safety.

**Keywords:** Transparent materials, functional materials, solar energy, information and communication technologies, mobility, built environment

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# Characterization of glass produced from glass wool batch containing simulated end of life LCD waste glass

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Due to the drastic growth of the liquid crystal display (hereafter LCD) industry in the last decade, lots of waste glass is being produced. There are three types of waste glass: 1) LCD cullet from LCD glass manufacturers, 2) LCD process waste glass (hereafter LPWG) from LCD panel manufacturers, and 3) end LCD waste glasses (hereafter designated EOL-LWG) from end-of-life LCD devices. Among them LCD cullet is being recycled into a raw material for commercial electric continuous fiber glass (E-glass). However, the recycling of LPWG and End of Life LCD waste glass (EOL-LWG) is limited due to various reasons such as contaminants, toxic components and inhomogeneous glass compositions etc. Especially, it seems to be difficult that EOL-LWG derived from glass produced before 2011 is recycled positively because it contains toxic components such as As<sub>2</sub>O<sub>5</sub> and Sb<sub>2</sub>O<sub>5</sub>.

In this study, several alkali borosilicate industrial glass wool batches with three kinds of simulated EOL-LWG up to 20wt% of resulting glass were prepared. The simulated EOL-LWG was a mixture of different glasses produced before 2011. Some melt properties such as viscosity and liquidus temperature related with glass production were determined. Additionally a chemical stability of resulting glasses was estimated by the toxicity characteristic leaching procedure (TCLP) method of the U.S. Environmental Protection Agency (EPA).

According to results, the forming temperature corresponding to 10<sup>3</sup> dPas and liquidus temperature showed no serious behavior within investigated range. In the solution extracted by TCLP method As and Sb were not detected. Under the control of compositional tolerance for EOL-LWG its recycling possibility is suggested as a raw material for glass wool.

**Keywords:** recycling, LCD waste glass, glass wool, toxic component, leaching

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# Intelligent Coatings for Energy-Efficient Glazing of Glasses

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Energy used in buildings, for heating, cooling and lighting, accounted for roughly 30% of China's and 40% of the EU's total energy consumption. These heating and cooling costs are directly influenced by architectural design. Increasingly, governments are regulating the energy efficiency of new or refurbished buildings, and one of the main features that can impact total building efficiency is glazing. In which, the thermochromic coating based on VO<sub>2</sub> is one of the most important materials. In this talk, we will present the state-of-arts of thermochromic materials and some results on the materials preparation by magnetron sputtering, chemical vapor deposition and sol-gel methods. The microstructural control, materials modeling and the mechanism of phase transformation will be also discussed.

**Keywords:** thin film, VO<sub>2</sub>, coatings, thermochromic, sputtering, sol, gel, CVD

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\*Speaker

# HERITAGE HISTORY 1

# The color of the stained glasses of the Reims Cathedral : a witness of Middle Age technologies

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We present spectroscopic and colorimetric data on stained glasses from the Cathedral of Reims (France), among the first French monuments registered as a UNESCO World Heritage Site. This investigation has taken advantage of the restoration of the Grande Rose window (built around 1275) on the western facade. Due to previous restorations over the past centuries, the western rose contains stained-glass pieces of a large variety of colors and periods (mainly from 13th, 16th and 20th century).

We have performed a systematic spectrometric and colorimetric analysis on the stained glasses just after their restoration, and we have used contactless devices, for allowing in situ measurements. Indeed, the analysis of historical stained glass windows has to follow standards of ethics, using only non-destructive and non-invasive techniques. For that purpose, a homemade portable UV-visible-NIR transmission spectrometer has been designed to investigate cultural heritage artifacts as historical glasses (Hunault et al, *Appl. Spectr.* 70, 778). We also systematically measured glass thicknesses, which evidenced variation of thickness depending on color. We wonder whether these differences were intentional or if different colors were produced by different glassmakers.

The assignment of the absorption bands and their relative intensity provide unique information about this glass, with special attention to the evolution of glass-making techniques and to the mastering of glass coloring. A particular attention was paid to the dispersion of the colorimetric parameters, because of the symbolic significance of most colors. The influence of the successive restoration periods was also systematically investigated.

This spectroscopic approach allows us to follow the evolution of color with the successive glass-making techniques and glass formulation recipes . In our case, we observed that modern glassmakers produce glass with colors that very close from the medieval glasses, making impossible authentication on the sole color criterion, except in the case of chromium colored glasses,

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for which we show the effort of glassmakers to adapt their compositions and glass-making to obtain a color similar to that of medieval glasses.

**Keywords:** stained glasses, glass color, optical absorption spectroscopy, transition elements

# Reconstruction of technology of layered red glass production based on chemical analysis of discovered glass fragment.

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In the 16th century, the Bohemians have succeeded in preparation of a more stable and colourless glass, which could be etched and cut with significantly less risk of breaking comparing to glass from Murano. Deposits of limestone and silica together with the newfound recipe for preparation of potassium rich flux (potash) enabled Bohemian industrial glass production to flourish. Bohemia's industry boomed, with over 34 factories during the 17th century producing top quality glass products. In the second half of the 19th century, Bohemians eager to expand export and mass-produce glass developed a line of vases in a single colour of opaque glass or in two colour cased glass, where one is ruby red. Reconstruction of technology for red glass, produced in central Bohemia, have been investigated. Glass fragment was found in the central part of the Czech Republic near Havlíčkov Brod, at a site of abandoned workshop producing glass between 18th and 19th Century. SEM EDS/WDS and LA ICP MS have been used to characterize and investigate the glass finding. Examination of a cross section revealed a chromatic layer placed between two colourless glassy phases. In the colourless layer, crystal assemblages of various shapes were identified. This glass compositionally belongs to the group of soda lime silica glasses. LA ICP MS confirmed the presence of manganese, copper together with another metals as cobalt, lead and arsenic in the chromatic layer. The role of particular elements contributing to coloration of intermediate layer and a technology of production of layered glass was discussed.

**Keywords:** glass, composition

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# Glass archaeometry in the aspect of cultural heritage

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Glass has been known for aged, as a evidence of the development of that civilization, its culture and industrial progress.

First of all we have to divide glass, as a material production, for natural glass and that create by man. Subject of this presentation has been focus on the discovery the past, and artefacts of previous generations

The possibility of testing materials has developed very slowly. Since the nineteenth century, and especially in the second half of the twentieth century, due to the overall development of science, with particular emphasis on materials science, the options for analyzing historical glass have become almost limitless.

Instrumental methods and computerization have evolved, and so has awareness of the need for interdisciplinary cooperation among conservators and archaeologists, as well as engineers and materials science scientists. This principle of combining sciences to decipher material history on many level also enabled technologists to be involved in archaeological research, specialists in materials science, materials experts to deepen the information about the nature of the material of the object and creation.

It is a field of archaeological research which aims to confirm the authenticity, age, and origin of finds and archaeological objects and to determine which technologies were used to create them on the basis of their chemical composition. In addition, it is important to establish the condition of the object through macroscopic and physical research. Such analysis of historic articles also contributes to the knowledge of the culture and way of life of our ancestors .

The interest in this issue is best demonstrated by the number of emerging articles about the study of the types of historical glass.

In addition, during a number of scientific conferences, separate thematic sections under the heading of archaeometry are prepared. This also creates the possibility of working partnerships with other research institutions. An example of the importance and development of the archaeometry of glass in the world is the creation of a separate technical committee which deals with archaeometry as part of the activities of the International Commission on Glass.

**Keywords:** glass, corrosion, culture herititage, culture development

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\*Speaker

# Identification of Factors Relevant to Preservation of Claude Laurent's Glass Flutes: Model Studies vs. Actual Observations

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The GWU-LOC-VSL team is studying glass flutes made in Paris by Claude Laurent from 1806-1848. Less than 200 flutes exist today worldwide, and 20 are housed in the Library of Congress's Dayton C. Miller (DCM) Collection. The project is aimed at improving care for these rare musical instruments through better understanding of glass deterioration observed in many of the flutes. Initial sampling of glass from damaged joints of two of the flutes enabled composition analyses and direct observation of a modified surface layer resulting from about 200 years of natural aging. These analyses have been supplemented by two complementary lines of inquiry: studies of glass simulants, and continuing non-destructive assessment of the actual flutes (microscopy, surface pH, fluorescence, XRF, fiber optic reflectance spectroscopy (FORS)). Unexpectedly, to date only 2 out of 20 DCM Collection Laurent flutes may be identified as high-leaded "crystal," while the remaining flutes are composed of potash glass formulations. The rarity of leaded glass instruments by Laurent and his workshop has been verified by examination of 21 additional flutes and piccolos in other collections. The two sampled DCM flutes contain only three major components: SiO<sub>2</sub>, K<sub>2</sub>O (ranging from 16.5 to 20.5 wt%), and CaO. These types of flutes are prone to attack by moisture, while the leaded glass flutes appear in relatively stable condition. Studies are proceeding toward assessment of the relative risk factors of the potash glass flutes. Simulated glasses of simplified compositions spanning the potassium range, plus two representing the actual flutes sampled, and one PbO-glass were prepared and subjected to aqueous attack by accelerated aging methods. Preliminary results have previously been reported, but this presentation will report the results of more extensive testing, provide quantitative values for kinetics of attack, and highlight variation as a function of composition. Results of the model studies will be compared to recent non-destructive analytical characterization of the actual flutes to assess the preservation needs of these exceptional historical artifacts.

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\*Speaker

**Keywords:** Nineteenth, century glass, Claude Laurent, tranverse flute, potash glass, leaching, microscopy

# From words to objects: the art of glassmaking through recipes

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Glass is part of our tangible cultural heritage, present in diverse cultural and creative expressions. In this research we aim to create new knowledge based on the link between historic documentary information on glass production and the produced historical glass objects. This is fundamental for the discovery of new information and insights into the history and conservation of our material culture, impacting its preservation, interpretation and appreciation. Representative recipes of glass-based paints, such as grisailles, yellow silver staining, enamels and sanguine red, are being selected from treatises and recipe books dated from the 15th century to the 19th century and reproduced in laboratory. These allows the characterization of this paint material with analytical techniques such as Optical Microscopy (MO), X-Ray Diffraction (XRD), Particle Induced X-ray Emission (PIXE), Scanning Electron Microscopy (SEM) and Colorimetry. The results are being correlated with historical glass paints applied on stained-glass aiming to understand how this historical written information represents the practices at the stained-glass workshops.

**Keywords:** historical reconstructions, conservation, archaeometry

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\*Speaker

# HERITAGE HISTORY 2

# Archaeometrical investigation of protohistoric glass from southern Italy: from Early Bronze Age to Advanced Iron Age (18th-6th century BC).

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This work reports the results of an archaeometrical investigation performed on 145 glass beads dated from the Early Bronze Age (18th cent BC) to the Advanced Iron Age (6th cent BC), coming from 14 Southern Italian sites. Moreover, it offers, for the first time, a general review of our knowledge on the protohistoric Italian glass. Since a quite large amount of data is available in literature on Bronze Age glass from Northern Italy (e.g.: Angelini et al., 2005), while very few are available for the South, the aims were: to determine the raw materials and the technologies employed for the glass production, to suggest hypotheses regarding their provenance, but also to compare the Northern and Southern Italian glass in order to verify their supply routes. The research was carried out with: ESEM-EDS for textural study; Electron Microprobe (EMPA) for major and minor elements, and LA-ICPMS for trace elements; isotopic analyses for the determination of the Sr and Nd isotopic signatures, were also performed. The results provided evidences of a great complexity in the chemical composition and production technologies, as enhanced by the presence of mixed alkali, plant ash and natron glass. Among the natron samples there are: classic natron, alumina cobalt blue produced with cobaltiferous alums as colorant, black glass with high iron (10% FeO) and high-alumina glass (10% Al<sub>2</sub>O<sub>3</sub>). Trace and REEs analyses provided more detailed information on the raw materials, while the comparison of our trace results with those reported in literature, and the Sr-Nd isotopic signatures, allow to make hypothesis on the glass provenance. This study demonstrates the existence of different trade routes, most of all in the Early and Middle Bronze Age 1-2, when Northern Italy was involved in the trades with the Central Europe, while the South was already inserted in the Mediterranean interactions.

## REFERENCES

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\*Speaker

**Keywords:** archaeometry, glass, bronze, iron ages, trace elements, provenance, Southern Italy

# A new style of inside painting glass sculptures

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Traditional inside painting techniques of Chinese snuff bottles have developed over more than 200 years into a popular form of Chinese folk art, often based on glass snuff bottles with painted decoration on the inside. The craftsmen who make these pieces usually pay more attention to inside painting skills and overlook their own artistic expression. The designs used tend to be repetitive and copies of existing designs from other media such as ink painting or photographs. In this research, a body of inside painted glass works was produced to show how the glass form and painted content were combined. These works also helped to establish possible ways to reduce the limitations of traditional inside painting of Chinese snuff bottles. It has attempted to create a ‘new style’ for Chinese traditional inside painting through the creation of contemporary glass sculptures.

**Keywords:** Inside painting, snuff bottles, new style, contemporary glass sculptures.

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\*Speaker



# Micromechanical properties of altered surfaces of archaeological glass fragments

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Surfaces of glasses exposed to weathering in aqueous environments undergo after long periods of time considerable alteration due to ion exchange, hydration and hydrolysis resulting in opaque crusts or iridescent layers. The morphology of the alteration layer of archaeological glass fragments depends on environment. For land-based environments banded layers (parallel to the surface) were observed, while marine environments showed besides banded textures, flaky and spongy morphologies of alteration. Going in hand with changes in the morphology and the chemical composition of the alterations, mechanical properties of the glass fragments and their alterations are observed to vary considerably which are tested by micro bending and Vickers indentation. Studies are intended to shed light on the mechanical robustness of archaeological glass fragments and the cohesion between alteration textures and unaltered glass.

**Keywords:** archaeological glass fragments, surface alterations, micromechanical properties

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\*Speaker

# Gentilshommes verriers, mythe ou legende?

Stephen Pollock-Hill \* 1

<sup>1</sup> Stephen Pollock-Hill (GMF Ed Trust Chairman and Trustee) – c/o British Glass Sheffield, United Kingdom

Gentilshommes verriers ,mythe ou legende?  
Gentlemen Glassmakers, myth or legend?

Throughout history, or at least since the time of the crusades, glassmaking has had an almost secret mystique about it; similar in a way to turning base metal into gold, akin to alchemy.

Why was this? Why did most of the seventeenth

and eighteenth century glass works in Europe, belong to aristocratic families, e.g. les Comtes de Vogue in France, Baccarat in Lorraine founded in 1764, by Prince Bishop Cardinal Louis-Joseph de Laval-Montmorency – (and recently sold to a Chinese company), Cristalleries de St Louis -1586 in Lorraine, Glasfabrik Freiherr von Pochinger(1568) in Frankenau, Bavaria, and The Duke of Buckingham's Plate Glass Works, Vauxhall, London.

These "men of glass," were often referred to in contemporary literature and documents as "gentilshommes verriers" (or gentlemen glassmakers), In England men like Sir Robert Mansell, George Ravenscroft, Thomas Webb, and Harry, later Lord Pilkington of St Helens, and his distant cousin, the scientist Sir Alastair Pilkington carried the fame of their achievements in glass, right up to 2009 Nobel winner Sir Charles Kao the inventor of modern fibre optic.

The speaker Stephen Pollock-Hill is a second generation glassmaker and the family own the ten acre site on which the glass works stands.

Although not a maker of flat glass, recently they have helped create a room of mirrors for the re-opening of the new poshest top night club in London Annabels.

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\*Speaker

**Keywords:** History, Heritage, scholar, gentilshommes verriers

# Investigating ancient glazing processes: Lead-glazed earthenware of Bernard Palissy (1510-1590)

Gauthier Roisine <sup>\*† 1</sup>, Anne Bouquillon <sup>2</sup>, Daniel Caurant<sup>‡ 1</sup>, Laurent Cormier <sup>3</sup>, Odile Majérus <sup>1</sup>, Gilles Wallez <sup>4</sup>, Thibault Charpentier <sup>5</sup>

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Bernard Palissy (1510-1590) produced outstanding lead-glazed ceramics that made him very famous during his life and are still regarded as an example of technical skill today. Since the sixteenth century, many potters have risen to the challenge heard by Palissy and have tried, more or less successfully, to imitate his work. The question of his original glazing process remains nonetheless unresolved.

By chance, we have today access to a unique archaeological material excavated between 1984 and 2003 from his workshop in Paris, that give us a chance to discover his manufacture process through a replication and comparison approach between glazes originating from Palissy's workshop and synthesized in our laboratory. In this work, we focus on the characterisation of yellow to brown transparent glazes.

The analysis of 15 archaeological samples (SEM-EDS) attests that Palissy used of an iron coloured (3-5 wt% Fe<sub>2</sub>O<sub>3</sub>) high lead alumino-silicate glaze (55-65 wt% PbO, 5-7 wt% Al<sub>2</sub>O<sub>3</sub>, 26-32 wt% SiO<sub>2</sub>). The iron richest glazes contain PbFe<sub>12</sub>O<sub>19</sub> crystalline inclusions, which are a marker of the firing process of the artist.

The replication of this chemical system allowed us to study its crystallisation behaviour. It appears that the nature of the iron bearing crystalline phases formed in the glaze during firing (Fe<sub>2</sub>O<sub>3</sub>, Pb<sub>2</sub>Fe<sub>2</sub>Si<sub>2</sub>O<sub>9</sub>, PbFe<sub>12</sub>O<sub>19</sub>), their abundance and microstructure strongly depend on the firing temperature, cooling rate and iron content (2.6 – 10.5 wt% Fe<sub>2</sub>O<sub>3</sub>). These results obtained from replicated glasses enlighten our observations of Palissy's work and allow us to

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make some assumptions about the temperatures Palissy may have used. Unfortunately, replicating the glaze alone is not completely satisfying because of the existence of chemical interactions between the ceramic body and the glaze. Therefore, we replicated glazes of different compositions with a ceramic body and we investigated their reactivity during various firing processes, through measuring the Al<sub>2</sub>O<sub>3</sub> composition profiles in the glazes. Understanding the thermal behaviour of the glaze and the paste together is essential to hypothesise the process used by Palissy.

**Keywords:** Palissy, lead glazes, magnetoplumbite, glaze, clay interaction

# Alteration mechanisms of medieval stained glass windows in atmospheric medium

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Medieval stained glass windows from the Northern Europe are sensitive to the atmospheric medium that causes degradations due to the low durable composition of the glass (SiO<sub>2</sub> content around 50 wt.% and high K<sub>2</sub>O and CaO content). The alteration appears as pits or as a flat continuous layer whose thickness can reach 200  $\mu\text{m}$ . In order to determine the formation mechanisms of this altered layer, different isotopic tracers were used. Furthermore, as the atmospheric medium is characterized by a variable relative humidity and rainfall events, different experimental devices were set up. In order to understand the alteration mechanisms during rainfall events, a dynamic experiment was performed with a solution doped in <sup>29</sup>Si. This allowed Si coming from the glass and Si coming from the solution to be discriminated. The analysis of the Si isotopic signature of the gel layer by SIMS highlighted that diffusion, but also hydrolysis/condensation reactions, are involved in the formation process. In unsaturated medium, experiments at different relative humidity values were carried out on model glass. The results have shown that interdiffusion is predominant in the first stages of alteration. Furthermore, in order to investigate the alteration mechanisms on ancient stained glass samples (once the altered layer is formed), these latter were exposed to a rainwater (in a first experiment) and to a water vapor (in a second experiment) both doped in deuterium and <sup>18</sup>O. NanoSIMS analyses have highlighted that the alteration continues at the interface between the altered layer and the pristine glass, mainly by interdiffusion. Associated kinetics were also determined. Their extrapolation over 650 years are consistent with the range of alteration thicknesses observed on ancient stained glass windows.

**Keywords:** stained glass, cultural heritage, alteration, atmosphere

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# Historical Reproduction of Grisailles: A preliminary study

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Grisaille is a glass-based paint applied on stained-glass panels, used, in general, for the creation of contours and shadows with dark colors (grey and brown hues). They are made by mixing metal oxides (iron and/or copper) with a ground lead-based glass, and applied on a glass panel with a binding agent, such as Arabic gum. After the annealing at temperatures between 650-700°C, the grisaille form a thin layer of glass with dispersed metal oxides which is adhered to the base glass.

This study is focused on a preliminary research of treatises and recipe books which describe the production of grisailles with the aim to investigate its historical evolution. This includes a general overview of the historical treatises that described this type of production, the interpretation, and identification of raw materials and the reproduction of selected recipes. The produced paints were characterized before and after their annealing by optical and scanning electron microscopy, ion beam analyses and X-ray diffraction.

Four recipes were selected to be reproduced, belonging to four different treatises, dated from the 10th to the 19th century. The treatises were written by Eraclius (10th century), Antoine de Pisa (14th-15th century), Pierre Le Vieil (17th century) and George Bontemps (19th century) allowing a representative analysis of the evolution of the grisaille production through history.

As principal conclusion, it was possible to understand that the production of grisailles did not change significantly through history, except for the source of some colorants, such as the replacement of burned metals for ochres and earths, and an evolution of the morphology of the grisailles towards a greater homogeneity. It was also observed that the differences in the hues of the paint after the annealing were due to a change in the metallic phases.

**Keywords:** Stained, Glass, Grisaille, Treatises

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# IONIC DIFFUSION & CONDUCTIVITY



# Ionic conduction pathways in chalcogenide glasses: experimental evidence and modelling

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Extended R&D in the field of alternative energy sources stimulates studies of all-solid-state lithium and sodium batteries for portable electronics, transport and stationary applications. Chalcogenide vitreous electrolytes and glass/ceramic composites belong to promising functional materials offering record-high ionic conductivity and advanced charge/discharge cycling. The origin of the superionic mobility in a chalcogenide glass remains an open question often related to preferential conduction pathways formed in the disordered network. Using pulsed neutron and high-energy X-ray diffraction combined with RMC/DFT modeling, we will unveil the nature of ionic conduction pathways in glassy chalcogenides. The tracer diffusion experiments and Raman spectroscopy measurements yield an independent verification of the proposed scenario providing a deeper insight into the interesting and practically important phenomenon.

**Keywords:** ion, conducting chalcogenide glasses, neutron diffraction, high, energy x, ray diffraction, RMC/DFT modelling, tracer diffusion

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# Structure, Ionic Mobility, and Mechanical Stiffness in Mixed-Network Former Glasses

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We investigated the adiabatic elastic properties and ionic conductivities of two series of mixed network former glasses, sodium borosilicates and sodium borogermanates using Brillouin light scattering (BLS) and dielectric impedance spectroscopy, respectively. Using data from NMR spectroscopy and BLS as input for a reaction equilibrium-based statistical thermodynamic model we constructed a detailed structural model of these glasses. This model yields statistical measures for the distribution of cation hopping pathways in these glasses. Our analysis reveals strong correlations between elastic and transport properties, which allow us to develop a more detailed formulation of transition state theory describing the modifier cation migration in these materials. We find that the structural deformation during a cation jump is almost entirely controlled by the bulk modulus. Our analysis allows us to assess the spatial extent of this deformation, as well as estimate the relative amounts of configurational and vibrational entropy changes associated with this thermally activated process. Funding: NSF-DMR\_1610742

**Keywords:** transition state theory, adiabatic elastic modulus, ionic conductivity, statistical thermodynamic model

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# New Fast Ion Conducting Glasses: Towards Enabling High Energy Density and Safe All Solid State Batteries

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Li batteries are fire and explosion hazards. They also operate at 10 times less energy density than theoretically possible. The first of these problems is caused by the flammable liquid electrolyte used in their construction that can spontaneously ignite or explode if lithium ion batteries are charged incorrectly, stored in hot conditions, or discharged too rapidly. The second of these problems is caused by the fact that to give these batteries the little safety they do have, they must use graphitic carbon that reduces the amount of lithium that can be stored to 10% of the theoretical value. In spite of these two critical problems, lithium batteries remain about the only choice manufacturers have to store electrical energy for portable electronics and automobile propulsion. In our research ISU, we are working to solve these two critical problems and at the same time make lithium and sodium batteries that are cheaper and can be charged much faster. The core break through that has led to this possibility is the discovery of new solid electrolytes that conduct lithium and sodium ions through the battery more safely and faster than the flammable liquid electrolytes used to day. In this talk, I will describe our recent research that has led to the break through achievements of our research group in this area.

**Keywords:** glass, solid state battery, solid electrolyte, lithium sodium

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\*Speaker

# Diffusion and Ionic Conduction in Glasses

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In this contribution studies of ionic conduction and of radiotracer diffusion in oxide glasses are summarized. In contrast to ionic conduction tracer diffusion is element-specific. The tracer experiments comprise measurements of Na and Rb diffusion in single and mixed alkali borate glasses and of Na and Ca diffusion in soda-lime silicate glasses as function of temperature and of composition. Diffusivities and ionic conductivities are Arrhenius activated and are compared via the Nernst-Einstein relation. Haven ratios for both silicate and borate glasses are deduced. Viscosity diffusion coefficients are deduced from viscosity data for a soda-lime silicate glass via the Stokes-Einstein relation. Viscosity diffusion is considerably slower than diffusion of the network modifiers Na and Ca indicating that the motion of the network formers and network modifiers are decoupled. The ionic conductivity in soda-lime glasses is dominated by Na ions.

**Keywords:** diffusion, ionic conduction, borate glass, silicate glass

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\*Speaker

# Development of down converting stable and efficient materials: Silver diffusion in glass

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Luminescent devices are significant part of daily life (e.g., LEDs). In this work new stable luminescent glass materials for down converting UV light to visible/NIR light were synthesized. Noble metal clusters are known to be able to confer photoluminescence to glasses and are expected to display high luminescence quantum yields when synthesized with different emissive ions. [1] Control of the size and shape of the small particles is imperative to increase the colour range and external quantum yields (EQY) of luminescent glasses, thus demanding investigation of the metal ions reduction mechanisms, nanoparticles formation and diffusion in glass.

In a first step silver in different concentrations was introduced in soda-lime silicate glasses. An ion exchange technique was used by immerse a glass piece in a solution containing silver, e.g. in a molten salt mixture of AgNO<sub>3</sub>/NaNO<sub>3</sub>, allowing the formation of homogeneous films in glass surfaces doped with silver clusters and/or larger nanoparticles (NPs), taking in consideration that oversized NPs may quench luminescence. The ion metal reduction was achieved by chemical agents present in the glass matrix. After silver diffusion and reduction, formation of metal clusters or NPs with controlled sizes was induced by heating at different temperatures, for different times. After annealing at 400 °C the samples were pale-yellow and transparent, yet when excited at 360 nm photoluminescence was observed with an emission band around 650 nm, consistent with Ag clusters as light emitting centres. Annealing at higher temperatures, c.a. 500 °C, lead to larger nanoparticles and a more intense yellow colour, however with same characteristic photoluminescence.

Different experimental techniques were used, namely XRF combined with the ion beam based spectrometries PIXE, RBS and NRA, to characterize the elemental glass compositions and depth distributions of the incorporated atoms, as well as absorption and emission spectroscopy to characterize the optical properties.

M. Eichelbaum, K. Rademann, A. Hoell, D. M Tatchev. W. Weigel, R.Stosser and G. Pacchioni,

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**Keywords:** silver clusters, photoluminescence, glass, metal ion diffusion

# Li conduction in Li<sub>2</sub>S-P<sub>2</sub>S<sub>5</sub> glasses: insights from dynamics and polarizability

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We investigated the dynamical and polarizable properties of Li<sub>2</sub>S-P<sub>2</sub>S<sub>5</sub> glasses, which is a fast Li-conducting material, by performing ab initio molecular dynamics simulations for 300 ps at 300 K. Structural properties a zone analysis based on Li migration highlighted the effective path along which Li diffuses in the materials. Our resultssuggested that all the Li ions did not have constant mobility, indicating that some of the Li ions were effectively available for conduction. The origin of the path that would support effective Li diffusion was analyzed in terms of the dynamics and polarizability of the sulfur surrounding the Li migration path.

**Keywords:** solid state electrolytes, ab initio molecular dynamics, polarizability

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# Ionic conductivity of binary alkali borate melts

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While electrical conductivity of borate glasses has been extensively studied, only few works were devoted to the charge transport in molten state of these oxides. In order to reach accurate conductivity data in the molten state, we used an experimental setup based on the four-electrode method which reduces polarization effects usually observed in the classical two-electrode method especially at high temperatures and low frequencies. Our device was successfully applied to study ionic transport of two series of binary alkali borate melts:  $\text{XLi}_2\text{O}-(100-\text{X})\text{B}_2\text{O}_3$  and  $\text{YNa}_2\text{O}-(100-\text{Y})\text{B}_2\text{O}_3$  ( $X = 5 - 45$  mol% and  $Y = 5 - 40$  mol in the frequency range 1Hz - 1 MHz. The data acquisition was performed during cooling from about 1050°C to 300°C, thus from the molten to the solid states. It is well known that below the glass transition temperature ( $T_g$ ) the conductivity follows an Arrhenius law which is characteristic of thermally activated transport while above  $T_g$  and in the molten state, the conductivity is well described by the phenomenological VTF (Vogel-Tamann-Fulcher) law. The VFT law suggests a cooperative nature in the transport mechanism where the deformation of the network enhances the mobility of the ionic charge carriers. Our results suggest that the well-known boron anomaly observed on several properties of borate glasses persists in the molten state, but takes place at lower alkali contents than in the solid state.

**Keywords:** alkali borate glasses and melts, ionic conductivity

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# IONIC EXCHANGE

# Strengthening of Alkali Alkaline Earth Silicate Glasses by Ion-Exchange

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This project involves investigation of the effects of changing, ionic species, process time and temperature on the enhancement of mechanical properties by ion-exchange. In the current work, a single-side ion exchange process has been used. In addition to ion exchange involving potassium, equivalent potassium containing glasses have been prepared to deconvolute the effect of potassium on mechanical properties. Other alkali metal ions have also been used for ion exchange to observe the effects of exchanging pair of ions. Observations are made whether the features are a direct consequence of ion exchange or due to the alkali metal species in the glass composition. SEM-EDX has provided concentration versus depth profiles of exchanged ions. FTIR and Raman spectroscopies have been used to investigate the structural differences between ion-exchanged glasses and the glasses that contain potassium. Physical and mechanical property evaluation has also been conducted through four-point bending, microhardness and scratch resistance tests. Nanoindentation has also used to compare hardness and elastic modulus of treated and untreated glass samples. Results and their relationship to the treatment conditions will be compared and discussed.

**Keywords:** ion exchange strengthening, alkali alkaline earth silicate glasses

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# Mechanics of Ion-Exchanged Glass

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Chemically strengthened cover glasses for portable electronics are based on a ternary alkali aluminosilicate glass system. Glasses within this system can be readily ion-exchanged when immersed in a molten alkali salt bath to produce high surface compressive stress and deep compressive stress layer. The ionic inter-diffusion of monovalent alkali ions within an aluminosilicate glass results in an invading ion concentration profile that has a complementary error function form. Due to the larger size of the invading alkali ion during typical ion-exchange processing, compressive stress is generated along the diffusion profile. The basics of fracture mechanics are reviewed and then used to describe advantages of ion-exchanged glasses, namely imparting high surface strength to allow highly flexible glass sheets and to provide retention of strength following sharp contact damage. A simple model is described that can accurately predict the retained strength as a function of flaw depth for a known stress profile. The sharp contact failure mode for cover glasses is of particular importance since it is the most commonly observed failure type in the field. It is demonstrated that sharp contact damage can be replicated in the lab using diamond indentation. Experimental data show that the resistance to sharp contact flaw generation is improved both with high compressive stress enveloping the deformation region and by utilizing glass compositions that are more resistance to subsurface damage during sharp contact events. The frangibility behavior of ion-exchanged glasses is also described in terms of stored strain energy and cracking responses are shown.

**Keywords:** Ion, Exchange, Cover Glass, Damage Resistance, Indentation

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\*Speaker

# Influence of processing temperature and time on the structure evolution and mechanical properties of ion-exchanged soda-lime-silicate glass

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Chemical strengthening of glass is carried out in a typical ion-exchange process where sodium atoms contained in the glass are substituted by potassium ions diffusing from the molten salt. The optimization of the fundamental parameters of the process, such as time and temperature, plays role in preventing stress relaxation and to guarantee efficient reinforcement of glass. The effect of different ion-exchange conditions on the mechanical behavior and the structure evolution of soda-lime silicate glass were studied in this work.

Glass samples were subjected to chemical strengthening in pure molten KNO<sub>3</sub> at different temperatures and times. Ion-exchanged glass was characterized from a mechanical (residual compression and case depth, strength, surface crack formation, scratch resistivity), chemical (surface composition, potassium penetration) and structural (by Nuclear Magnetic Resonance (NMR) and micro-Raman spectroscopies) point of view.

The results show that the case depth increases with time and temperature of the process at the expense of a reduction in the residual stress. The same occurs for potassium surface concentration and penetration. The crack initiation tendency decreases in samples treated at lower temperature for shorter period. Furthermore, scratch test revealed a decrease in the length of the plastic regime of the samples by increasing the time and temperature of the exchange process. This is in good agreement with the NMR and micro-Raman results, where higher distribution of Q<sub>3</sub> and Q<sub>2</sub> species are observed and indicated network distortion for longer treatment times.

**Keywords:** Ion exchange, Chemical tempering, Chemical strengthening, Soda lime silicate glass, Nuclear Magnetic Resonance Spectroscopy, micro Raman Spectroscopy

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\*Speaker

# Calculation of residual stress in Alkali-Silicate glasses after Ion Exchange

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Chemical strengthening by ion exchange is becoming a widely used technology to increase glass strength . Structural applications of glass in consumer electronics, transportations, and architecture has generated a significant increase of interest in glass chemical strengthening by ion exchange. The determination of residual stress profile induced by ion exchange is of critical importance in process design and final product assessment. Experimental methods and international standards are generally limited to the determination of surface compression (Sc) and compression layer depth (Cd).Mathematical modeling, when compared with experimental results, can be useful to check our understanding of the physics and chemistry of the ion exchange process. Predictions of stress profile based on mathematical models have been proposed in the literature. Here it is presented an approach to mathematical modeling of residual stress profile considering: ion exchange kinetics, stress relaxation, constant and concentration dependent Linear Network Dilatation coefficient (LNDC – B). Applications examples to soda-lime silicate glass will be presented and discussed. A short discussion of effects due to time dependent boundary conditions for ion concentration will also be presented. A side discussion will be introduced on the "zero time surface compression value" and its connection to the recently debated LNDC anomaly. A final discussion will also be proposed for glass strength assessment on the basis of a calculated stress profile.

**Keywords:** Chemical strengthening, Ion Exchange, Residual Stress profile, Mathematical modeling, Strength

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\*Speaker

# Chemical strengthening of magnesium doped LAS glass-ceramics

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Recently, ion-exchange (IOX) in glasses has found a renewed interest with a lot of new development and research in industrial and academic laboratories along with the commercialization of products with outstanding damage resistance (ie Gorilla glasses).

In some cases, glass-ceramics can present better mechanical properties as compared to glasses due to greater toughness and elastic modulus. In addition, likewise glasses, IOX can further improve the glass-ceramic strength through surface compression build up.

However, there has been little research on this area worldwide. In the past years, Corning investigated chemical strengthening of various glass-ceramic systems. Here, we focus on magnesium rich beta-quartz solid solution after treatment in molten lithium salt. In this approach, the magnesium ions from crystals are replaced by lithium ions from the bath.

Particular emphasis will be given to demonstrate the origins of surface compression following cationic interdiffusion.

**Keywords:** glass, ceramic, damage resistance, ion, exchange, chemical strengthening

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# Structural adaptation in Na<sup>+</sup>/K<sup>+</sup> ion exchanged glasses leading to a relaxation of the compressive stress

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A major limitation in many technological applications of glassy materials is their brittle fracture behavior [1]. However, exchanging smaller ions such as Na<sup>+</sup> in the glass structure with larger ions such as K<sup>+</sup> leads to chemical strengthening, as it allows for developing high surface compressive stress, which in turn drastically improves the modulus of rupture of the treated glass [2]. The magnitude of this surface compressive stress depends on the extent of stress and structural relaxation occurring during the ion exchange [2,3]. Therefore, the optimization of the ion-exchange process requires a fundamental understanding of the nature of this relaxation process [3].

In the present work, we investigated how the relaxation of the compressive stress developed in Na<sup>+</sup>/K<sup>+</sup> ion-exchanged binary Na-silicate and ternary Na,Mg-, Na,Ba- and Na,Ca- silicate glasses affects the glass structure. For this purpose, two experimental methods were used:  $\mu$ -XANES (X-ray Absorption Near Edge Structure measurements) and nuclear magnetic resonance (NMR) spectroscopy. The  $\mu$ -XANES allowed the study of the environment of Ca<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup> and Mg<sup>2+</sup>, while NMR probed the environment of <sup>23</sup>Na and <sup>29</sup>Si.

In the Na<sup>+</sup>/K<sup>+</sup> ion exchanged glasses, the K<sup>+</sup>-foreign cations are introduced in the cages of the Na<sup>+</sup>-host cations. Due to stress relaxation, the size of the K-O coordination shell in ion-exchanged glasses increases. This increase is achieved by two structural adaptation mechanisms: a contraction of the Na-O, Ca-O and Mg-O coordination shell and both a shortening of the Si-NBO distances and an opening of the Q<sub>4</sub> Si-O-Si angles.

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**Keywords:** Ion, exchange, NMR, stress relaxation, structure



# Boron effects on chemical strengthened glass

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Chemical strengthened glass is produced by an ion-exchange stuffing process where small radius alkali ions within the base glass are replaced with larger radius alkali ions from a molten salt. To achieve a desirable strength in a reasonable process time, the base glass has to be carefully designed. In this study, we investigated the boron effects on the compressive stress (CS) and depth of layer (DOL) achieved from ion-exchange. A series of glass with compositions of  $15\text{Na}_2\text{O}\cdot 15\text{Al}_2\text{O}_3\cdot x\text{B}_2\text{O}_3\cdot (70-x)\text{SiO}_2$ , where  $x=0, 5, 10$  and  $15$ , has been melted and ion-exchanged in potassium salt bath at  $380\text{ }^\circ\text{C}$  for 2, 4, 6, 8, and 10 hours. For each glass, DOL increases with ion-exchange time, but CS gradually decreases, which is due to force balance. Across the series, both DOL and CS decrease as the amount of boron is increasing. With boron content increasing, the atomic density (number of atoms in a unit volume) increases, therefore the packing density increases and free volume decreases. Interestingly, the number of Na ion in a unit volume is decreasing as boron content increases. As boron content is increasing, the atoms are more closely packed, which slows down the ion-exchange process. On the other hand, the number of  $\text{Na}^+$  in unit volume is decreasing as boron content increases, which also slows down the inter-diffusion of alkali ions. Both facts explain why smaller DOL and CS have been observed in high boron glasses.

**Keywords:** boron, ion, exchange, atomic packing density

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\*Speaker

# LASER INTERACTION

# Femtosecond laser three-dimensional exposure of silica substrate in the non-ablative regime : from laser-induced modifications to applications

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Thanks to non-linear absorption processes, non-ablative femtosecond laser pulses applied to fused silica induce bulk morphological transformations in the material associated with a variety of local changes of physical properties. These structural changes includes locally densified glass matrices, self-organized nanostructures as well as the formation of polymorphic phases. As a direct consequence, the material experiences localized volume variation resulting in either tensile or compressive stress, which intensity and direction are both controlled by the pulse energy and the laser polarization, respectively. Here, we will discuss these laser modifications, both from the viewpoint of stress-states and structural changes induced in the material. In particular, we will show how these controlled states along with this ability to tune material properties can be used for novel applications in optomechanics, such as tunable Duffing oscillators, embedded optical wave plates, but also, as a means to investigate mechanical properties at the small scales and for the packaging of complex optical devices. Finally, we will conclude by showing the existence of intermittent behavior observed while writing in material and illustrates how this apparent erratic behavior bearing randomness provides useful information related to fracture mechanics at small scales.

**Keywords:** Femtosecond lasers, fused silica, high pressure polymorphic phases, glass micro, mechanics.

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\*Speaker

# Femtosecond laser-written nanogratings in alkali silicate glasses

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Birefringent periodical nanostructures induced by a series of femtosecond laser pulses in the bulk of glass which are known as nanogratings have drawn a lot of attention due to possibility to control their orientation and optical retardance by the parameters of laser treatment and have already been used in applications such as polatization converters and ultrastable data storage. Most of the studies of this phenomenon were performed in fused silica. Recently, inscription of nanogratings was also demonstrated in several multicomponent glasses though studies of possibility, conditions and mechanism of their inscription depending on glass composition are still scarce.

Here, we have demonstrated possibility of nanograting formation in binary R<sub>2</sub>O-SiO<sub>2</sub> glasses (R = Li, Na, K) and investigated their inscription conditions and properties depending on the alkaline cation type and, in the case of Na, on its content. By example of sodium silicate glasses, the number of laser pulses required to induce nanogratings is shown to depend exponentially on the contents of Na<sub>2</sub>O changing from ~10<sup>2</sup> for pure SiO<sub>2</sub> to 10<sup>6</sup>-10<sup>7</sup> for 23Na<sub>2</sub>O77SiO<sub>2</sub> glass at a certain pulse energy.

Conditions of nanograting formation have been found to strongly depend on the alkali cation type. As it has been demonstrated in 15Na<sub>2</sub>O85SiO<sub>2</sub> glass, most of sodium ions migrate from the laser-irradiated area along with formation of a SiO<sub>2</sub>-like nanograting. Na<sup>+</sup> cations remaining within the nanograting are accumulated near or inside the 20-30 nm thick nanoplanes whereas composition of regions between the nanoplanes approaches to pure SiO<sub>2</sub> making drastic nanoscale chemical differentiation. However, formation of nanogratings in 23K<sub>2</sub>O77SiO<sub>2</sub> glass at similar laser exposure conditions isn't accompanied by noticeable migration K<sup>+</sup> cations out of the nanograting. Thus, depletion of alkaline cations within the laser-exposed area is shown to be unnecessary for nanograting appearance in glasses.

The study was financially supported by RFBR (grants 16-03-00541 and 17-03-01363).

**Keywords:** nanostructure, nanograting, form birefringence, alkali silicate glasses, femtosecond laser treatment, nanoscale atomic rearrangement

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# The impact of the silver-containing phosphate glass composition on femtosecond laser induced optical properties

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The manufacturing of innovating and novel photonic materials is inevitably linked to the development of non-conventional fabrication techniques for designing multiscale structured photonic materials. In the two last decades, Direct Laser Writing (DLW) using femtosecond laser has been investigated in transparent glasses. In the specific case of silver-containing phosphate glass, DLW leads to the formation of silver clusters which exhibit photoluminescence properties in the entire visible range and can be at the origin of a local refractive index modification. Non-linear optical absorption and cumulative thermal effect are responsible for these silver clusters formation at the edge of the voxel of interaction. Rewritable phenomenon, even for high energy deposition, dependent on the glass composition has been demonstrated.

The phosphate glass composition has a determinant impact on the nature of the clusters and the photo-generated properties. Polyphosphate, pyrophosphate and orthophosphate glass composition have been investigated in order to establish the impact of the phosphate network on the glass photosensitivity. Raman and infrared spectroscopies have allowed characterizing the glass structure. Luminescence spectroscopy of the silver ions has been investigated. The study has allowed undergoing a systematic investigation of the relationship between the glass structure,

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the silver ions environment in phosphate glass and the overall material photosensitivity. Fiber drawing of the most promising composition has been demonstrated. The results obtained contribute to demonstrate that silver containing phosphate glasses are excellent candidates for the development of micro-optic systems embedded into glass fiber for cutting-edge technologies.

**Keywords:** Photosensitive glass, silver, containing glass, phosphate glass, matter, laser interaction, femtosecond laser, spectroscopy

# Glass and silicon welding by femtosecond laser: set up improvement through modeling

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In Photovoltaic and Microelectronics industries many devices combine materials of different physical and mechanical properties such as silicon and glass are used. Welding them is a complex application that still can be improved in terms of speed, preservation of mechanical properties. Conventional welding methods (anodic fusion, adhesive bonding, and junction by fusing, optical contacting) and continuous laser welding are relatively effective but can be improved in terms of machining speed, thermal and chemical resistance, seam limited length, long term stability, complex pressure tools....

In this work a femtosecond laser emitting at 1030 and 515 nm is used to weld both glass on glass (sodalime, borosilicate, aluminosilicate) and glass on silicon (mono and polycrystalline). Different ranges of thickness are tested for glass plate (from 0.7 to 2 mm) and for silicon wafer (from 100 to 300  $\mu\text{m}$ ).

Power, pulse duration, frequency, beam diameter focussing and process speed are the key parameters to empower this application. Even with few values for each parameter, the number of experimentations can be tremendous. To reduce with efficiency the time to provide good beads and to optimise the machining speed, numerical modelling is combined with experiments works. Different welding trajectories and strategies configuration (with or without mechanical pressure, parts roughness) are tested.

Finite element method (FEM) calculation based on laser beam set up is used to model the melted zone morphology. Transient thermal calculation is done to analyse temperature field.

These numerical works help to optimise focus plane, power and machining speed ranges.

Numerical results analyses led to understand melting temperature is reached from the 6th pulse.

Different welding strategies led to reach 3 m/s machining speed for glass on silicon welding. Heat treatments reveal that welded samples resist to 200 °C thermal shock while the beads are still watertight.

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**Keywords:** Finite Element Method, Laser beam, laser welding, welding trajectories, welding strategy, soda lime, borosilicate mono and polycrystalline silicon wafer, residual stresses and modelling



# Low loss fluoride optical fibers: properties and application

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Heavy Metal Fluoride Glasses (HMFG) were discovered in 1974 by Poulain *et al.* [1]. More than 40 years later, tremendous research and development efforts have resulted in a notable improvement of fluoride fibers quality. Their optical transmission in the mid IR extends up to 4.2  $\mu\text{m}$  for fluorozirconate glass fibers and 5.2  $\mu\text{m}$  for fluoroindates with minimum losses reaching 1.04 dB/km ad 2.2 dB/km for these fibers, respectively.

Present fibers pave the way to numerous passive applications.

- Remote detection of optical signals from 0.5 up to 5.5  $\mu\text{m}$  (Spectrometry, Thermometry).
- Pigtailling Quantum Cascade Lasers from 2 up to 5  $\mu\text{m}$ .
- Low birefringence fibers for astronomical instruments.
- Polarization maintaining fibers (airgap, panda, elliptic core fibers) for instrumentation.
- Laser power transmission, e.g. Er:YAG laser. Indeed, ZBLAN fibers withstand 1.6 J pulses at 2.94  $\mu\text{m}$ . At other wavelengths they can handle more than 188W continuous wave laser beam.

Applications for active fibers are based on rare-earth-doped fibers or on non-linearity. Fluoride glass fibers offer two main advantages for active applications: their high solubility of rare earth ions, up to 10 mol % and their low phonon energy: 580  $\text{cm}^{-1}$  for ZBLAN and 510  $\text{cm}^{-1}$  for fluoroindate glass. As a consequence, laser transitions are possible from energy levels that are inactive in silica fibers. For example, lasing around 2.8  $\mu\text{m}$  has been reported, with a record value of 30.5 W at 2.94  $\mu\text{m}$  in CW operation [2].

Optical nonlinearity is small in fluoride glasses. However, low optical losses make possible to use long fiber lengths. As a result, supercontinuum laser sources have been developed in a broad spectral range, typically from 0.8 up to 4.8  $\mu\text{m}$ . Also, deep-ultraviolet supercontinuum starting from 200 nm has been demonstrated using photonic crystal fluoride fiber [3]. Fluoride fibers are less sensitive to ultraviolet related optical damages than silica fibers.

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**Keywords:** Fluoride Fiber, Fiber laser, Supercontinuum

# Femtosecond laser induced structural transformations in transparent oxide glasses.

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The increase of demand in optical telecommunication rate is such that optical integration is a requisite for the foreseen development. In this way, direct laser writing in glasses could be a solution especially when using femtosecond laser. According to the pulse energy at moderate repetition rate (< a few 100kHz), the irradiation changes the fictive temperature and thus produces a change of refractive index. On increase of the pulse energy, some glasses can be locally decomposed into reduced glass and oxygen gas that self-organized under the light into nanogratings giving rise to large form birefringence, very thermally resistant and orientable by turning the laser polarization. This is useful for achieving optical waveguides but also any kind of lenses.

Among them, we demonstrated the possibility to achieve an achromatic rotator by combining several irradiated layers. But we find also, that according to some specific conditions, only one irradiation may also produce light rotatory power. On this point, we do not know today if this chiral property arises from rotatory combination of linear property or from chiral arrangements at the molecular level.

The local creation of second order optical susceptibility for frequency conversion can be achieved by driving the glass to crystalize. The thermal problem, here, is similar to the one with CW laser but with fs laser the material can be transparent and the modification in the bulk. This will be shown in Li<sub>2</sub>O-Nb<sub>2</sub>O<sub>5</sub>-SiO<sub>2</sub> glass.

For this glass, the direction of the crystals is controllable for a range of parameters with the direction of polarization and so the orientation of the susceptibility. This is a real advanced because the electromagnetic field direction in a waveguide is not free.

Finally, we found that when the glass is not congruent, phase separation during crystallization may also induce similar nanogratings like in SiO<sub>2</sub>.

**Keywords:** oxyde glass, femtosecond laser, crystallization, optical properties, silica glass

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# Polarization dependence of femtosecond laser induced circular birefringence in silica glass

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From a practical point of view, femtosecond-IR lasers can now generate pulses with ultra-high intensity of tera or even peta W/cm<sup>2</sup>. This kind of laser leads to radically different laser-matter interaction from that achieved with a conventional laser. Highly non-linear multiphoton processes are observed, so even transparent material can absorb this light when the intensity is high enough. This allows 3D direct writing when the beam is strongly focused into transparent materials, particularly silica-based glasses. The mechanism of interaction of the femtosecond laser light with dielectric materials is not fully understood but one recognized specificity due to the very small pulse duration is that the action of the light on electrons and ions is decoupled. Then, by choosing the correct configuration of the beam for controlling the ponderomotive force, we can imagine forcing the electrons to move to one side of the beam, creating an inhomogeneous plasma. This may be the clue to an innovative aspect in materials science. Many recent works on pure silica have been conducted, and several properties have been demonstrated in this glass: average index changes, linear birefringence LB and linear dichroism LD. We recently revealed a chiral mechanical structure by measuring the surface topography of laser tracks written in opposite directions that could lead to circular properties. Taylor reported highly ordered chiral-like nanostructures using circular polarized laser light but no circular optical properties. We recently report on the creation of circular optical properties and non-reversible measurements according to the probe face. Here it is shown that by controlling the laser-writing configuration, we can create a quite high ellipticity of 40deg/mm revealing the creation of a large circular dichroism (CD), a useful range for potential applications. As the writing polarization is adjustable from 0 to 360°, the ellipticity maximum appears for linear polarization oriented at 112° and 292°. In addition, ellipticity measurements are non-reversible (the values are different when change the light propagation). This is due to the co-existence of anisotropic LBLD, which exhibit a different spatial distribution from the CD.

**Keywords:** Lasers and laser optics, silica glass, chiral media

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# 3D Glass Decoration by Nonlinear Absorption of Ultrafast Lasers

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In the frame of decorative applications, several techniques exist nowadays to color various kinds of glassware. Nevertheless, most of these processes employ toxic chemical additives and are characterized by long processing time. It is well known that precipitation of metallic nanoparticles in glass by laser processing allows for 3D intra-volume glass coloring with high-resolution patterning into bulk glass. In this work an ultrafast laser with a central wavelength 1030 nm was employed to irradiate FOTURAN ® photosensitive glass doped with Ag nanoparticles, and the color variation is obtained by simply varying the laser and process parameters. The laser-irradiated samples were annealed in oven at different temperatures around the glass-transition temperature to assess the effect of annealing on the final colorization. All treated samples were characterized by measuring the absorption coefficient in the visible spectrum by a SHIMADZU spectrometer UV3600PLUS. Results show that the absorption coefficient increases when the cumulative energy employed during the process increases. The post-irradiation annealing process enhances the coloring effect. Finally, thicker samples of FOTURAN ® II, which is an improved photo-sensitive glass based on the well-known FOTURAN ®, were treated with the best parameters studied in the first part with a 3D pattern to evaluate the process resolution.

**Keywords:** Glass decoration, ultrafast laser, nonlinear absorption

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# METALLIC GLASSES

# Metallic Glasses

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In this talk, we provide an introduction to metallic glasses, including recent developments on the range of structures and properties that can be achieved, and the growing possibilities for their applications. Even after more than 50 years of study, metallic glasses can be considered relative newcomers to the world of glasses, and they continue to provide surprises. There is current interest in the use of thermomechanical processing to extend the range of the glassy state, and metallic glasses are ideally suited for this [1]. In addition to the effects of plastic deformation, there are significant effects even well within the (nominally) elastic regime [2]. We explore the remarkably wide range of energy that can be achieved in the metallic glassy state, from very high (‘rejuvenated’) to very low (‘relaxed’ and even ‘ultrastable’). We also explore the extent to which directionality (anisotropy) can be induced in metallic glasses [3]. In each case, we examine the potential applications of the properties that can be induced in stable and unstable states [4].

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A.L. Greer, New horizons for glass formation and stability *Nature Mater.* **14** (2015) 542–546.

**Keywords:** metallic glasses, rejuvenation, mechanical properties, anisotropy

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# Surface hardening of Zr-Cu based bulk metallic glasses using gaseous thermochemical treatment

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Gaseous thermochemical surface treatment is commonly applied for enhancing the metallic material performance with respect to their wear, tribological and corrosion resistance. In thermochemical processing, interstitial elements are introduced in the metallic substrate at elevated temperatures in order to deliberately change the chemical composition of the surface. Amorphous multi-component metallic systems, viz. bulk metallic glasses have been extensively researched in the past decades due to their promising structural capabilities in engineering applications. The present research investigates thermochemical treatment by gaseous oxidizing of Zr-Cu based bulk metallic glass systems with high glass forming ability. The metallic glass systems are treated below their glass transition temperatures in atmospheres imposing high oxygen partial pressures. X-ray diffraction analysis, light optical microscopy (LOM), scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) and microhardness testing were utilized for evaluating the hardened oxygen-containing case developed during the treatment. The oxide layer was found to consist of two different layers, an outer layer comprised of copper oxide islands due to the outward diffusion of Cu and an inner layer consisting of different oxide zones. For all the studied Zr-Cu based BMGs, the inner oxide layer mostly consists of tetragonal ZrO<sub>2</sub> and minor amounts of CuO, Al<sub>2</sub>O<sub>3</sub> and monoclinic ZrO<sub>2</sub>. In silver containing BMG, a small fraction of expelled non-oxidized silver, as a consequence of volume and thermal expansion, can be seen on the top surface which is covered by copper oxide particles. The surface hardness of thermochemical treated BMG samples reached approximately 1200 HV (except Ag containing Zr- based BMG). The results shows that a homogenous hardened case can be achieved after conducting gaseous thermochemical treatment without devitrification of the amorphous substrate.

**Keywords:** ZrCu bulk metallic glasses, Gaseous thermochemical treatment, Surface hardness

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# Glassy state formation and thermal stability in (Hf,Cr)-Co-B alloys

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Research on the new permanent magnet materials is focused on the boost of their magnetic properties, to obtain at least half of the value of energy product of Nd-Fe-B materials. Substitution of Cr atoms is proposed to improve magnetic properties of Hf<sub>2</sub>Co<sub>11</sub>B alloys by grain refinement, expected increase of magnetic anisotropy. Results of the Miedema's model calculations for Hf<sub>2-x</sub>Cr<sub>x</sub>Co<sub>11</sub>B ( $0 < x < 2$ ) were confronted with the experimental results for the melt-spun alloys. Formation enthalpy of Hf<sub>2</sub>Co<sub>11</sub>B amorphous alloy = -20.6 kJ/mol and other determined parameters indicate its moderate glass forming ability (GFA). = -0.5 kJ/mol for the Cr<sub>2</sub>Co<sub>11</sub>B alloy suggests its very low ability to form amorphous phase, which can be explained by similar atomic radii of Cr and Co and smaller interfacial enthalpy of Cr-Co than Hf-Co pair. This results correspond well with X-ray diffraction experiments, where the presence of fully amorphous structure was confirmed for the alloys with high Hf content ( $1 < x < 2$ ). In the ribbons with the lower Hf content ( $0.5 < x < 0$ ) crystalline phases were formed at the expense of amorphous one. Thermal stability is usually proportional to GFA and in fact the increase of crystallization temperature and thermal stability with increasing Hf content is reported. **Acknowledgement**

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**Keywords:** glass forminy ability, thermal stability, formation enthalpy

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# Zr61Ti2Cu25Al12 bulk metallic glass: Failure under torsional loading and Mode III fracture toughness

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From torsional tests of cylindrical samples, we have determined the torsional properties of high-toughness Zr61Ti2Cu25Al12 (ZT1) bulk metallic glass (BMG), including its shear yield strength,  $\tau_y=950$  MPa, its shear elastic strain limits,  $\gamma_C=3.0\%$ , and its shear modulus,  $G=31.5$  GPa. Under torsional loading, the BMG fails via a major shear band, without obvious macroscopic plasticity on the specimen surface. The shear band maintained stable propagation by a distance of  $\sim 300$  mm ( $\sim 20\%$  of cylinder radius) before final catastrophic failure, owing to the constraint of stress gradient along the radial direction. The intrinsic mode III fracture initiation toughness is measured for the Zr61Ti2Cu25Al12 BMG, which is known to have a high mode I fracture toughness ( $K_{IC}$ ). The plastic strain intensity factor  $G_{III}$  was used as a measure of the fracture resistance under elastic-plastic conditions. The intrinsic mode III fracture initiation toughness of ZT1 BMG,  $G_{IIIIC}$ , is found to be  $29 \mu\text{m}$ , equivalent to a  $K_{IIIIC}$  of  $51 \text{ MPa}\sqrt{\text{m}}$ . The corresponding fracture energy release rate is similar to or higher than that of conventional engineering metals such as high-strength aluminum alloys and some steels. The subcritical crack growth in ZT1 prior to catastrophic fracture is characterized by an extension of a microscopically zig-zag crack front. ZT1 exhibits a relatively low ratio of  $K_{IIIIC}/K_{IC}$  of  $\sim 0.39$ , indicating that the material is more susceptible to mode III fracture. In engineering design with BMGs, the mode III fracture toughness is thus a useful baseline to ensure the reliability of structural components.

**Keywords:** Metallic glass, Fracture toughness, Torsion, Shear band, Zirconium

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# OPTOELECTRONICS AND OPTICAL PROPERTIES 1

# Redox in glasses: interactions with radiation

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Redox processes can exert significant influences on the processing and properties of glasses, both during production and in-service. For example, control of oxygen partial pressures during glass melting and cooling control the oxidation state of multivalent species therein, influencing foaming (or its avoidance), refining, optical properties such as absorption and fluorescence, chemical durability and crystallization behaviour. However, a less-researched aspect of glass redox is in the interaction of multivalent species in glasses with radiation. This can manifest through interactions with high-energy radiation including UV, which causes solarisation (see, for example, [1]), and even higher energies such as X-rays and  $\gamma$ -rays [2] which can lead to colour centres, point defects and modifications of glass structure or properties. Here we will illustrate, with examples from our recent research, and from other research (see, for example, [3]), interactions of multivalent species in silicate and borosilicate glasses of relevance to technical and radioactive waste glasses, with UV and  $\gamma$ -rays. We will show that, by using selected multivalent transition metal dopants, the optical absorption and fluorescence behaviour of glasses can, to an extent, be tailored or controlled; and the effects of high-energy radiation upon the redox, structure and properties of oxide glasses can be managed or, in some cases, mitigated.

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**Keywords:** glass, radiation, redox, gamma, UV, transition

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\*Speaker

# Coloration of alkali borate glasses by transition d and f elements: a review

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The presence of transition elements in alkali borate glasses is at the origin of one of the most noticeable chemical dependence of the color of oxide glasses. We compare the chemical dependence of optical absorption data on borate glasses containing Cr, Co, Ni, Cu and U. Alkali concentration in borate glasses cause an important modification in the speciation of transition elements, with major modifications observed when IIIB is present, i.e. at concentrations lower than 20 mol%. The variations of coordination numbers, crystal-field splitting, site distribution or site geometry depend on the existence of either only one or several sites occupied by the transition element. These spectroscopic properties will be discussed at the light of recent findings on the medium-range organization in borate glasses, in particular on the role played by IIIB in the geometry of borate super-units. The local rigidity induced by planar IIIB triangles also explains the formation of ordered element clusters, already demonstrated by EXAFS and XANES in low-alkali borate glasses containing Ni, Co or Zn.

**Keywords:** glass color, transition elements, borate glasses, optical spectroscopy

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# Spectral-luminescent properties of silver ion-exchanged aluminosilicate glass doped with $\text{Eu}^{3+}$ ions

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Nowadays, silver nanostructures are of great interest for many applications of photonics due to their unique optical, non-linear and electrical properties. Silver clusters (SCs) in glass well-known to possess intense and broadband luminescence in the visible. Glasses with luminescent SCs were proposed to be used as phosphors for white LEDs, down-shifting glasses for solar cells and optical data storage media. On the other hand, well-known rare earth ions are characterized by narrow and weak absorption bands. Energy transfer from SCs can be used for improving characteristics of optical glasses doped with rare earth ions.

Glasses based on the  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{ZnO}-\text{SiO}_2-\text{F}$  system doped with  $\text{Sb}_2\text{O}_3$  (0.002% mol.) and  $\text{Eu}_2\text{O}_3$  (0-0.5% mol.) were synthesized. Silver ions were incorporated into the glass by ion exchange (IE) diffusion. In order to form SCs the ion-exchanged samples were heat-treated at temperatures in the range of 350-500°C. In this work we presents results on study of influence ion-exchange duration, heat treatment temperature and duration on the energy transfer from SCs to  $\text{Eu}^{3+}$  ions.

As-prepared samples show no luminescence under UV excitation at 350 nm. Broadband and intense luminescence related to SCs are observed in the glass after the IE and subsequent heat treatment. Intensity of SCs luminescence, as well as  $\text{Eu}^{3+}$  ions emission, increases with rising the (HT) temperature from 350 to 450 °C. Moreover, intensity of the  $\text{Eu}^{3+}$  emission in the glasses after formation of SCs is much higher than that in the as-prepared glasses due to energy transfer from SCs to  $\text{Eu}^{3+}$  ions. Formation of silver nanoparticles, which are characterized by the surface plasmon resonance, in the ion-exchanged glass samples heat-treated at 500 °C results in luminescence quenching.

Thus, we observed effective energy transfer from SCs to  $\text{Eu}^{3+}$  ions in silver ion-exchanges aluminosilicate glass. The developed glass can be used as down-convertors for solar cells and phosphors for LEDs.

This work was supported by the Ministry of Education and Science of Russian Federation (Project 16.1651.2017/4.6).

**Keywords:** silver clusters, europium, silicate glass, ion exchange, luminescence

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\*Speaker

# Absorption spectrum analysis of Fe-Ce- and Fe-Cu-doped soda-lime-silica glasses melted with a refiner

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A detailed fitting analysis of the absorption spectra shows significant differences in the structures and concentrations of the Fe<sup>2+</sup> and Fe<sup>3+</sup> ions and the Ce- or Cu- ions, dependent on the mutual co-dopant concentrations. The differences are related to the glass composition: 15soda-15 calcia-70 silica with Na<sub>2</sub>SO<sub>4</sub> refiner, and on the melting conditions: oxidizing and reducing. The dopant concentrations of Cu, Ce and Fe ions in the studied glasses are low, i.e. below 2 weight %, and the analysis results suggest that there is no 5-coordinated Fe-ions in these glasses. The fitting parameters obtained for the Fe- and Cu-ion structures are those published in Refs. 1-2 for the 15-15-70-glass. The parameters obtained for the Ce- ions are close to those earlier found in Ref. 3, and the Ce<sup>3+</sup> charge transfer peak position (wavenumber) varies also with the concentration of the dopant.

The reflectance, over the range from 250 nm and upwards, was seen to follow the refractive index defined as a Cauchy- equation, fitted to the refractive indices measured at several visible and near IR wavelengths. The effect of the reflection loss subtraction method on the absorptance fitting results was found to be one important factor. However, at the low dopant concentrations, the reflectance from the second glass surface at the UV-edge, is dependent on the high absorption inside the glass at the charge transfer peaks of Cu, Ce and Fe ions, but the reflectance seems not to be caused by a large increase of the refractive index. Thus, the charge-transfer occurs between the closest ions (between Fe- and O-ions, and between Cu and O ions and the Ce- and O- ions) in the studied glasses.

**Keywords:** Absorption spectroscopy, doped soda, lime, silica glass, Fe, Cu, Ce, fitting analysis, effect of reflectance

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\*Speaker

# Measurement of internal transmittance and refractive index of optical glasses at cryogenic temperatures

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The authors have developed a unique Cryogenic Vacuum facility for measuring the temperature dependency of internal transmission and refractive index of optical glasses at cryogenic temperatures. The sample temperature can be set in the range 35 K – 375 K and the wavelength range covered using a combination with different instruments is currently 180 nm – 25,000 nm. This poster gives a short description of the facility and some results obtained on optical glasses that were selected by the European Space Agency for instrument development for future scientific missions.

**Keywords:** refractive index, internal transmittance, cryogenic, optical

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\*Speaker



# **OPTOELECTRONICS AND OPTICAL PROPERTIES 2**

# Cobalt oxide doped zinc-boron-phosphate glasses, preparation and properties

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Boron-phosphate glasses combine the properties of phosphate glasses such as high solubility for rare-earth ions and excellent optical properties with the high thermal, chemical and mechanical properties introduced by boron oxide [1]. The obtaining and properties of boron-phosphate glasses doped with cobalt oxide are investigated in this work. The glass was prepared by classical melting-quenching method but using the wet preparation of raw materials [1]. The amount of CoO was of 0.5 and 3.0 mol% and the melting temperature of 1300 °C for 2h. UV VIS transmittance shows a minimum in the domain of 500-700 nm. The FTIR maxima are attributed to the stretching vibrations of the P-O-P bonds in units Q2 and Q1 at 770 and 870-890 cm<sup>-1</sup> respectively and to the symmetrical and asymmetrical stretching of the PO<sub>3</sub><sup>2-</sup> units at 1030 and 1220 cm<sup>-1</sup>, respectively. The vibrations of O3B-O-BO4 bonds can be identified at 770 cm<sup>-1</sup> and asymmetric vibrations of O3B-O-B-O bonds in triangular borate units (BO<sub>3</sub> and BO<sub>2</sub>O-) from piro and orthoborate groups at 1030 cm<sup>-1</sup>. The mechanical properties, hardness (H), Young's modulus (E) and fracture toughness (KIC) of boron phosphate glasses, evaluated by micro- and nanoindentation techniques, showed higher values than those for alumino-phosphate glasses. DSC analyze of samples thermal treated at 800 and 900 °C indicates the crystallization temperatures around 660 and 790°C for the XRD identified crystalline compounds Al(PO<sub>3</sub>)<sub>2</sub> and BPO<sub>4</sub>. The magnetic susceptibility values lies between 1.8 x 10<sup>-5</sup> emu / g / Oe and 9.5 x 10<sup>-5</sup> emu / g / Oe, directly proportional to Co oxide concentration.

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**Keywords:** Boron, phosphate glasses, mechanical properties, FTIR, Raman, DSC, magnetic properties

# Size and temperature effect on the photoluminescent properties of Europium-doped silica nanoparticles

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Optical fibers containing rare-earth (RE) doped nanoparticles are investigated to develop new devices such as fiber lasers or amplifiers [1]. Thanks to this route, alteration of the spectroscopic properties of RE ions have been already reported [2,3]. However, the broad size distribution of vitreous nanoparticles does not allow to discriminate between the role of their composition and their size on the luminescent properties as already reported for crystalline nanoparticles [4]. In this context, we take advantage of the sol-gel process to prepare vitreous nanoparticles with controlled sizes to study their luminescent properties before and after annealing at 900°C and compare their properties with the Eu-doped silica bulk.

The classic sol-gel process remains one of the most important approach for the preparation of such nanoparticles with diameter larger than 50 nm using the Stöber method [5]. Smaller ones (around 10 nm, Fig. 1.a) can be obtained by Sol-Gel in reverse micro emulsion method (water in oil) [6, 7]. In this case, the hydrolysis and the polycondensation take place in the hydrophilic micelles that play the role of nanoreactors.

For this study, silica nanoparticles with several molar contents of europium (0.2, 0.5 and 1%) were prepared in one step.

All nanoparticles were characterized by Transmission Electron Microscopy (TEM) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The effects of the size of the nanoparticles and their Eu content (Fig. 1.b) as well as the annealing temperature effect on their photoluminescent properties have been investigated. These correlations and results will be presented and discussed.

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**Keywords:** Silica nanoparticles, Sol, Gel, Europium, Photoluminescence.

# Preparation and application of phosphor-in-glass for Fabricating white LEDs

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Phosphor-in-glass (PiG) as fluorescent conversion material has been widely applied in high-power light-emitting diode (LED) owing to its good thermal stability, high thermal conductivity, and low thermal expansion coefficient. However, the preparation technology and optical performances of present PiG are difficult to satisfy the packaging requirement of high-power white LED. Thus, a preparation method based on screen-printing and low-temperature sintering was proposed to prepare PiG in this paper. Preparation technology and properties characterization of PiG were studied. The PiG was prepared by screen-printing and low-temperature sintering. The effects of sintering temperature on the performances of PiG were investigated, and the results indicate that the optimized sintering temperature is 600. In addition, the properties of PiG were analyzed, including microstructure and constituent analysis, phase analysis, transmittance, and emission spectra and excitation spectra.

The yellow PiG was prepared and used to package LED. The effect of yellow phosphor content on the optical performances of white LED was investigated, indicating that when the ratio of yellow phosphor is 40%, the optimized optical performances of LED are achieved. In addition, the reliability of PiG and PiG-based white LED was measured in different aging condition. Compared with the phosphor-in-silicone, the PiG and PiG-based white LED achieve superior thermal reliability.

The yellow and red PiG was prepared and used to package LED. The effect of yellow and red phosphors content on the performances of white LED was studied. The results indicate that when the ratio of yellow phosphor is 40% and the ratio of red phosphor is 9%, the optimal optical performances of LED were achieved. In addition, in order to inhibit spectral overlap, the multilayered PiG and patterned PiG were proposed, thus the optical performances of LED were improved.

**Keywords:** White LEDs, Phosphor, in, glass, Screen, printing, Optical performance, Application

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\*Speaker

# Devitrification behavior of sol-gel derived ZrO<sub>2</sub>-SiO<sub>2</sub> rare-earth doped glass: correlation between structural and optical properties.

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Efficiency of the most common single-junction Si solar cells is limited to 30% because of the mismatch between the incident solar spectrum and the spectral absorption properties of the material. The photon down-conversion phenomenon is considered as an effective approach for improving of the solar cells performance. Particularly cooperative energy transfer from single Tb<sup>3+</sup> to two Yb<sup>3+</sup> ions, with quantum efficiency up to 196% has been observed.

In present study rare-earth doped ZrO<sub>2</sub>-SiO<sub>2</sub> glass is considered as a potential down-converter for solar energy applications. The base glass has high thermal stability and chemical durability, whereas crystalline products formed during devitrification, in particular ZrO<sub>2</sub>, can improve its optical properties. 30 ZrO<sub>2</sub>-70 SiO<sub>2</sub> glasses doped with 1 mol % Tb<sup>3+</sup> or 1 mol % Tb<sup>3+</sup> and 10 mol % Yb<sup>3+</sup> were synthesized by sol-gel method. The obtained gels were heated at different temperatures and times (1000°C : 2h, 5h, 10h, 30h; 1100°C : 2h, 5h, 10h, 30h).

By means of fluorescence spectroscopy it was found that efficiency of the down-conversion photoluminescence depends on the gel heat-treatment procedure. At the same time alteration of Tb<sup>3+</sup> and Yb<sup>3+</sup> emission spectra were observed, evidencing about changes in local environment of the rare-earth ions. Raman spectroscopy investigation revealed possible formation of up to 3 different crystalline phases in the samples, including monoclinic and tetragonal ZrO<sub>2</sub>. According to the XRD analysis, the latter phase found to be dominant in the samples.

To understand influence of these crystalline phases on the luminescence properties several micro-2D maps under 488, 532 and 780 nm laser excitation were collected, allowing to correlate emission of the rare-earth ions with the host matrix structural changes. It was demonstrated that the observed alteration of the emission spectra is largely related to the incorporation of Tb<sup>3+</sup> and Yb<sup>3+</sup> into the crystalline phases. It is shown that the final performance of the down-conversion is determined by efficiency of Tb-Yb energy transfer as well as the ions emission itself in the different phases formed and redistribution of the rare-earth elements during devitrification of the glass.

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\*Speaker

**Keywords:** down, conversion, sol, gel, crystallization, rare, earth, luminescence



# Elongation, break-up, dissolution and growth of nanoparticles during the fiber drawing of silica-based optical preforms

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Rare-earth-doped (RE) silica-based optical fiber lasers and amplifiers are developed for numerous applications. However, silica glass has certain characteristics (high phonon energy, low RE solubility, ...) which may be detrimental for the luminescence properties of RE. To overcome this issue, the incorporation of RE in nanoparticles is investigated to tailor the spectroscopic properties through the control of their composition [1]. Such optical fibers are elaborated by a high temperature fiber drawing (2000°C) of nanoparticles-doped optical preforms.

This communication focuses on the thermodynamical and morphological changes undergone by nanoparticles throughout the fiber drawing. Dissolution and growth of particles induced by high temperatures will be discussed. Also, tomography-based (FIB/SEM) and X-ray nanotomography Multiscale imagery show that nanoparticles elongate and can even break-up during the fiber drawing [2]. Such modifications are explained by Rayleigh-Plateau instabilities and the competition between viscous forces and surface tension. These observations allow us to envision a new top-down strategy, the use of these phenomena to tailor optical properties through the control of the size and shape of nanoparticles during the drawing step.

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**Keywords:** optical fibers, silica, nanoparticles, fiber drawing, break up

# Photoluminescence from PbSe and Sr<sup>2+</sup>-doped PbSe quantum dots embedded in silicate glass

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Glasses doped with quantum dots (QDs) have been intensively investigated in recent years, due to the tunable absorption and photoluminescence in a wide wavelength range induced by the quantum confinement effects. This work reports the photoluminescence from lead selenide (PbSe) and Sr<sup>2+</sup>-doped PbSe QDs in silicate glasses. PbSe QDs were precipitated in the glass system with nominal composition of 50SiO<sub>2</sub>-25Na<sub>2</sub>O-8.2ZnO-10BaO (or SrO)-5Al<sub>2</sub>O<sub>3</sub>-0.6PbO-1.2ZnSe (in mol%). When BaO was replaced by SrO, the Sr<sup>2+</sup>-doped PbSe QDs formed and showed large blue-shifts in both absorption and photoluminescence compared to the PbSe QDs. The incorporation of Sr into PbSe QDs leads to the increasing in the band gap, which resulted the large blue-shifts. The PbSe and Pb<sub>1-x</sub>Sr<sub>x</sub>Se QDs were excited with the pumper power from 100 to 600 mW at 294K. When the pumper power increased from 100 to 600 mW, the photoluminescence bands from the pure PbSe quantum dots showed a blue-shift of  $\sim 4$  meV, and the full width at half maximum (FWHM) increased from 168 to 204 nm. These changes were due to the increased in the local temperatures induced by pumper power. While, the photoluminescence bands from the Pb<sub>1-x</sub>Sr<sub>x</sub>Se quantum dots showed a red-shift of  $\sim 26$  meV, and the FWHM increased from 196 to 232 nm. This heating induced red-shift was attributed to the negative temperature coefficient  $dE/dT$  of the Pb<sub>1-x</sub>Sr<sub>x</sub>Se QDs.

**Keywords:** Sr<sup>2+</sup> doped PbSe, laser induced heating, photoluminescence

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# Mutual Effect of Quantum Dots and Rare Earth Ions in glass Matrix

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Both rare earth doped glass and ceramics, and quantum dots (QDs) in glass matrix have attracted much interests for their promising potential applications for optical and photonics devices, solar cells and others. In general, rare earth ions can be the nucleation agent of crystallization for oxide glass, oxy-fluoride glass and others, while the crystallization can improve the luminescence performance by aggregation and local environment change of rare earth ions. However, the function of rare earth ions on the chalcogenide based QDs was not clear yet. The interactions between rare earth ions and QDs for the luminescence were rarely investigated. In this research, the mutual effects of rare earth ions and QDs in silicate glass matrix was studied. Nd<sup>3+</sup>, Er<sup>3+</sup> single doped silicate glass specimens with additional CdO and ZnSe, for CdSe QDs formation, were prepared by conventional melt-quenching method. The CdSe QDs with different diameters was fabricated by the subsequent heat treatment under different temperatures and durations. The absorption and photoluminescence peaks showed red shift because of increasing CdSe QDs diameter. In fact, the glass with Nd<sup>3+</sup> or Er<sup>3+</sup> ions presented absorptions and photoluminescence peaks with longer wavelength, accordingly lager CdSe QDs. X-Ray Diffraction, Raman spectra, Transmission Electron Microscope (TEM) also confirmed that the formation of CdSe QDs favored by the rare earth ions. Moreover, the infrared luminescence from Nd<sup>3+</sup>, Er<sup>3+</sup> ions were enhanced by the formation of CdSe QDs. The Energy dispersive X-Ray Spectroscopy (EDS) and Electron Energy Loss Spectroscopy (EELS) proved the aggregation of rare earth ions into CdSe QDs, for low phonon energy surroundings, which enhanced the luminescence from rare earth ions.

**Keywords:** Photoluminescence, Semiconductor Nanocrystals, Local Environment, Nucleation Agent

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# Upconverter phosphate glasses prepared using direct doping method

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Laser glasses are glasses doped with rare-earth (RE) elements. Since the invention of the first solid-state laser in 1960, many important successes have been achieved in diode laser pumped solid-state lasers, followed by the blooming research for new laser glasses. A major research focus in laser glasses is glass for upconversion. Upconversion (UC) is a phenomenon where the serial absorption of two or more photons causes light emission at shorter wavelength than the excitation source. Phosphate glasses could be good glass candidates due to their *eco-friendly* compatibility. However, these glasses have a large phonon energy, which is disadvantageous to the UC emission

Therefore, we investigate new phosphate-based glass composites to be used as soft upconverters.

In this presentation, we will demonstrate that upconversion can be obtained in phosphate glass composites which contain a low doping level of Er<sup>3+</sup> (0.01 at%) and Yb<sup>3+</sup> (0.06 at%). This achievement is possible by adding Er<sup>3+</sup>, Yb<sup>3+</sup> codoped nanoparticles (NPs) in the glasses using direct doping process. We will explain that it is crucial to control the melting process in order to balance the survival and dispersion of the particles in the glass composites. Finally, we will demonstrate that the corrosion behavior of the glass melt is another important parameter to consider in order to engineer new glass composites using this direct doping method.

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**Keywords:** phosphate glass, NaYF<sub>4</sub>:Yb, Er particles, direct doping method, upconversion

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\*Speaker

# OXYFLUORIDE, OXYNITRIDE GLASSES

# The structural role of fluorine in ionic glasses via fluorine-19 MAS NMR

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Ionic glasses, defined as compositions with more modifying ions than network formers, are of interest since their properties are dominated by ionic interactions, allowing an opportunity to understand the role of these interactions in structure-property relationships. Recent publications have demonstrated the stability of fluoro-phospho-sulfate (FPS) glasses over large compositional ranges. The addition of F- *via* AlF<sub>3</sub> has been found to greatly increase the stability of the glass-forming region of the FPS family, leading us to question the exact role of the fluorine in the glass structure. Furthermore, FPS glasses have been found to possess high ionic conductivity, indicating that F- may be mobile in these structures at elevated temperatures. The fluorine peaks resolved in fluorine-19 MAS NMR are highly sensitive to the identity of neighbours; for example, F-Na-O, F-Al-O and M-F-M-O (where M = metal) units are discernible. This allows for the quantification of terminal and cross-linking fluorine atoms in FPS glasses, which will then be related to the mechanical and thermal properties, and the ionic conductivity of these glasses. Terminal fluorine atoms are interesting as they essentially remove cations from the glass network leading to a paucity of charge-compensators in the phospho-sulfate region which coincides with an increase in Al coordination (AlO<sub>x</sub>F<sub>y</sub>). It is expected that at low fluorine content, more terminal fluorines are present compared with at higher fluorine content, where non-bridging oxygens are replaced by cross-linking fluorines (M-F-M).

**Keywords:** ionic glasses, NMR, structure, property relationships, fluoride

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# Transparent 80SiO<sub>2</sub>-20LnF<sub>3</sub> sol-gel oxyfluoride glass-ceramics for photonics

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The usual method to prepare oxyfluoride glass-ceramics (OxGCs) is traditional glass melt-quenching (MQ) [1,2]. Nevertheless, the MQ method presents some drawbacks, such as the high melting temperatures (1400-1700 °C) that lead to significant fluorine loss, up to 30-40 wt%, thus limiting the final crystal content (~ 10 wt%). In addition, due to frequent phase separation, it is a challenge to prepare samples with high optical quality. To overcome these limitations, the Sol-Gel (SG) route has been considered as a promising alternative process to obtain transparent OxGCs. In fact, SG is a practical, very flexible and relatively cheap method to fabricate novel and innovative materials at temperatures much lower than those used for MQ materials. The low temperature allows higher amounts of fluoride nano-crystals to be introduced with much better dispersion than in MQ compositions. Moreover, higher homogeneity can be obtained with no phase separation. However, to date results concerning SG OxGCs have treated very small active-phase concentrations (< 10 mol%) and all the benefits that this process offers have not been exploited.. In this work, we present the synthesis and properties of novel 80SiO<sub>2</sub>-20LnF<sub>3</sub> GCs (Ln=La, Gd) doped with Rare-Earth (RE) ions [3]. Structural features obtained by XRD, HRTEM, EDXS, XAS, FTIR and NMR are studied. A crystal fraction of 18 wt%, the highest value reported for SG OxGCs, was obtained by Rietveld refinement. The incorporation of RE ions in fluoride crystals will also be shown, along with photoluminescence properties. Enhanced optical emissions are obtained for the GC samples due to the low phonon energy of the fluoride crystals.

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**Keywords:** sol, gel, oxyfluoride, glass, ceramics, photonics, rare, earths

# Oxynitride phosphate glasses: new strategies of synthesis for new applications

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Oxynitride phosphate glasses, or nitrated phosphates, were firstly obtained by Roger Marchand at the University of Rennes 1 in the early 80's through reaction of NH<sub>3</sub> with a NaPO<sub>3</sub> glass [1]. Further studies soon arrived and were mainly done in France, USA and Spain, but the method of synthesis did not practically change. Meanwhile a great number of compositions were designed and important structural studies developed with the help of NMR and XPS spectroscopies, their applicability has been very limited and often regarded as unfeasible due to the inherent difficulties when handling ammonia. The potential use of oxynitride phosphates as low temperature sealing glasses has undoubtedly been the main option for their application, but there has been other fields where the incorporation of nitrogen produces very interesting modifications, not only increasing the thermal and chemical stability but also giving rise to an important improvement of the ionic conductivity, such as in the case of the so-called LiPON materials [2,3]. On the other hand, if the phosphate glass susceptible of nitridation must contain other elements, e.g. F, S or transition metal ions, the reaction with NH<sub>3</sub> needs to be reconsidered as other reactions may take place during the synthesis, and the processing of the oxynitride glass becomes more complicated and not only depending on the viscosity of the melt. This talk will review the processing and structure of the oxynitride phosphate glasses and the works in which additional steps of synthesis were needed to obtain glasses with new chemical, electrical or even optical functionalities [4].

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**Keywords:** Phosphate Glasses, Oxynitride Glasses, Nitridation, Structure

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# Structural Studies of fluorophosphate Laser Glasses by Solid State NMR

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In this presentation, we will report the structure study of BaF<sub>2</sub>-YF<sub>3</sub>-Na<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub>-NaF glass system by solid state NMR. Based on <sup>23</sup>Na, <sup>31</sup>P, and <sup>19</sup>F high resolution solid state NMR as well as on <sup>31</sup>P/<sup>19</sup>F and <sup>23</sup>Na/<sup>19</sup>F double resonance results, we develop a quantitative structural description on the atomic scale. <sup>19</sup>F NMR results indicate a systematic dependence of the fluoride speciation on the content of YF<sub>3</sub>. F<sup>-</sup> ions were transferred from P<sup>5+</sup> ions to Ba<sup>2+</sup> and Y<sup>3+</sup> ions with the increasing of YF<sub>3</sub>. Both F<sup>-</sup> and Y<sup>3+</sup> ions were homogeneously distributed in the glasses. No nanophase segregation was observed. P<sup>5+</sup> ions mainly exist as [PO<sub>4</sub>]<sup>3-</sup> groups with minute [PO<sub>3</sub>F]<sup>2-</sup> groups.

**Keywords:** fluorophosphate glass, glass structure, solid state NMR

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# Ordering of Ba site in MgF<sub>2</sub>-rich barium fluoroborate glasses and their highly efficient photoluminescence

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New oxyfluoride glasses of  $x\text{MgF}_2-(66.7-2x/3)\text{BaO}-(33.3-x/3)\text{B}_2\text{O}_3$  ( $x=10-50$ ) (in mol%) were prepared by using a conventional melt-quenching method. The glass forming region is wider than oxide (MgO-BaO-B<sub>2</sub>O<sub>3</sub>) system. Glass structure was investigated by <sup>11</sup>B- and <sup>19</sup>F-MAS NMR, Raman scattering spectroscopy, X-ray diffraction, and EXAFS.

It was indicated that the glass with  $x=40$  is composed of BO<sub>3</sub> units mainly, e.g., 92.8% of BO<sub>3</sub> and 7.2% of BO<sub>4</sub> units by <sup>11</sup>B-NMR and fluorine between Mg and Ba ions by <sup>19</sup>F-NMR. Three kinds of distances of Ba-Ba bonding were found in X-ray diffraction. The distances are consistent with the Ba-Ba distances of the out-of-plane direction and the in-plane direction in the oxyfluoride crystal of BaMgBO<sub>3</sub>F, composed of MgO<sub>4</sub>-BO<sub>3</sub> oxide layers and Ba-F fluoride layers.

Glasses have wide UV transmittance region and it enhanced with addition of MgF<sub>2</sub>, i.e., ~220 nm for 10MgF<sub>2</sub> and ~180 nm for 50MgF<sub>2</sub> of UV cutoff. Photoluminescence properties of Eu<sup>3+</sup>-doped glasses were investigated. Quantum yield of glasses increased with addition of MgF<sub>2</sub>, i.e., red photoluminescence with 82 % for 10MgF<sub>2</sub> and 98% for 50MgF<sub>2</sub> of quantum yield in the visible region at the excitation of the wavelength 393 nm.

**Keywords:** Oxyfluoride glasses, Borates, Photoluminescence, X, ray diffraction, Rare earth

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# **MECHANICAL PROPERTIES 1**

# In-Situ Raman Spectroscopy During Indentation to Study Plastic Deformation in Silicate Glasses

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Understanding plastic deformation in silicate glasses is extremely important in the development of glasses with improved resistance to mechanical failure. Plastic deformation under a point contact determines the stress state, which determines whether a surface flaw forms, which in turn determines the strength of the glass. Unfortunately, relatively little is known about the atomic scale mechanisms that control plasticity in silicate glasses. To date, most effort has focused on the continuum concepts of shear and densification. Raman spectroscopy is a powerful tool for investigating structure of glass. This method has been used to study glasses deformed by indentation ex-situ, however this approach can only interrogate the unloaded glass after deformation. To investigate the structure of plastically deformed glass under load, we have developed an instrument in which the deformed material under the indenter can be investigated in-situ, while the load is being applied. We show that we are able to track changes in spectra which can be correlated to ring size, bond angles, and other structural motifs with load. By tracking these changes, we could identify transient structural changes which no longer exist after load is removed. We are also able to investigate these quantities with position under the indenter using simple mapping and to comment on the relative amounts of shear and densification modes. Additional experiments to study the effect of composition, water content and strain rate, as well as applications to other nanomechanical tests are described.

**Keywords:** Raman spectroscopy, indentation, plastic deformation, hardness

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# Combined Experimental and Computational Study of Damage in Silica Glass due to Laser Shock

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Fracture initiation and propagation under laser shock is the main focus of the current study. The shock was generated by a high intensity laser using the ELFIE facility at the LULI, UMR 7605 at the French École Polytechnique. Front and rear face damages of the samples were observed and quantified by optical methods and X-ray micro-CT. They ranged from no damage at all to a completely damaged sample on both front and rear faces. Micro-CT showed that the most damaged samples also have several types of internal failure.

Peridynamic approach was used to explore the underlying mechanisms leading to damage initiation and propagation in silica samples. This method is a non-local formulation that uses integrals instead of tensors, thus removing the singularities caused by geometric discontinuities. The laser-shock experiments were simulated by using a peridynamic grid matching the size of the shocked silica samples. The loading conditions were determined by one-dimensional laser-matter simulations using the ESTHER code (developed by the CEA). They were applied to material points on the front face of the mesh corresponding to the experimental laser irradiated zone. Two specific cases were considered: High Flux (HF) and Low Flux (LF). These cases represent clear differences in both loading conditions and the observed failure modes. In the current study the HF case was used to refine the peridynamic material parameters allowing for a satisfactory description of the experimentally observed damage on both the front and rear faces. This setup was then used in LF case and damage predictions were compared to those of the recovered sample to test the accuracy of the method.

Although the comparisons between experimental measurements and peridynamic predictions are encouraging in multiple aspects, considering the lack of current data on such studies, results are also discussed in terms of qualitative or quantitative matching in order to set the limitations of the numerical approach.

**Keywords:** laser shock, damage, fracture, modeling, peridynamics

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# Fracture toughness and indentation cracking resistance in the Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> chemical system

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Due to an increasing demand for oxide glasses with a better mechanical performance, there is a need to improve our understanding of the composition-structure-mechanical property relations in these brittle materials. At present, some properties such as Young's modulus can to a large extent be predicted based on the chemical composition, while others – in particular fracture-related properties – are typically optimized based on a trial-and-error approach. In this work, we study the mechanical properties of a series of twenty glasses in the quaternary Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system with fixed soda content, thus accessing different structural domains. Ultrasonic echography is used to determine the elastic moduli and Poisson's ratio, while Vicker's indentation is used to determine hardness, as well as the resistance to indentation cracking. Furthermore, the Single-Edge-Pre-cracked-Beam (SEPB) method is used to estimate the fracture toughness ( $K_{Ic}$ ) for some compositions of interest.  $K_{Ic}$  data are then compared to the predicted values derived by means of a model based on the strength of the bonds supposed to be involved in the fracture process. The correlations among crack resistance, toughness, and elasticity are discussed in the light of structural features such as the fraction of non-bridging oxygens and boron speciation.

**Keywords:** fracture toughness, indentation cracking, SEPB, mechanical properties

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# Dynamic behavior of ZrCuAl Bulk Metallic Glasses under high pressure and high strain rate induced by laser shock

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High Velocity debris shielding is of concern since the amount of orbiting space objects is continuously increasing. Thus, the space industry is always searching for innovative and effective materials combining high mechanical properties and lightweight. The Bulk Metallic Glasses family appears to be suitable for such applications. Therefore, the suitability of a ternary  $Zr_xCu(90-x)Al_{10}$  Bulk Metallic Glass (with  $x=45, 50, 55, 60$ ) is investigated by characterizing its dynamic behavior at high pressure and high strain rate ( $10^7$ - $10^8$  1/s). Laser irradiation of various pulse durations (350 fs, 600 ps and 5 ns) were used to generate different shock waves profiles to study the strain rate dependency on the spalling process. Ejecta velocities were measured for several sample thicknesses and pulse durations by Photonic Doppler Velocimetry and transverse shadowgraphy. Spall velocity diagram for 350 fs shots emphasize two distinct velocity domains that may be attributed to a rheological/material behavior change. Scanning Electron Microscopy observations performed on the recovered fracture surfaces highlight the presence of a peculiar feature known as "Cup and Cone". The presence of cups and cones and their morphologies are revealed to be strongly strain rate and compositional dependent. This last dependency can be correlated to specimens Poisson's ratios that are known to have a role on the fracture behavior of Bulk Metallic Glasses. Furthermore, cups are found on sample while cones are observed on spall. By investigating the cups and cones morphologies, two distinct regions are observed: a smooth viscous-like in the center and a flat peripheral one with a large vein-pattern. Energy Dispersive Spectroscopy measurements conducted on these features bring an atomic segregation out taking place during spallation. A mechanism for the initiation and the growth of these cups and cones but also a process for atomic segregation during spallation will be presented.

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**Keywords:** Bulk Metallic Glasses, Dynamic Behavior, Laser Shock, Spallation

# Fractal Geometry: A Key to Understanding the Nature of Glass Fracture

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Failure of materials affects every aspect of research, material development and production. Fracture surface features contain quantitative information about the stress and energy associated with a specific fracture event. Fracture surfaces of all materials examined can be characterized using fractal geometry. Fractal geometry is a mathematical tool that quantitatively describes irregular surfaces. Fractal objects, such as fracture surfaces, are characterized by their fractal dimension,  $D$ , which is the dimension in which the proper measurement of a fractal object is made.  $D^*$  is the fractional part of the fractal dimension and represents the amount of tortuosity out of the plane. The fractal dimensional increment,  $D^*$ , is directly related to the fracture energy,  $g$ , during fracture for many materials, i.e.,  $g = E a_0 D^*$  where  $E$  is the elastic modulus and  $a_0$  is a material structural parameter. Of course, this means that  $D^*$  can be related to the fracture toughness,  $KC = E a_0^{1/2} D^{*1/2}$ , as well. These equations then provide a link to fracture mechanics and quantitative fractography. The combination of atomistic modeling, experimental measurements and the application of fracture mechanics and fractal geometry leads to a suggested sequence and organization of the brittle fracture process. By applying fractographic principles combined with fractal analysis and fracture mechanics, several different types of problems can be solved. The combined analyses can be used to determine whether a product has been manufactured properly, to identify toughening mechanisms in composites and to identify the type of loading during fracture. Examples of each application will be discussed in terms of fracture surface analysis and microstructural characterization.

**Keywords:** Fracture, fractal geometry, fractography, fracture mechanics

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\*Speaker

# The Fracture Toughness of Inorganic Glasses

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Measuring the fracture toughness (K<sub>Ic</sub>) of glasses still remains a difficult task, raising experimental and theoretical problems as well. The available methods to estimate K<sub>Ic</sub> are reviewed. The critical flaw size, and the indentation load for the onset of crack initiation are discussed, in the light of the fundamentals of fracture mechanics and classical background regarding the mechanics of brittle materials. Analytical expressions were further proposed to predict the fracture energy and fracture toughness of glasses from different chemical systems from their nominal compositions. The theoretical values were compared with the experimental ones, as obtained by self-consistent methods such as the SEPB method. The remarkable agreement observed in most cases suggests that measured K<sub>Ic</sub> values correspond to the crack propagation regime (as opposed to the crack initiation threshold), and supports previous investigations in glasses and ceramics, which showed that a crack tip is nearly atomically sharp in these materials (but for metallic glasses).

**Keywords:** glass, fracture toughness, SEPB, theoretical approach

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\*Speaker

# Effect of Valence Change on Surface Stresses in EuPO<sub>3</sub> Glasses

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Effects of heat treatment in reducing and oxidizing atmospheres on the valence states and resulting stresses was examined in europium metaphosphate glasses. Glasses were prepared through a melt-quench method, cut and polished to an optical quality. Samples were heat treated above and below T<sub>g</sub>. Surface stresses created by the valence changes were probed through the number of cracks generated around Vickers indents and birefringence measurements. Changes in structure and valence state were observed through Raman spectra. An increased number of cracks were observed with heat treating Eu<sup>3+</sup> metaphosphate glasses in a reducing environment, corresponding to the generation of tensile stresses caused by a change from Eu<sup>3+</sup> to Eu<sup>2+</sup>. A corresponding change in the area of the O-P-O bridging oxygen Raman peak was observed.

**Keywords:** Glass, Metaphosphate, Valence change, Surface Stresses, Raman Spectroscopy

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# Innovative ion implantation technologies for cutting-edge materials : Scratch resistant glass, a first case study

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Ion implantation technologies have been used for many years in electronic industries but never on a large scale for materials surface treatment and especially for flat glass materials. This technology consists in bombarding in a vacuum chamber the surface of a material with highly energetic ions. The ions penetrate violently into the surface of the material, then stop and lose their energy because of a cascade of collisions. The surface reorganization and the implantation of ions into the surface of the material can modify the physico-chemical properties of various materials from polymers to metals, from glass to crystals.

The judicious choice of the implanted ions allows obtaining re-alloying, amorphization or nano-restructuring of the surface, improving the material's properties or adding new functionalities. These properties are typically hardness, friction coefficient, resistance to cracking, or resistance to corrosion. Another advantage of this technology over its alternatives is its environmental friendliness (no emission, no additional heating and final product recyclability).

A new design of an ECR ion source-based micro-implanter, producing multi-charged ions (dissociation of the molecule and up to 4 positive charges) by employing high frequency microwaves, was used to obtain high productivity and large surface area treatment at affordable cost. Furthermore, the utilization of ions with different charge allows simultaneous ion implantation at different depth.

This presentation will focus on flat glass materials as a first case study. The description of certain effects of ion implantation on glass materials has been described in scientific publications since the 80's. It was for instance shown that ion implantation could improve glass scratch resistance properties on a small scale. We will demonstrate how we can reach outstanding improvements on large glass panels with good uniformity considering the final target in glass industry : 6m x 3m.

**Keywords:** ion implantation, properties

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# **MECHANICAL PROPERTIES 2**

# On the role of amorphous overlays on the mechanical properties of Ni nanoparticles under compression

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Nano-objects like nanowires, nanoparticles and thin films are used in various fields of applications as nano-electronics, pharmaceuticals, catalysis or additives and lubricants. Nano-crystals exhibit particularly promising mechanical properties: they show a size-dependent elastic regime as well as increased yield strength and ductility compared to their bulk counterpart that is associated to surface dislocation nucleation. However, a significant data spread is observed and the sample surface state has to be taken into account. For example, *in situ* TEM experiments have identified the presence of an amorphous overlay at the top of metallic, ceramic or semiconductor nano-structures. Very few studies investigate the role of these amorphous shells on the mechanical properties of nano-crystals. In this context, we use Molecular Dynamics (MD) simulations to investigate the influence of amorphous overlays on the mechanical properties of nanoparticles under compression. To avoid glass composition complexity, we choose to make a Ni monoatomic system for both the crystalline and amorphous phases. The first part of the study will focus on the sample fabrication methodology *i.e.* making a monoatomic bulk metallic glass and then creating a core/crystalline-shell/amorphous Ni nanoparticle. Based on multiple EAM potentials and fabrication method tests, a unique methodology that stabilizes the monoatomic amorphous-crystalline interface is proposed. Then, compression MD tests using a flat punch virtual indenter will be presented. In particular, we will discuss the mechanical response disparities between crystalline, core-shell and purely glassy 20 nm nanospheres. A specific attention will be paid to address the major differences in terms of dislocation-based plastic deformation processes.

**Keywords:** nanoparticles, amorphous, crystalline interface, monoatomic glass, Molecular Dynamics, compression

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# Erosion of Glass Substrates due to Microparticles

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Electromagnetic (EM) window and dome material performance suffers from inadequate fracture resistance to sand particles and rain drops. Airborne sand particle impacts cause local damages that manifest themselves as radial and lateral cracking. Increased roughness through damage on the surface of the EM structures degrades the transmission properties and may lead to loss of communication. Specifically, lateral cracking is suspected of playing a larger role in loss of transmission due to surface damage on EM window and dome materials. In order to mitigate such transmission problems due to sand impact damage, in-depth understanding of the origins of distinct fracture modes is necessary. Previous work involves theoretical approaches utilizing elasticity and plasticity formulations, as well as experimental work.

While it is valuable to understand the erosion resistance of different materials when impacted by specific size erodents, the previously mentioned studies did not explore a direct relationship between impacting particle shape and subsequent damage modes. Not many studies have been published to assess the effect of impacting geometry on damage quantities and mechanisms. The limited research found in a literature survey pertained more to drop-weight impact on composite materials

In order to further the understanding of erosion due to irregularly shaped particles, first impact experiments were performed. Impacting velocity, rebound velocity, and particle volume were estimated from high-speed video footage. Impact events were also correlated to damage sites, and damage was characterized using optical and scanning electron microscopy. To explore the effect of impact geometry, bond-based peridynamic simulations were carried out. Sand particles were characterized using x-ray micro-CT. Particles from the virtual library were matched to particles from specific impacts in the experiments, and PD simulations were performed using those particles at different orientations at impact. Also, further PD simulations were conducted using sphere and cylinder impacters, to show ideal contact geometry: a perfectly round surface for the sphere, and a perfectly flat surface for the cylinder face. Damage quantified from the results of the PD simulations was compared to the corresponding damage from impact experiments.

**Keywords:** impact, damage, fracture, modeling, experiments, characterization, peridynamics

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# Statistical analysis of subcritical crack growth in water bearing soda-lime silicate glasses

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It is well known that subcritical crack growth (SCCG) in glasses is highly affected by the presence of water in the surrounding atmosphere of a propagating crack. Despite this, there is less knowledge on the influence of structurally bound water on crack propagation. For this purpose, soda-lime silicate glasses of up to 8 wt.% water were synthesized using an internally heated pressure vessel at 0.5 GPa. As the sample size is limited by this preparation route, standard test geometries, which allow to determine the stress intensity factor as a function of the crack length, such as double cantilever beam, are not feasible. Thus, radial cracks in hydrous glasses were initiated by Vickers indentation and the decelerating SCCG was captured by 60 seconds video sequences of high recording rate (30 frames per second). An automated image analysis algorithm was used for the precise and operator-independent analysis of the crack length of each video frame. Approximately 150 cracks per glass composition were analyzed to demonstrate statistical significance with respect to the broad scatter in Vickers-induced SCCG recently found for non-hydrated glasses. The results show that also for hydrated glasses the proper approach is to use averaged SCCG data of a large number of cracks to develop a precise analytic formulation of the effect of structurally dissolved water on SCCG.

**Keywords:** SCCG, Stress intensity, Wiederhorn, Hydrated Glasses, Statistics

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\*Speaker

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# In-situ observation of the formation of indentation cracks in glass by means of synchrotron X-ray tomography

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Damage caused by sharp contact loading at the surface of glass is a major fundamental problem in glass science, for the glass industry, and for end-users as well. Different microcracking patterns are observed, and cracks may form either on loading or on unloading depending on the glass composition. The driving forces associated with these cracks are intimately related to the elastic response, and to the permanent deformation processes, such as densification and isochoric shear. A specific mechanical testing set-up was used for the situ observation of the displacement field and crack formation during a Vickers indentation process by means of a synchrotron X-ray tomography. Results are discussed in the light of available analytical expressions for the indentation problem.

**Keywords:** Indentation cracks, in situ Xray tomography

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\*Speaker

# Synthesis by SPS of new glass matrix composite with functional properties - toward self-healing glass

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Dense glass matrix particulate composites containing 2 %V of magnetic Fe<sub>3</sub>O<sub>4</sub> particles, 70 nm size in average, were synthesized by means of Spark Plasma Sintering (SPS). We show in this study that a temperature as high as 330°C can be induced in the composite by applying an alternating magnetic field for a few minutes. This finding opens new possibilities for crack-healing and health recovery in damaged glassy materials. The elaboration, the magnetic, and the mechanical properties of this novel functional glass-based composite are presented.

**Keywords:** Composite, magnetism, Fe<sub>3</sub>O<sub>4</sub>, Self, healing, glass

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# SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O Glasses: Understanding how microscale changes alter macroscale fracture properties

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Oxide glasses find extensive uses in our world today due to their amorphous structure, optical transparency, electrical and heat insulation, and large hardness. However, oxide glasses have a major drawback: brittleness. Their failure properties are driven by the mesoscale structure of the glasses. Linking these mesoscale variations to the overall macroscale properties provides new insight onto the controlling factors of glass failure. This is intrinsically important in assessing the life-time of materials. Herein, minute structural variations are controlled by selecting the chemical compositions of 7 SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O ternary glass systems. These changes lead to mesoscale changes as revealed by a novel parameter coined the depolymerization index. This parameter reveals surprising trends with the stress corrosion cracking behavior in Region I. The presentation will focus on stress corrosion fracture damage and how it varies with chemical composition and the depolymerization index.

**Keywords:** SiO<sub>2</sub>, Na<sub>2</sub>O, B<sub>2</sub>O<sub>3</sub> glasses, Stress corrosion cracking, fracture, Physical properties, structural properties

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\*Speaker

# Effect of Humidity and Included OH and During Indentation of Silica Glass

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It has been shown that the presence of water can dramatically impact the fracture and hardness of silicate glasses during indentation. Despite how dramatic this effect is, it is often overlooked due to the difficulty in conducting well-controlled experiments. It is argued that water permeates the indented regions, disrupting the network with non-bridging OH groups. However, it is not known how this can occur on the timescale of a typical indentation. To study these effects, we performed a series of indentations on a set of SiO<sub>2</sub> glasses prepared with OH contents from 10 to 1000 ppm. Each glass was both indented in a humidity controlled glovebox at a range of humidities and indented directly through water droplets. Additionally, to probe the kinetics of water's interaction with the sub-indenter region, we varied the loading rates of the indentations across several orders of magnitude. The implications for hardness testing of glass will be discussed.

**Keywords:** Nanoindentation, Humidity, Water Content, Strain Rate

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\*Speaker

# The Single-Edge Precracked Beam (SEPB) method to assess the fracture toughness, the fracture energy and the stress corrosion cracking of glass

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We show that the Single-Edge Precracked Beam (SEPB) test is not only suitable to the determination of the fracture toughness ( $KIc$ ) of glass, but also offers a unique opportunity to assess the slow crack growth behavior in a single experiment lasting for few minutes. Besides, we found that it is possible to get either a stable or an unstable final fracture regime (pre-cracked specimen) depending on the testing parameters, and that the unstable case is preferable for the estimation of  $KIc$ . The "pop-in" precrack was found mostly to close completely once the load was suppressed on the bridge-flexure device. This led to a reopening event on the loading curves. It is noteworthy that all these original observations were made possible thanks to the design of very stiff testing apparatus ( $6.7 \text{ MN.m}^{-1}$ ) allowing for a cross-head speed as small as  $0.01 \mu\text{m.s}^{-1}$ . Results obtained on four grades of commercially available glasses are compared to those stemming from Vickers indentation cracking and chevron notched experiments.

**Keywords:** Fracture toughness, Vickers indentation fracture (VIF), Chevron, Notched Beam (CNB), Single Edge Precracked Beam (SEPB), Stress corrosion

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# Ex-situ Raman Investigation of Indentations in Vitreous Silica

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Decades of research have led to the conclusion that glass plastically deforms by two mechanisms: densification and shear. In indentation, densification has been associated with "anomalous" glasses containing low amounts of modifiers, whereas shear has been associated with "normal" glasses rich in modifiers. We have combined Raman spectroscopy with indentation techniques to probe local structural changes in silica glass induced by densification. We collected spectra of pristine silica which and compared them to spectra obtained from inside indentations at different loads. We observed large structural changes in the silica which vary continuously with increasing indentation load. In this talk, we clarify the role of the stress state in the atomic mechanisms of plastic deformation by comparing our indentations to the results of many other studies in which silica was hydrostatically compressed at various maximum pressures and temperatures. We are able to attribute differences in the spectra to specific factors such as: shear stress, stress gradients and temperature. We observe that the structural changes induced by indentation are most similar to the structural changes induced by high temperature hydrostatic compression.

**Keywords:** Densification, plasticity, silica, Raman, indentation

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\*Speaker



# PHASE CHANGE MATERIALS

# Ge-Sb-S-Se-Te amorphous chalcogenide thin films for nonlinear optics in the Mid-Infrared

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Chalcogenide materials exhibit a unique portfolio of properties which has led to their wide use for non-volatile memory applications such as optical data storage or more recently Phase-Change Random Access Memory. Some chalcogenide glasses (CGs) are showing a high transparency window in the infrared range and large optical nonlinearities offering also opportunities for elaboration of innovative mid-infrared (MIR) components such as MIR supercontinuum (SC) sources. Up to now, state-of-the-art MIR SC sources have been mainly demonstrated with CGs containing Arsenic. However, the REACH European recommendation and the World Health Organization have both identified Arsenic as one of the ten most harmful chemicals for human health. In that context, we study here the linear and nonlinear optical properties of As-free amorphous chalcogenide thin films with a particular emphasis on their compatibility with CMOS technologies for future realization of on-chip MIR components. Magnetron co-sputtering of chalcogenide compounds targets in an industrial 200 mm deposition tool allowed us to tailor the composition of the amorphous GeSb<sub>w</sub>S<sub>x</sub>Se<sub>y</sub>Te<sub>z</sub> films aiming at finding the best compromise between good glass stability of S-based chalcogenide and the huge nonlinear refractive index of Te-based compositions. Modeling of spectroscopic ellipsometry measurements on the films allowed to determine their linear optical constants and to approximate their optical band gap energy. Optical attenuation at 1548 nm was obtained using M-line technique. FTIR and Raman allowed to get information on the amorphous structure of the films. Advanced optical characterizations of nonlinearities in rib and ridge waveguides with a tailored group velocity dispersion were performed and compared to the nonlinear refractive Kerr index of each CGs calculated by means of analytical and empirical models. Finally, the origin of the enhanced optical nonlinearities observed in some of the amorphous GeSb<sub>w</sub>S<sub>x</sub>Se<sub>y</sub>Te<sub>z</sub> chalcogenide compositions will be

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\*Speaker

probed by means of ab initio simulations.

**Keywords:** Chalcogenide Glasses, Nonlinear Optics, Physical Vapor Deposition, SuperContinuum Generation, Mid InfraRed

# Ab initio modelling of radiation damage in amorphous phase-change memory materials: The case of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>

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Radiation-hard non-volatile memories with large capacity and low production cost are in high demand by the space community for implementation in solid-state data recorders. In phase-change memories, binary data are represented as a structural phase rather than by stored electrical charge; thus, these devices are supposed to be tolerant to ionising radiation effects. Radiation effects on phase-change memories have been investigated by several experimental studies, while radiation-hard memories of relatively small size are already available by BAE systems. In this work, we present the first *ab initio* calculations of radiation-damage in amorphous phase-change materials by carrying out a thermal-spike simulation in order to examine the effect of the ionizing radiation on the short- and medium-range order of the amorphous network and shed light on its atomistic structure. The local environments of irradiated amorphous Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> have been investigated by employing a mixed Born-Oppenheimer and generalised Langevin molecular-dynamics approach in order to model the radiation-damage cascade, dissipate the heat from the irradiated area and probe the structural evolution of the amorphous network. Density-functional theory calculations, with hybrid-functionals, have been used to characterise the electronic structure of the irradiated glass and identify the effect of the ionising radiation on the electronic properties of the glass. The most significant damage of the amorphous network occurs at approximately 300 fs after the detonation of the thermal-spike, since a considerable loss of the quasi-binary chemical order and substantial modifications of the medium-range order were quantified at that time. The equilibrated glass shows a recovery from the damage imposed during ion irradiation, as it manages to maintain its amorphous network. Specific structural rearrangements inside the glass were observed in the modelled glass systems. The total electronic density of states exhibits negligible differences in the electronic structure of the glass before and after irradiation, while the absolute value of the band gap also was not significantly affected. Our simulations manifest the remarkable ability of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> phase-change random-access memory material to be radiation-tolerant, and hence indicating its potential applications in future space and other radiation-present environments.

**Keywords:** phase change memory, radiation hardness, molecular dynamics simulations, atomistic structure

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\*Speaker

# Laser-Induced Modification and Formation of Periodic Surface Structures ("Ripples") of Amorphous GST225 Phase Change Materials

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We studied the surface modification of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> (GST225) amorphous thin films under impulse laser irradiation. GST225 composition is one of the extensively investigated phase change memory (PCM) materials, which is currently used for rewritable data storage applications based on structural phase transitions.

The GST225 amorphous thin films have been prepared by both the vacuum thermal evaporation and *dc* magnetron sputtering. We used nanosecond ( $\lambda=532$  nm, 16 ns) and femtosecond ( $\lambda=515$  nm, 600 fs) lasers to study surface modification. Different methods have been used to determine the composition, in-depth elemental distribution and phase state of thin films (EDX, AES, TOF SIMS surface analysis, XRD). All specimens were studied using TEM/SEM, Raman spectroscopy and AFM.

It is shown that, with specially selected parameters of laser influence, it is possible to realize different types of surface structures. We observed fully crystallized spots in amorphous GST225 matrix in the case of "weak" laser intensity. The rise of laser power caused the formation of crystalline ring-shaped roll spots with amorphous central part. Subsequent increase of laser influence permitted to form periodic surface structures (ripples) with a period of  $\sim 500$  nm in an outlying area of spot. In these structures it is possible realize the periodic modulation of the refractive index due to solidification after the laser action of the crests and valleys of the gratings in different phase states whose dielectric constants differ greatly from one another. We observed the destruction of an amorphous film also, and the partial evaporation of the material in the central part in the case of laser pumping intensity above the threshold. This effect is due to a sharp increase of lattice vibrations amplitude, since when a sufficiently short and powerful laser pulse is applied, the light energy is transferred from the free carriers to the lattice and it causes its rapid melting.

This study was supported by RFBR (17-03-00450) and MES RF (14.Z50.31.0009).

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**Keywords:** phase change memory, amorphous thin films, laser modification

# Controllable crystallization and interface microstructure stability of new phase-change films

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The new phase-change thin films with single element doping, pseudo-binary homogeneous phase, and nano-composite structure have been investigated. It is found that together with well-documented results of Zn-doped Sb<sub>2</sub>Te<sub>3</sub>, Sb<sub>2</sub>Te, Sb<sub>7</sub>Te<sub>3</sub>, and Sb<sub>3</sub>Te systems, we plotted the ternary amorphous-phase forming-region of Zn-Sb-Te. Zn-doped Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> and Sb:Te films exhibit excellent properties, such as nanocrystals uniform distribution, no phase separation, fast speed, reverse optical cycle. The addition of Mg into Sb<sub>7</sub>Te<sub>3</sub> can increase the crystallization temperature, crystalline activation energy and change growth mode, while hindering grain growth and suppressing phase separation from Sb+Sb<sub>2</sub>Te, Sb<sub>2</sub>Te, to Sb phases. In nano-composite structure films with one-dimensional growth mode, the Sb<sub>2</sub>Te-rich nanocrystals, surrounded by TiO<sub>2</sub> amorphous phases, are observed in the annealed Sb<sub>2</sub>Te-TiO<sub>2</sub> composite films. The segregated domains exhibit obvious chalcogenide/TiO<sub>x</sub> interfaces, which elevate crystallization temperature, impede the grain growth and increase crystalline resistance. NiO-doped ZnSb can directly crystallize into a stable ZnSb phase at temperatures greater than 320 °C with suppression of a metastable ZnSb phase. These characteristics enlarge the amorphous/crystalline resistance ratio by approximately five orders of magnitude. The improved thermal stability, larger resistance ratio and direct transition to a stable phase with ultrafast one-dimensional crystal growth indicate the good potential of these materials in phase change memory applications. This work is helpful to explore a new generation of phase change storage film applied in phase-change memory.

**Keywords:** Phase change films, Crystallization, Thermal stability, Interface

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\*Speaker

# Phase Change Materials by Design: Taming Bond No. 6

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Phase change media utilize a remarkable property portfolio including the ability to rapidly switch between the amorphous and crystalline state, which differ significantly in their properties. This material combination makes them very attractive for data storage applications in rewriteable optical data storage, where the pronounced difference of optical properties between the amorphous and crystalline state is used. This unconventional class of materials is also the basis of a storage concept to replace flash memory. This talk will discuss the unique material properties, which characterize phase change materials. In particular, it will be shown that only a rather small group of materials utilizes a unique bonding mechanism ('Bond No. 6'), which can explain many of the characteristic features of crystalline phase change materials. Different pieces of evidence for the existence of this novel bond will be presented. This insight is subsequently employed to predict systematic property trends and to explore the limits in stoichiometry for such memory applications. It will also be demonstrated how this concept can be used to tailor the electrical and thermal conductivity of phase change materials. Yet, the discoveries presented here also force us to revisit the concept of chemical bonds and bring back a history of vivid scientific disputes about 'the nature of the chemical bond'. Finally, we will employ these concepts to identify property trends for chalcogenide glasses.

**Keywords:** chalcogenide glasses, phase change materials, electronic memory, fast crystallization

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\*Speaker



# **PRESSURE AND DENSIFICATION**

# Structure of (11B2O3)0.3(GeO2)0.7 glass at pressures up to 8.2 GPa

Michela Buscemi <sup>\*† 1</sup>, Anita Zeidler <sup>1</sup>, Philip S. Salmon <sup>1</sup>, Gregory S. Moody <sup>1</sup>, Henry E. Fischer <sup>2</sup>

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*The B2O3-GeO2 system is one of the few oxide glass-forming materials that comprises solely network-forming cations, and the local motifs in the pure component glasses B2O3 and GeO2, are rather different [1]. Boron oxide, or B2O3, is formed of corner-sharing planar triangles that link to create B3O6 boroxol rings. The structure of glassy germania, or GeO2 is based on corner-sharing tetrahedra.*

*Investigating the structure of glasses under high pressures allows changes in their atomic level structure to be followed gradually.*

*Structural variation that occur in (11B2O3)0.3(GeO2)0.7 glass under pressure were investigated by using neutron diffraction at pressures up to 8.2(5) GPa. The coordination numbers  $n_{BO}$  and  $n_{GeO}$  start to increase at 5.4(5) GPa, and they reach values of  $n_{BO} = 3.5(1)$  and  $n_{GeO} = 4.5(1)$  at 8.2(5) GPa.*

*The pressure dependence of coordination numbers and bond distances is presented and the results are compared to those obtained via the same experimental method for pure B2O3 and GeO2.*

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**Keywords:** glasses under pressure, coordination numbers, bond distances, atomic level structure

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# A Laser shocked induced densification of silica glass studied by both experience and molecular dynamic simulation.

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Understanding and modeling the mechanical behaviour of silicate glasses under both high pressure (up to several GPa) and high strain rate (up to  $10^9$  s<sup>-1</sup>) loading conditions encountered during hypervelocite impacts is of interest for applications such as high power laser facility (National Ignition Facility in USA or Laser MegaJoule in France) or aerospace fields (solar panel and window). Pure silica, borosilicate or soda lime glasses have been studied for strain rate about  $10^5$  s<sup>-1</sup> using plate impact or explosive device to obtain Hugoniot curve and observe failure wave mechanism. To study these materials under hypervelocite impact conditions, laser shock experiments instrumented by VISAR and transverse shadowgraphy were performed using high-power laser facilities. Pressures in the range of tens of GPa were generated with very limited to no surface damage for pure silica glass. Laser shock experiments allow for the recovering of the impacted sample for post-mortem investigations such as 3D confocal Raman spectroscopy to study for instance residual structural modifications. Raman spectroscopy results are presented for different loading conditions and discussed in the light of the literature (quasi-static loading and thermal history). Furthermore the time scale compatibility of both laser shock tests and Molecular Dynamic simulations offers a real opportunity for a comparison and discussion of the results in terms of residual densification ratio and structural modifications.

**Keywords:** Silica glass, laser shock, Densification, Raman spectroscopy, Molecular Dynamics

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# Pressure dependence of density and structural relaxation of glass near the glass transition region

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A simplified and effective pressure cell together with an experimental procedure has been developed and applied to compress samples of SCHOTT N-BK7 glass under static high pressures in a piston-cylinder apparatus. Results from the density and volume recovery measurements show that, the glass samples were effectively densified in piston-cylinder apparatus with the density at room temperature increasing linearly with frozen-in pressure. To explain the experimental data, we developed a mathematical model based on a suggestion by Gupta (1988) with two internal parameters, named fictive temperature ( $T_f$ ) and fictive pressure ( $P_f$ ), which fits the experimental data well.

**Keywords:** Glass, High pressure, Piston cylinder apparatus, Structural relaxation, Fictive temperature, Fictive pressure.

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# Relaxation processes of densified silicate glasses having different thermo-mechanical histories

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Depending on the thermo-mechanical history, SiO<sub>2</sub> glass samples, with same density, exhibit structural differences (ring population, intertetrahedral angles, ...). From these results, it's interesting to wonder about the role of pressure and temperature during the densification process. One possibility, little studied in the literature, to more understand these structural and thermodynamic differences, is to study the relaxation mechanisms during a temperature annealing.

We have studied relaxation during different high temperature annealing, far below glass transition temperature, densified silicate glasses in order to more understand structural processes occurring during annealing for both pure SiO<sub>2</sub> and Na<sub>2</sub>O-SiO<sub>2</sub> glasses. For that, we have prepared several recovered densified samples from Belt press (High temperature and high pressure) and from diamond anvil cell (room temperature, high pressure). In-situ experiments (Raman spectroscopy, X-ray diffraction, small angle X-ray scattering (SAXS)) have been done during annealing.

Our results put in light that, during temperature annealing, the density decreases monotonously while the structural evolution shows a non-monotonous behaviour. Indeed, both density fluctuations from SAXS and D2 band area, related to 3-fold ring population, from Raman spectroscopy first increase before decrease during the temperature annealing. Then, the relaxation occurs from a transitory state which leads to an inhomogeneity increase during the process. Moreover, the role of sodium cations leads to a more compact glass with a decrease of the free volume and an increase of disorder. Nevertheless, in the sodo-silicate glasses, the transitory state has been also put in evidence during the relaxation process of these recovered densified glasses.

**Keywords:** Silicate glasses, vibrational spectroscopies, high pressure, temperature relaxation, small angle X, ray scattering, structure

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\*Speaker

# Densification and relaxation of densified glasses under electron irradiation in silica and phosphate glasses

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It is possible to permanently densify oxide glasses under High Pressure (HP) either at room or high temperature. In silica glass, electron irradiation can also lead to a density increase but it is less efficient (a few % against 20% under HP). In this work, we are interested in the density variations of phosphate and silica glasses under 2.5 MeV electron irradiation. A significant density increase (up to 13%) was obtained in Zn metaphosphate after a 4x10<sup>9</sup> Gy integrated dose. Note this value is comparable to what was obtained under 2 GPa at T<sub>g</sub> [1]. The increase of glass density will be analyzed in different metaphosphate and polyphosphate glasses as a function of the integrated dose, the initial polymerization degree of polyphosphate glasses as well as the presence of Zn. This will be discussed in terms of structural variations analyzed by Raman spectroscopy and solid state NMR of <sup>31</sup>P.

In pre-densified silica glasses either by HP-HT or by an increase of the fictive temperature, the relaxation of densified silica occurs under 2.5 MeV electrons. The density decrease depends on the irradiation dose and applied temperature during HP (e.g. higher HP temperature lower relaxation). As a result of irradiation, we observed an unusual intensity increase of D1 and D2 Raman bands whereas there is a strong decrease of glass density in 350 and 440°C treated HP samples. This indicates that bond breaking mechanism leads to the formation of 3 and 4 membered rings at the expense of higher membered rings as shown by MD calculation under laser irradiation [2], which does not systematically traduce an increase of the silica density. This depends on the initial structure of the glass and rings statistic.

Kapoor S et al. *Front. Mater.* 4 (2017) 1.

N. Shchleblanov, M. Povarnitsyn *EPL* 114 (2016) 26004.

**Keywords:** structure, density, relaxation, irradiation, silica, phosphate

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\*Speaker

# Spectroscopy as a tool for local density measurement in vitreous silica

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The paper will discuss the possibility for light spectroscopies, *e.g.* Brillouin Light Scattering or Raman Scattering, to locally monitor the densification of amorphous silica. It is indeed well-known that silica significantly densifies under high stresses, either elastically as for example during a high-pressure experiment in a diamond-anvil cell below about 10 GPa or plastically above that limit. Further, this elastic limit strongly depends on the temperature. Irradiation-induced density changes are also observed using ultra-short laser pulses, neutrons or other particles. All these different routes lead to substantial structural modifications which in turn alter the response of silica to light spectroscopy in a complex manner.

**Keywords:** Spectroscopy, Silica, Densification, High Pressure

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\*Speaker

# High Pressure behaviour of v-SiO<sub>2</sub> : Brillouin and polarized Raman study

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High-pressure Brillouin [1] and polarized Raman spectra [2] of vitreous silica are measured up to 8 GPa in diamond-anvil cell at room temperature. On one hand, Brillouin frequencies show that the well-known anomalous maximum in the pressure dependence of the compressibility is suppressed by He incorporation into the silica network. This shows that the elastic anomaly relates to the collapse of the largest interstitial voids in the structure. On the other hand, the combined use of either a nonpenetrating pressurizing medium-argon-or a penetrating one-helium and Neon, allows one to separate density from stress effects on the Raman frequencies.

C. Weigel, A. Polian, M. Kint, B. Rufflé, M. Foret, and R. Vacher, Phys. Rev. Lett. 109, 245504, 2012

C. Weigel, M. Foret, B. Hehlen, M. Kint, S. Clément, A. Polian, R. Vacher, and B. Rufflé, Phys. Rev. B 93, 224303, 2016

**Keywords:** high pressure, elastic properties, structure, silica

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\*Speaker



# PROPERTIES 1

# Redox-induced precipitation of nickel and cobalt metal nano-particles in silicate glasses

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Optical and magnetic properties of transition metal nanoparticles (Co, Ni, Fe) in oxide glasses are currently receiving attention for potential applications in data storage and as magnetic resonance contrast media. The glass matrix thereby acts as a stabilizer preventing metal oxidation as well as agglomeration of the particles. As the particle size plays a significant role for the material properties, controlling growth rate and final size distribution is a prerequisite for future applications. The time-dependent size evolution of Ni and Co metal nanoparticles is therefore studied in borosilicate base glasses. To trigger redox-induced precipitation, the glasses were treated under a hydrogen stream while running a defined time-temperature protocol. Particle size distributions were determined on small scales by analysis of electron microscopy (TEM, SEM) images, whereas UV-Vis-NIR spectroscopy was used to identify mean particle sizes of Ni and Co nano-particles.

**Keywords:** Reduction, Nanoparticles, Kinetics, Cobalt, Nickel

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\*Speaker

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# The Effect of Cation Species on the Sulfur Solubility of CaO-FeO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> Melts

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The charge compensation effect of Ca<sup>2+</sup> and Fe<sup>2+</sup> on the sulfur solubility of CaO-FeO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> melts has been studied. The content of cation species (MO, M=Ca, Fe) and anion groups (AlO<sub>4</sub><sup>-</sup>, SiO<sub>4</sub><sup>-</sup>) were varied to determine the effect of charge compensation [1,2] on the sulfur solubility in high temperature ionic melts. The coordination number of aluminum ion in the super-cooled liquids was identified by deconvolution with PeakFit<sup>TM</sup> 4.0 of <sup>27</sup>Al 500MHz Solid NMR Spectra. [3] The proportion of Q<sub>n</sub> was analyzed by Raman spectroscopy. [4] As a result, the sulfide capacity represents a linear relationship according to the MO activity, as an index of the basicity. In the case of the cationic excess region (M<sub>2+</sub>/Al<sub>3+</sub> > 1.0), the sulfide capacity is directly proportional to the basicity due to high S<sup>2-</sup> stabilization by excess cation. However, in the case of the cation deficient region (M<sub>2+</sub>/Al<sub>3+</sub> < 1.0), the sulfide capacity was shown to be constant depending on the basicity.

Charge Balancing Join :  $(Ca^{2+}+Fe^{2+})/(Fe^{3+}+2XAl_2O_3)=1$  (1)

The reason is that S<sup>2-</sup> activity coefficient of the melts increase due to the absence of M<sub>2+</sub> required for charge balancing with AlO<sub>4</sub><sup>-</sup> and FeO<sub>4</sub><sup>-</sup>. Also, the sulfur stabilization region was determined by the kind of the cation species (M<sub>2+</sub>). The charge balancing region is changed by the stabilization of Al<sub>3+</sub> with Fe<sup>3+</sup> [5] and influences on the cation substitution effect on the sulfur solubility.

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\*Speaker

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**Keywords:** Sulfur solubility Charge Compensation, Iron Redox Equilibria, Cation Substitution, Aluminosilicate melts

# A dislocation based model of rotating-lattice single crystal growth on glass surface by CW-laser

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We recently demonstrated the fabrication of rotating lattice single (RLS) crystal architecture of unlimited dimensions in various glasses. The RLS crystal is a novel form of solid, in which active properties can be designed on atomic scale by appropriate choice of process parameters. An analysis of lattice orientation of lines written with different laser speed by electron back scattered diffraction (EBSD) shows a direct impact of the trajectory of laser beam and the shape of crystal-glass interface on lattice rotation. We proposed a model of RLS crystal lattice in which rotation is created through the introduction of unpaired edge dislocations during glass to single crystal transformation. In general, these dislocations are of one dominant sign such that extra half planes are added from the free crystal surface, thereby inducing clockwise lattice rotation. We have now obtained evidence of this critical assumption of our model through direct observation of dislocations using transmission electron microscopy of Sb<sub>2</sub>S<sub>3</sub> samples prepared by the lift-out technique using focused ion beam. We will further explore the process of crystal growth within Sb<sub>2</sub>S<sub>3</sub> glass by moving CW laser beam, which occurs in solid state and under strong temperature gradient. Then the growth can occur by the classical mechanism as atoms reorganize and jump across the growing interface. Alternatively, nuclei/embryo may form ahead of the interface, which then attach to the crystal via recently proposed ‘particle attachment’ mechanism. We will note that the crystal growth model based on particle attachment and introduction of dislocations maybe applied to other solid-solid as well as liquid-solid transformations.

**Keywords:** laser crystallization, single crystal, rotating lattice, transmission electron microscopy, EBSD

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\*Speaker

# Microstructuring the optical properties in ionic glasses by thermal poling: the influence of the sodium content

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In the design of microphotonic devices, it is of the utmost importance to control optical properties at different scales. For this reason, new materials and processes have been developed. Thermal poling induces in ionic glasses strong composition and structural modifications as well as index change and second-order nonlinear (SONL) response which is usually forbidden in such centrosymmetric media.

In this work borophosphate niobium and sodium glasses have been studied. Different content of sodium from 3 at% up to 10 at% have been tested while the ratio between the other compounds has been kept unchanged. In the first place the influence of the sodium content on both the structure and the linear optical properties, namely the index, have been discussed. In the second place the evolution of the linear and nonlinear optical properties induced by thermal poling have been quantified. Strong variations of the index ranging from 0.005 to 0.015 have been observed along with a SONL response (with  $\chi(2)$  from 2 pm/V up to 4 pm/V) both function of the initial sodium content. It has consequently been shown that the sodium ratio was a key parameter allowing one to tune the amplitude of the index change as well as the SONL efficiency induced by thermal poling.

Finally, using thermal poling as an imprinting process, structuring of optical functionalities has been controlled at the micrometric scale leading to the conception of an optical grating with both linear and nonlinear responses.

**Keywords:** thermal poling, optics, microstructuring

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# Redox (and acid-base) properties of aluminosilicate melts: the ionic-polymeric description

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The properties of melts and glasses of interest in Earth Sciences and glass-making industry are heavily affected by redox equilibria. These are not only sensitive to changes in intensive parameters, such as temperature and oxygen fugacity ( $fO_2$ ), because extensive parameters (composition) have major effects. This compositional control, which includes the amphoteric behaviour of some components, demands the understanding of the link between redox, acid-base properties and structure. Nevertheless, a precise and coherent chemical "syntax" is required to write chemical exchanges in aluminosilicate melts. These are in fact a special category of fused salts (oxides, in our case), in which the silicate structure is such that cations and anions have actual charges lower than formal ones, and the residual charge distribution from bonding of bridging oxygen to silicon allows oxygen bonding with other cations. This characteristics makes the relative contribution of non-bridging and bridging oxygens to the oxygen coordination of the other cations poorly known, avoiding to readily distinguish solute and solvent like in aqueous solutions and consequently the complexes needed to define acid-base reactions. Therefore, the distinction between solute and solvent becomes blurred in such systems, because speciation is not only complex, but it changes with the marked depolymerization of the silicate framework that obtains from pure  $SiO_2$  to metal-oxide rich compositions. So-called ionic-polymeric models highlight the mutual correspondence between polymerization and acid-base properties of dissolved oxides through the Lux-Flood formalism for molten oxides. They thus provide the syntax to write chemical exchanges, but have no pretension to structural description. The unique validity of ionic-polymeric approaches is shown for iron redox equilibria, for which no shift of activity coefficient can explain observations. We also show the case of redox interactions involving sulfur species, and the effects that arise on biphasic gas-melt equilibria in presence of halogens, water and carbon dioxide.

**Keywords:** Redox, acid, base properties, amphoteric behaviour, iron, sulfur, polymerization, Lux, Flood formalism

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\*Speaker

# PROPERTIES 2



# Ceria nanocubes stabilized in Silica Aerogels

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CeO<sub>2</sub> based nanomaterials possess exceptional properties due to their ability of acting as an "oxygen buffer" releasing or storing oxygen atoms reversibly, while retaining the fluorite structure. This can be exploited in a variety of important industrial processes of great interest for energy and the environment, spanning energy conversion (fuel cells and renewable production of fuels from solar energy), energy storage (lithium-air batteries), and environmental protection and remediation (treatment of toxic contaminants in water). The exceptional reactivity originates from the labile and reversible redox cycle between Ce<sup>4+</sup> and Ce<sup>3+</sup>, where oxygen ions are released and stored through the formation of oxygen vacancy defects. This is particularly enhanced at the nanoscale and the reactivity of ceria nanomaterials is also strongly dependent on the shape of the nanoparticles because it influences the amount of oxygen vacancies that are present. In particular, ceria nanocubes show an enhanced reactivity due to the large fraction of highly reactive {100} facets. However, the control of both size and shape of nanoparticles require the use of surfactants which act as an "organic armour" that makes those facets less accessible. Also, after thermal treatments needed to remove the surfactants and obtain clean surfaces the ceria nanoparticles undergo coalescence, leading to a drastic decrease in surface area and reactivity. These problems can be overcome by using porous matrices to host nanoparticles keeping them apart and avoiding coalescence. Silica Aerogels are used in this study to stabilise ceria nanocubes and maximise their reactivity taking advantage of their highly extended open porosity (up to 98%), and high surface areas.

**Keywords:** Nanostructures, ceria, oxygen storage capacity

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\*Speaker

# Glass characterization by Raman microscopy, Glow Discharge Optical Emission Spectrometry and Spectroscopic Ellipsometry

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Whether in construction, automotive or transport, the use of glass is constantly increasing. Glazed surfaces no longer serve simply to allow the natural light in and the occupants to see outside, but they can become truly multifunctional materials by combining a wide number of properties. Glass is also designed to optimize solar energy conversion. The analysis of inclusions and bubbles in bulk, the control of coatings on surfaces, the monitoring of ion exchange involved in the strengthening are some examples of challenges to take up in glasses technologies. The portofolio of HORIBA Scientific offers different techniques that are optimized for the investigation of elemental, structural and optical properties of glasses.

Confocal Raman microscopy offers the possibility to detect, characterize and identify glass imperfections. Thanks to the high confocality, it is possible to well characterize "glass nodes", bubbles gas, zirconia or other types of inclusions.

With the use of Pulsed Radio Frequency source (pulsed RF), Glow Discharge - Optical Emission Spectroscopy, offers the possibility of depth profiling tens of microns of glasses without inducing thermal stress allowing monitoring ion exchange processes (IOX) or studying thin layers (down to the nanometre) on top of the glasses as in PV.

Last, but not least, Spectroscopic Ellipsometry (SE) enables to determine thickness and optical constants of thin films with a sensitivity at the atomic scale. It can be applied to improve processes of anti-reflection or mirror structures, to study electrochromic glasses such as WO<sub>3</sub> or to identify and characterize the air and tin sides of float glass. Applied to bulk glass, SE can measure absorption curves or residual birefringence.

This presentation will illustrate solutions proposed by HORIBA Scientific for glass materials applications both in research and industry.

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**Keywords:** Glass characterization, Raman microscopy, Glow Discharge Optical Emission Spectroscopy, Spectroscopic Ellipsometry

# Electric field-induced softening (EFIS) of alkali silicate glasses

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We report on a new phenomenon in alkali silicate glasses, termed electric field induced softening (EFIS), whereby electric fields produce abrupt softening and viscous flow at furnace temperatures well below the glass transition temperature. The experiments are carried out with cylindrical specimens sandwiched between two metal electrodes, under a compressive stress. The strain, the specimen temperature (obtained with a pyrometer), and the optical emission spectrum are measured simultaneously as a function of time. The softening is accompanied by an abrupt increase in electrical conductivity as well as photoemission. The effect is more pronounced (that is, it occurs at a lower temperature) with AC field of  $\sim 1$  kHz than with DC electric field. Unusual events at the metal-glass interface, resembling dielectric breakdown are observed, which, however, are less localized in AC than in DC experiments. These observations suggest the following sequence of events: polarization of the sample from ion displacement under the application of electric field as in electro-thermal poling, formation of an alkali ion depletion layer, development of large internal electric fields across this layer, electrolysis and charge injection followed by dielectric breakdown, and very high localized heating near the anode, ultimately leading to thermal runaway and softening throughout the sample. The results suggest that AC electric field assisted softening may be better suited to practical applications of this phenomenon. The magnitude of EFIS is significantly larger in single alkali than in relatively lower conductivity mixed-alkali glass of same mole fraction of silica, raising the possibility that EFIS can be induced in highly conductive classes even at ambient furnace temperature.

**Keywords:** Glass softening, Electrical properties, Thermally stimulated current, Alkali migration, Dielectric breakdown, Thermal runaway

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\*Speaker

# Temperature Dependent Optical and Electrical Properties of Heavy Metal Oxide Glasses

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Tellurite and antimonite based heavy metal oxide (HMO) glasses are considered as promising amorphous semiconducting materials due to their medium optical band gap energy values that are comparable with conventional semiconductors. Therefore, these glasses are studied for different potential applications in non-linear optical devices such as ultra-fast switches, power limiters and broad band optical amplifiers. It is well known that the addition of transition metal oxides to HMO glasses improves non-linear optical properties, enhances electrical conductivity, increases refractive index and expands the transmission range up to the middle infrared region of the electromagnetic spectrum. In the present work, MoO<sub>3</sub> and WO<sub>3</sub> were included in TeO<sub>2</sub> and Sb<sub>2</sub>O<sub>3</sub> glass network in different concentrations since these transition metal oxides have the potential to improve optical and electrical properties of glasses and enhance their optical sensitivity and non-linear optical features due to their different oxidation states in the glass network. Accordingly, a series of glasses were synthesized in the WO<sub>3</sub>-MoO<sub>3</sub>-TeO<sub>2</sub> and WO<sub>3</sub>-MoO<sub>3</sub>-Sb<sub>2</sub>O<sub>3</sub> ternary systems using conventional melt-quenching technique. Optical and electrical properties of these glasses were investigated as a function of temperature using in-situ UV-Vis spectroscopy and electrical conductivity measurement setup. The authors of this study gratefully acknowledge The Scientific & Technological Research Council of Turkey (TUBITAK) for the financial support under the project numbered 116M210.

**Keywords:** Heavy metal oxide glasses, TeO<sub>2</sub>, Sb<sub>2</sub>O<sub>3</sub>, optical properties, electrical properties

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\*Speaker

# Thermal Conductivities of R<sub>2</sub>O-SiO<sub>2</sub> and CaO-R<sub>2</sub>O-SiO<sub>2</sub> (R=Li, Na, K) Melts

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The thermal effusivities of the R<sub>2</sub>O-SiO<sub>2</sub>, and CaO-R<sub>2</sub>O-SiO<sub>2</sub> (R=Li, Na, K) melts were measured by using the front heating-front detection laser flash method. Then, the thermal conductivity was evaluated by combining the present thermal effusivity data with specific heat capacity and density. The relation among ionic radii of cations (Li<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup>) and the number of non-bridging oxygens per tetrahedral cations (NBO/T) and the thermal conductivity of R<sub>2</sub>O-SiO<sub>2</sub> and CaO-R<sub>2</sub>O-SiO<sub>2</sub> melts was evaluated. It was found that the temperature dependences of the thermal conductivities of the R<sub>2</sub>O-SiO<sub>2</sub> and CaO-R<sub>2</sub>O-SiO<sub>2</sub> melts were small over the temperature range investigated. It was also found that the thermal conductivities of CaO-R<sub>2</sub>O-SiO<sub>2</sub> melts were larger than those of R<sub>2</sub>O-SiO<sub>2</sub> melts. It can be presumed that the network frame of CaO-R<sub>2</sub>O-SiO<sub>2</sub> melt became dense due to the ion bonding between Ca<sup>2+</sup> and non-bridging oxygen. Accordingly, the increase of the mean free path of phonon in CaO-R<sub>2</sub>O-SiO<sub>2</sub> melts brought the large thermal conductivity. It was noteworthy that the thermal conductivities of the Li<sub>2</sub>O-SiO<sub>2</sub> and CaO-Li<sub>2</sub>O-SiO<sub>2</sub> melts were larger than those of another R<sub>2</sub>O-SiO<sub>2</sub> and CaO-R<sub>2</sub>O-SiO<sub>2</sub> melts. It can be considered that the large thermal conductivities of the Li<sub>2</sub>O-SiO<sub>2</sub> and CaO-Li<sub>2</sub>O-SiO<sub>2</sub> melts affected by the relatively large ionic radius of Li<sup>+</sup> among those of cations

**Keywords:** CaO, R<sub>2</sub>O, SiO<sub>2</sub> (R=Li, Na, K), melt, front heating, front detection laser flash method, ion radius of cation, NBO/T, thermal conductivity

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\*Speaker

# Silicate glass structures with low hydrogen permeability

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Efficient energy provision using fuel cells requires effective hydrogen storage capacities. Glass is a material of low intrinsic hydrogen permeability and is therefore a promising material for hydrogen storage containers or diffusion barriers. Pioneer work on oxidic glasses seems to indicate a correlation between glass composition and hydrogen permeation, which was mainly derived from the behavior of silica glass. In this study, we focus on the relationship between topologic (free volume; network polymerization) and thermodynamic (configurational entropy) glass parameters. Experiments were performed well below the glass transition temperature, which excludes significant structural relaxation and chemical dissolution of hydrogen. The compositional dependence of seven glasses on the SiO<sub>2</sub>-NaAlO<sub>2</sub> join pointed out that in fully polymerized glasses the H<sub>2</sub> permeability cannot be solely derived from the total free volume of the glass structure. Hence, evidence is provided that the size distribution of free volume contributes to hydrogen diffusion and solubility. Additionally, results indicate that hydrogen permeability of the glasses is affected by the configurational heat capacity  $\Delta C_p$  at T<sub>g</sub>.

**Keywords:** hydrogen permeability, sodium aluminosilicate

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\*Speaker

# Measuring the difference in refractive index between tin and glass side of float glass

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The surface refractive index of float glass appears to be different from the bulk refractive index which is commonly used in designing optical coatings for glazing. furthermore, due to the diffusion of tin into the surface of float glass in contact with the tin bath during production, the properties of tin and glass side are known to be different. The work presented in this paper focusses on determining the differences in refractive index corresponding to these surfaces. It is shown that with proper sample preparation and the measurement procedure used by the author, sufficiently accurate results can be obtained using a spectrophotometer equipped with a simple reflection accessory. Results of the surface refractive indices are presented for a silicate float glass in the measurement range 250 nm - 2,500 nm

**Keywords:** refractive index, float glass, tin side

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\*Speaker



# Effect of Macrostructure on Thermal Conductivity of Foam Glass

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Cathode ray tube (CRT) panel glass can be recycled into foam glass. The foam glass is used as an insulating material for building constructions. Thermal conductivity is therefore a crucial property of the foam glass. Density has a major impact on the thermal conductivity [1,2]. At low densities, the cellular structure of insulation materials becomes important. For example, the conduction path through the solid matrix becomes longer or radiative heat transfer increases. The impact of the foam structure on the overall thermal conductivity of foam glass remains almost completely untouched. In this study, we prepared foam glasses from CRT panel glass using Mn<sub>3</sub>O<sub>4</sub>, carbon, and different content of K<sub>3</sub>PO<sub>4</sub>. All foam glasses are experimentally analyzed regarding foam density, porosity, and thermal conductivity. These data are compared to 3D structural data on wall thickness and pore size obtained from X-ray microtomography (XMT) analysis. The pore size distribution, average pore size, and wall thickness varies among the samples, though, neither increasing or decreasing pore size, nor narrowing or broadening size distribution is found in a consistent manner with varying K<sub>3</sub>PO<sub>4</sub> content. Moreover, the wall thickness is found to have no significant influence on the porosity and thermal conductivity. However, the relation between average pore size and thermal conductivity indicates a correlation for foam glasses with porosities between 87–90 %.

R.R. Petersen, J. König, Y. Yue, The mechanism of foaming and thermal conductivity of glasses foamed with MnO<sub>2</sub>, *J. Non. Cryst. Solids.* 425 (2015) 74–82.

J. König, R.R. Petersen, Y. Yue, Fabrication of highly insulating foam glass made from CRT panel glass, *Ceram. Int.* 41 (2015) 9793–9800.

**Keywords:** Thermal conductivity, Porosity, Pore structure, Cathode ray tube panel glass

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\*Speaker

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# PROPERTIES 3

# Kinetics of phase separation in barium borosilicate glass thin films deposited by magnetron sputtering

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Liquid/liquid phase separation has already been studied in bulk glasses where the morphological evolution and the growth of phase domains during the coarsening stage are of particular interest. It is known that growth law highly depends on the morphology of domains. When droplets are formed, their growth is limited by diffusion and their size scales with time to the third. On the contrary, the coarsening of interconnected domains is controlled by hydrodynamic transport mechanisms and characteristic size scales linearly with time.

In this study we investigate phase separation in glass thin films in order to use this phenomenon as a glass surface nano-structuring method. From a process point of view, industrial glass surfaces are often functionalized by magnetron sputtering. Metallic and dielectric thin films are deposited in order to add new optical, morphological or mechanical properties. In order to understand kinetics and mechanisms of phase separation, thin layers of barium borosilicate glass are deposited by magnetron sputtering with thickness range between 20 and 200 nm. They were studied after annealing at high temperature, from 700°C to 1000°C. Kinetics has been determined by several techniques such as AFM, postmortem SEM and in-situ SEM. Thanks to Python image processing, statistical data showed a good agreement between these techniques. Growth kinetics in barium borosilicate glass thin films are found significantly slower compared to the bulk.

As in bulk glasses, composition, temperature and annealing time impact the final morphology of phase separation. Besides we have observed that droplets growth is also influenced by additional parameters such as glass layer thickness and the nature of substrate. All these parameters allow to control morphologies and size of objects obtained by phase separation.

**Keywords:** Phase separation, glass thin film, barium borosilicate, nanostructuration

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\*Speaker

# Optical and chemical functionalities controlled at the micrometer scale in glassy materials by an imprinting thermo-electrical process.

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We report on the ability of a thermal poling treatment to be considered as an imprinting process modifying linear and nonlinear optical properties as well as surface chemistry of glassy materials.

Concerning optical properties, the formation of gradient of refractive index (GRIN) with large variations (up to 5.10<sup>-2</sup>) have been optimized. The effectiveness of this imprinting process of GRIN has been demonstrated by forming matrices of micro-lenses (sizes from 5 to 100 $\mu$ m) on large area (several tens of centimeters square). [1] Using the same process, second order optical properties have been implemented in isotropic materials at the micrometer scale. Moreover, a geometry control of the electro-optical anisotropy induced has been demonstrated and controlled in periodic structure as shown by the fabrication of second harmonic generation gratings. [2] Such patterning of both linear and nonlinear optical responses can be obtained successfully on both oxide and chalcogenide glasses.

Finally, by combing specific structural rearrangements and charge implementations, we have demonstrated very strong and localized influence of the  $\mu$ -poling treatment on surface reactivity, surface potential, and surface durability. [3-4]

M. Dussauze, A. Lopicard, F. Bondu, V. Rodriguez, F. Adamietz, T. Cardinal, E. Fargin, K. Richardson; 2016; EP16176689.4 (European Patent under PCT extension evaluation)

M. Dussauze, V. Rodriguez, F. Adamietz, G. Yang, F. Bondu, A. Lopicard, M. Chafer, T. Cardinal, E. Fargin, Adv. Optical Mater. (2016) 4, 6, 929–935

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\*Speaker

A. Lopicard, T. Cardinal, E. Fargin, F. Adamietz, V. Rodriguez, K. Richardson, M. Dussauze, Chemical Physics Letters, Volume 664, 1 November 2016, Pages 10-15.

M. Parailous, M. Dussauze, T. Cardinal, A. Poulon, E. Fargin; PCT/FR2016/05884. (Patent)

**Keywords:** optical glasses, chalcogenide, poling, GRIN, Second Harmonic Generation, Surface chemistry

# Poled glasses: relaxation and surface relief formation

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Thermal poling of glasses, that is, applying several hundred volts DC to a glass plate glass placed between two electrodes, heating it up to a temperature sufficient to activate ionic conductivity, and subsequent cooling under the applied voltage, results in structural and compositional modifications of multicomponent glasses. These modifications lead to relaxation of the glass structure and change of their surface reactivity. We present studies of a) relief formation on the surface of differently poled soda-lime glasses because of their volume relaxation in the course of poling and secondary heat treatment; b) compositional/structural and chemical reactivity relaxation under the secondary heat-treatment of these glasses; c) thermally stimulated depolarization current (TSDC) of "frozen" electric charge relaxation. Profilometry of the step at the interface of poled and unpoled glass surface allowed us to see the relation between the electric charge transferred in the course of the poling and the height of the surface relief formed and to reveal the peculiarities corresponding to higher poling voltages and poling conditions. Temporal behavior of the step under the secondary heat treatment allowed characterizing volume relaxation processes occurring under the heat treatment. Studied influence of the secondary heat treatment on the composition/structure and etching rate of the poled glass region provided us with the information on relaxation processes occurring under thermal processing of the poled glasses. The TSDC studies brought out three temperature regions which we attributed to the relaxation via 1) a turn of non-bridging oxygen bonds (250-300K range), 2) cation migration (600-700K range), and 3) switching of the oxygen bonds (viscous flow temperature range, 900 – 1000K range). Additionally, etching of the glasses with the use of poled region as a mask was applied for the formation of the surface relief essentially higher than one formed due to the volume relaxation in glass poling. The study has been supported by Russian Science Foundation grant No. 16-12-10044.

**Keywords:** sodalime glass, poling, thermal treatment, relaxation, TSDC, etching

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\*Speaker

# Magneto-optic glass for fast infrared modulators

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Fast infrared modulators, with a response time to an electric signal of less than 1  $\mu$ s, are required for high speed processing of optical signals in free space communications. For these modulators, new materials with a high magneto-optic coefficient are needed. Because the magneto-optic coefficient of heavy metal glasses doped with magnetic spinel nanoparticles can reach very high values, these materials are promising for such application. In this work, we developed a new glass based on a PbO-Bi<sub>2</sub>O<sub>3</sub>-Ga<sub>2</sub>O<sub>3</sub> system, which was doped with magnetic spinel nanoparticles. The glass was melted at 1000 °C for 40 min and then cast into a steel mould. Using the additions of Fe<sub>2</sub>O<sub>3</sub> and/or NiO the spinel nanoparticles of a defined size were successfully precipitated during heat treatment. The magneto-optic coefficient of the glass was measured in an optical system comprising a laser source, a polariser, a chopper, a quarter wave plate, a glass sample, an analyser, a diaphragm and a detector with an amplifier. The laser light source was operated in a continuous regime at a wavelength of 2090 nm. The maximum of the transmittance peak was influenced by the magnetic field applied on the glass sample inside a solenoid electromagnet. From the rotation angle of the analyser, the magneto-optical coefficient was calculated. Its value was maximized by optimizing the glass composition and the heat-treatment process. Another advantage of this glass was that in the range of 550–2750 nm it had a transmittance of above 70 %, which is high enough to achieve low optical signal attenuation in the near infrared region. Collectively, our results indicate that the developed glass with magnetic spinel nanoparticles of the optimized size could be applied to the construction of fast infrared modulators.

**Keywords:** optics, magneto, optic glass

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\*Speaker

# The Effect of Alkaline Earths on Fictive-Temperature Dependent Glass Properties

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Glass structure and properties vary as a function of thermal history, a phenomenon that is recorded by a parameter called fictive temperature. The fictive temperature of a glass changes such that the faster the cooling rate the glass experiences during quenching, the higher the fictive temperature. By varying fictive temperature, the glass structure and properties can be changed considerably. The extent to which these changes occur (i.e. the thermal history sensitivity of the glass) is determined by the bulk composition.

In this study, simple ternary and quaternary systems are used to investigate the compositional effect of alkaline earth (AE) modifiers on fictive-temperature dependent glass properties such as Young's modulus, refractive index, and density. The model system is comprised of 74 mol% SiO<sub>2</sub>, 16 mol% Al<sub>2</sub>O<sub>3</sub>, 10 mol% RO, where RO content is the sum of one or more of the following: MgO, CaO, SrO, and BaO. Preliminary results show that the properties of glasses with lower field strength AEs experience smaller changes as a function of fictive temperature than glasses with higher field strength AEs. We show that this reduction in the changes to thermal history sensitive glass properties is due to a more loosely-packed glass structure in the case of lower field strength-containing glasses. Single versus mixed AE effects are also investigated. By understanding the effect of AE modifiers on the thermal history sensitivity of simple systems, we hope to gain insight into the effect of AEs on the thermal history sensitive properties of more complex systems.

**Keywords:** Alkaline Earth, Fictive Temperature, Young's Modulus

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\*Speaker



# **SIMULATION MODELING 1**

# MD Simulations of the melting of sodium and lithium metasilicates

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Melting has been described as the single most important phase change in fundamental (materials) science. However, none of the theories put forward come close to explaining experimental observations, and this particularly true of the melting of silicate materials. The "reverse" reactions, crystallization and its solid-state counterpart, devitrification, also fall into the not-completely-understood category.

Whereas the timeframes associated with nucleation and growth make devitrification difficult to probe by standard atomistic simulation techniques such as molecular dynamics, melting does not suffer from such drawbacks. In this presentation, we describe the application of molecular dynamics to probe the structural changes that occur on heating crystalline sodium and lithium metasilicates to above their melting temperatures. The behavior of these two silicates is different; sodium silicate shows a pronounced pre-melting regime, associated with an excess heat capacity, whereas the lithium metasilicate does not. In melting, however, both show a change from a single distribution of Q<sub>2</sub> units in the crystal to a distribution of multiple Q<sub>n</sub> units in the melt (and subsequent glass).

The simulations allow us to shed light on the role played by the alkali ions in the pre-melting regime, as well as identifying the initial mechanisms that lead to the reduction in the number of Q<sub>2</sub> species. It is hoped also that these results may provide some insight into the reverse process of nucleation and growth.

**Keywords:** Molecular Dynamics, melting, alkali silicates

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\*Speaker

# Developing interaction potentials for modelling oxide glasses

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We propose a new scheme to parametrize effective pair potentials that can be used to simulate oxide glasses. As input data for the optimization we use the radial distribution functions of the liquid and the vibrational density of state of the glass, both obtained from ab initio simulations, as well as experimental data on the pressure and/or composition dependence of the density and the elastic moduli of the glass [1].

For the case of silica we find that this new scheme allows to find potentials that are significantly accurate than previous ones even if the functional form is the same, thus demonstrating that even simple two-body potentials can be superior to more complex three-body potentials. We have tested the new potential by calculating the pressure dependence of the elastic moduli and find a good agreement with the corresponding experimental data.

For binary alkali (lithium, sodium, potassium) silicate glasses, the new potentials allow to reproduce the composition dependence of both density and elastic moduli. Further, we examine the capabilities of these potentials for studying ternary compositions containing two alkali oxides, and we find that they are reliable even if they have been developed for binary compositions.

Simplicity of the functional form also makes these potentials computationally more efficient than potentials with more complex functional forms, and hence more suitable for simulations involving large length and/or time scales.

S. Sundararaman, L. Huang, S. Ispas, and W. Kob, "New optimization scheme to obtain interaction potentials for oxide glasses", to be submitted (2017)

**Keywords:** atomistic simulation, oxide glasses, interaction potential, fitting scheme, mechanical properties

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\*Speaker

# Using molecular dynamics to descend into the structural complexity of EuF3 doped ZrF4-BaF2-LaF3-AlF3-NaF (ZBLAN) glass

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The ZrF<sub>4</sub>-BaF<sub>2</sub>-LaF<sub>3</sub>-AlF<sub>3</sub>-NaF (ZBLAN) family of fluorozirconate glasses was developed due to the ease with which lanthanides can be incorporated for optical applications. The ZBLAN glasses are also interesting because they do not have a close analogue among other glass forming systems. As in oxide glasses the short range order is based on smaller cations surrounded by larger anions, but ZBLAN glasses do not follow the Zachariasen rules. Here we present a detailed classical molecular dynamics modelling of a series of ZB, ZBL, ZBA, ZBN, ZBLA and ZBLAN glasses. This methodology helps to identify the short range order and structural role relevant to each cation. The culmination is a 100Å size model of Eu doped ZBLAN glass of relevance for optical applications.

The structural units of binary fluorozirconate glasses were carefully studied as they do not follow the Zachariasen glass model. The coordination number for

**Keywords:** ZBLAN, lanthanide, fluoride glasses, short range order, molecular dynamics

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\*Speaker

# Atomistic study of two-level systems in amorphous silica

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We model at the atomic-scale internal friction in amorphous silica at low frequencies. To this aim, we explore the potential energy landscape of multiple glass samples to identify two-level systems (TLSs). We discuss the properties of TLSs, particularly their energy asymmetry and barrier as well as their deformation potential, computed as longitudinal and transverse averages of the full deformation potential tensors. The discrete sampling is used to predict dissipation in the classical regime. Comparison with experimental data shows a better agreement with poorly relaxed thin films than well relaxed vitreous silica, as expected from the large quench rates used to produce numerical glasses. The TLSs are categorized in three types that are shown to affect dissipation in different temperature ranges. The sampling is also used to discuss critically the usual approximations employed in the literature to represent the statistical properties of TLSs. Reference:

T. Damart, D. Rodney, 'Atomistic study of two-level systems in amorphous silica ', Physical Review B 97, 014201 (2018).

**Keywords:** internal friction, atomistic modeling

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\*Speaker

# A novel numerical method for exploring challenging phase-transitions: From liquid-crystal to amorphous-amorphous transformations

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Atomistic simulations, such as Molecular Dynamics, are powerful computational tools for investigating both ordered and disordered systems. However, in many situations, in particular those involving a kinetic barrier, one faces the *time scale problem*: the simulated time length is much too short to observe important phenomena (e.g. crystallisation from the liquid, relaxation in the vitreous state, etc). Thus, *enhanced sampling* methods (such as metadynamics) have been developed in the last decades and have proven efficient in many specific cases. However, a general and transferable method, that would reveal simultaneously the atomistic mechanism and the energetics of transformations has been lacking.

Water is a challenging system in this context because of its rich poly(a)morphism. Here, we show that using a novel set of coordinates, capturing changes in the topology of the interatomic network, we are able to systematically track transitions among liquid, amorphous and crystalline forms throughout the whole phase diagram of water [1], including the nucleation of crystals above and below the melting point. Our general approach is not specific to water and we will address on-going works in silica and B<sub>2</sub>O<sub>3</sub>. Both systems show a rich polymorphism as well as possible liquid-liquid transitions [2, 3]. The methodology will be used to establish connections between the liquid, glass and crystalline phases.

1) Navigating at will on the water phase-diagram, S. Pipolo, M. Salanne, G. Ferlat, S. Klotz, A.M. Saitta, F. Pietrucci. Phys. Rev. Lett., **119**, 245701 (2017).

2) Rings in network glasses: the B<sub>2</sub>O<sub>3</sub> case. G. Ferlat, in "Frontiers and challenges in molecular dynamics simulations of structurally disordered materials", Eds: C. Massobrio, J. Du, P. S. Salmon, M. Bernasconi, Springer (2015).

3) Hidden polymorphs drive vitrification in B<sub>2</sub>O<sub>3</sub>, G. Ferlat, A.P. Seitsonen, M. Lazzeri, F. Mauri, Nature Mat. **11**, 925 (2012).

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**Keywords:** water, boron oxide, crystallization, nucleation, vitrification

# **SIMULATION MODELING 2**



# XPDF and molecular dynamics analysis of the significance of bond angle change in the deformation of amorphous silica

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The deformation mode of amorphous materials differs from that of their crystalline counterparts in an important respect: whilst ordered materials possessing an atomic lattice arrangement deform in an affine way, glasses contain structural inhomogeneities down to Ångstrom length scales of interatomic bonds. Regions of denser packing exist alongside less dense domains, meaning that strain inhomogeneity manifests itself throughout structural scales. In this study we set ourselves the objective of elucidating how this non-uniform deformation is accommodated in amorphous silica: what mechanisms are responsible for different modes? With the help of X-ray Pair Distribution Function (XPDF) analysis and molecular dynamics simulation we were able to reveal that short range stretching of atomic bonds does not match the long range macroscopic strain. Instead, locally strain is accommodated by bond angle changes that we refer to as "scissoring" action. The relationships between macro and atomic level strains demonstrate that atomic rearrangement (bond angle change), rather than bond stretching, is the dominating strain accommodation mechanism up to length scales of approximately 15 Å in this material, even under moderate non-hydrostatic applied stress states down to ~100 MPa. <https://www.nature.com/articles/s41598-018-19900-2>

**Keywords:** strain, pair distribution function, synchrotron, silica

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\*Speaker

# On the utility of topological principles for determining the fragility of network glass-formers

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Models based on topological principles such as the rigidity percolation have been invoked to predict many physical properties of network glass formers such as density, relaxation, hardness as well as fragility. Here we investigate the structural, calorimetric and transport properties of four covalent and ionic network glass formers to examine the correlation between fragility and topology. It is found that topological principles are usually not an effective predictor of fragility although they can be useful in explaining some unusual behavior such as fragile to strong transitions. Instead it is found that structural and chemical contributions such as network dimensionality, chemical stoichiometry or structural heterogeneity have greater and clearer contributions to the fragility.

**Keywords:** fragility, topology, chalcogenide glass, zinc chloride, network glass

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\*Speaker

# Microscopic dynamics and thermodynamics on a dipolar glass former

Gemma Sesé \* <sup>1</sup>, Ricardo Palomar <sup>1</sup>, Jordi Ortiz De Urbina <sup>1</sup>

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Free energy and entropy have been evaluated for a supercooled dipolar model liquid, and their connections with structure and dynamics on the supercooled state have been explored by using perturbative calculations, molecular dynamics simulations and instantaneous normal mode analysis. A model is proposed in order to analyze translation and rotation contributions to entropy separately. The approach states that both of them contain gas-like and solid-like terms. Results are consistent with a preferential intrabasin energy landscape dynamics in the supercooled state. A logarithmic correlation between excess entropy associated with translation and the corresponding imaginary modes is encountered. Rosenfeld scaling law between reduced diffusion and excess entropy is tested, and it is obtained that it is valid within the same temperature range as the Arrhenius law for diffusion. The microscopic origin of the breakdown of Rosenfeld scaling at low temperatures is investigated and it results from an increasing relevance of mode-coupling contributions to diffusion.

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**Keywords:** Excess entropy, imaginary frequency normal modes, Rosenfeld scaling

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\*Speaker

# Amorphous plasticity from atomic scale to mesoscopic scale

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In crystalline materials, plasticity results from the motion of defects of the crystalline lattice, dislocations. The absence of structural order in glasses requires to look for alternative microscopic mechanisms for the plastic deformation. A common hypothesis consists in considering series of localized rearrangements of the amorphous structure : Shear Transformations. In this talk we review recent results obtained for the characterization of such Shear Transformations at the atomic scale.

We first present a recent numerical method allowing to characterize local yield thresholds in model glasses prepared by molecular dynamics. We discuss their connection to the plastic activity observed upon shearing and their dependence on the protocol of preparation of the glass. We then present recent results obtained with lattice models of amorphous plasticity at a mesoscopic scale

and discuss first attempts of coarse-graining the plastic behavior of glasses from atomic scale to mesoscopic scale.

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B. Tyukodi et al. From depinning transition to plastic yielding of amorphous media: A soft-modes perspective, Phys Rev. E 93, 063005 (2016)

**Keywords:** plasticity, Shear Transformations, Molecular Dynamics, mesoscopic scale, lattice models

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\*Speaker

# Structural Mechanisms of Plastic Deformation in Hydrostatically Compressed Calcium Aluminosilicates

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From the very first observations of plastic deformation in silicate glasses by Bernhardt and Taylor in the middle of the 19th century, glass scientists have been trying to understand plastic deformation in glasses. Current understanding has disentangled plastic deformation into continuum phenomena: densification and shear and attempted to quantify the relative contributions. In indentation, glasses are identified as anomalous and normal depending on whether they deform predominantly by densification and shear, respectively. However, despite our definitions of plastic deformation modes on a continuum scale, we still understand little about the atomic mechanisms which constitute each mode and how imposed stresses correlate with each mode. We conducted a series of molecular dynamics simulations in order to better understand the atomic mechanisms of plasticity when glass is subjected to hydrostatic stresses up to 15 GPa. Using a Pedone potential, we simulated calcium aluminosilicate glasses through the range of normal to anomalous glasses. The glasses ranged from 50%-100% SiO<sub>2</sub> along the tectosilicate line, which by simple models are expected to contain no NBOs. We show that throughout the composition range there are variations in the deviatoric strain heterogeneity and degree of densification which can be correlated to structural changes such as coordination number, bond angle distribution, ring size distribution, and the degree of ring puckering. With a better understanding of the connection between hydrostatic stress and atomic mechanisms of plasticity, we can begin to understand how glasses deform plastically at the structural level. Since plasticity occurs just before failure, it is important to understand atomic mechanisms of plasticity in complex, real-world stress states.

**Keywords:** Plasticity Mechanisms, Silicate Glass, Molecular Dynamics, Ring Puckering

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\*Speaker

# Fracture of sodium-silicate glasses: Insights from atomistic computer simulations

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Understanding the fracture behavior of glasses at the atomic scale is of fundamental importance for improving the mechanical properties of these materials. Using an interaction potential that has been parametrized via *ab initio* calculations [1,2], we have carried out molecular dynamics simulations in order to investigate the influences of system size, sample geometry, and strain rate on the fracture behavior of sodium silicate glasses. In contrast to earlier simulation studies on fracture, in which the bulk glass sample has often been put directly under stress, we have applied here uniaxial tension to a glass sample that has stress-free surfaces, i.e. we adopt a setup that is close to the one used in experiments on fracture studies. Our results show that the used interatomic potential captures reasonably well the brittle fracture on the nanoscale of silica glass and the enhanced ductility when sodium oxide is added to the glass network. We have found that below a critical strain rate of around 0.5/ns the stress-strain curve remains basically unchanged. By investigating the formation, growth and coalescence of cavities in the strained glass samples we find that in sodium silicate glasses the formation of cavities is being more pronounced than in silica glass. The analysis of atomic energy, local stress and strain, and atomic displacements have confirmed the presence and the development of mechanically weak zones in the glass network, resulting in paths along which the cracks advance.

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S. Sundararaman, L. Huang, S. Ispas, and W. Kob, "New optimization scheme to obtain interaction potentials for oxide glasses", to be submitted (2017)

**Keywords:** silicate glasses, atomistic simulations, fracture behavior

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# Dispersion of the elasto-optic tensor

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The elasto-optic tensor describes the relationship between strain and index of refraction, and thus is the key glass property describing the stress-optic coefficient and stimulated Brillouin scattering. As such, understanding its structural origin is critical in glass design. We showed experimentally that the dispersion of the shear component of the elasto-optic tensor is qualitatively different for different additives, such that barium gives positive dispersion and lead gives negative. We also developed in separate work a bond-based model for the full elasto-optic tensor. Here we build on these studies by developing a bond-based model of dispersion for the elasto-optic tensor, and in this way providing an explanation for the qualitatively different behavior of additives such as barium and lead, based on the nature of the bonds they form with oxygen. These results should lead to chemical design rules for generating glass with desired elasto-optic response, at all wavelengths.

**Keywords:** Elasto, optic response, stress, optic response, theory, dispersion

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# SPECIAL GLASSES AND CROSS-CUTTING



# The atomic structure of glassy carbon foams

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Recently, there has been an intense interest in carbon foams for a variety of engineering applications due to their superior mechanical, electrical and thermal properties. Glassy carbon foams are produced by the pyrolysis process using organic resins as the precursors. By controlling the synthesis conditions it is possible to adjust the porous structure of the foams in terms of bulk density, cell size and connectivity, but also the atomic structure which directly affects their final properties. Glassy carbon foams have disordered structure that is intermediate between crystalline graphite and amorphous carbon. Since the atomic arrangement is complex allowing coexistence of different bonds between carbon atoms, and very sensitive to the synthesis temperature, there is a need to use advanced tools for their characterization. Here, we use methodology based on the molecular dynamics simulations and their experimental verification by the wide-angle X-ray scattering to describe the atomic structure of glassy carbon foams pyrolyzed at different temperatures. The obtained diffraction data are converted to a real space representation in the form of the atomic pair distribution function. The applied pair distribution function analysis shows that the glassy carbon foams have a local order extending on the length scale of nanometers, in which carbon atoms are arranged in fullerene-related, curved units. The results of the computer simulations suggest that the curvature can arise from the presence of topological defects in the form of nonhexagonal carbon rings.

**Keywords:** glassy carbon foams, atomic structure, pair distribution function

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# Glass formation and mechanical properties of melt-quenched glasses of mixed metal node Zn/Co ZIF-62

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Recently, the newly-discovered melt-quenched Zeolitic Imidazolate Framework (ZIF) glasses have been attracting a lot of attention owing to their particularly high thermal, mechanical and chemical stability [1-4]. ZIF structures are built analogously to zeolites, but ZIF consists of transition metal ions that are bonded to imidazolate ligands, creating a three dimensional framework. However, for ZIF crystals, there are many questions that need to be answered. For instance, what is the microscopic mechanism of ZIF glass formation? How does the chemical composition influence ZIF glass properties?

In this work, we explore the impact of the change of metal ion type on the glass formation of ZIF-62 ( $\text{Zn}_{(1-x)}\text{Co}_x(\text{Im})_{1.75}(\text{bIm})_{0.25}$ ). This is done by substituting zinc ions for cobalt ions during synthesis of the ZIF-62 crystal and by characterizing the morphology of crystalline powders obtained during synthesis using Scanning Electron Microscopy. <sup>1</sup>H and <sup>13</sup>C Liquid Nuclear Magnetic Resonance measurements were conducted to determine the content of two types of organic ligands in both crystalline and amorphous phases, whereas X-ray Photoelectron Spectroscopy measurements were performed to detect any possible bond changes. Inductively Coupled Plasma Mass Spectrometry was performed to quantify the content of metal nodes in the frameworks. The melting temperature of ZIF-62 crystals, as well as the glass transition temperature of ZIF-62 glasses have been determined using Differential Scanning Calorimetry. Thermogravimetry was used to observe desolvation and decomposition. Both nanoindentation and microindentation were applied to measure mechanical properties of ZIF-62 glasses. We have found that substitution of second transition metal ions for Zn greatly lowers the glass forming ability of ZIF-62. The structural origin of this phenomenon has been discussed in this work. Furthermore, we have discovered Zn/Co substitution has only minor impact on the properties.

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T.D. Bennett, J.C. Tan, Y.Z. Yue, et al., *Nat. Commun.* 6 (2015) 8079.

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H.Z. Tao, T.D. Bennett, Y.Z. Yue, *Adv. Mater.* 29 (2017) 1601705.

A. Qiao, T.D. Bennett, H.Z. Tao, et al., *Sci. Adv.* 2018, under revision.

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\*Speaker

**Keywords:** Melt Quenched Zeolitic Imidazolate Framework Glasses, Structure of glasses, Glass properties, Glass formation

# Kinetics of decelerated melting

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Melting presents one of the most prominent phenomena in condensed matter science. Its microscopic understanding, however, is still fragmented, ranging from simplistic theory to the observation of melting point depressions. Here, we combine a multi-method experimental approach with computational simulation to study the microscopic mechanism of melting between these two extremes. We exploit crystalline structures in which melting occurs into a metastable liquid close to its glass transition temperature. The associated sluggish dynamics real-time observation of homogeneous melting. In-depth information on the structural signature is obtained from various independent spectroscopic and scattering methods, revealing a step-wise nature of the transition before reaching the liquid state. A kinetic model is derived in which the first reaction step is promoted by local instability events, and the second is driven by diffusive mobility. Computational simulation provides further confirmation for the sequential reaction steps and for the details of the associated structural dynamics, reconciling concepts of surface and bulk melting. This successful quantitative modelling of the low temperature melting of zeolite crystals, reconciling homogeneous with heterogeneous processes, should serve as a platform for understanding the inherent instability of other zeolite structures, as well as the prolific and more complex nano-porous metal organic frameworks.

**Keywords:** melting, liquid, kinetics, zeolites, MOF

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\*Speaker

# Metal-Organic Framework Glass Formation and "Reordering"

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Metal-organic frameworks (MOFs) are microporous inorganic-organic hybrid materials. Recently, some types of MOFs can be vitrified by melt-quenching technique [1-4]. However, we still do not exactly know why some MOFs can be vitrified, but some not. We also do not know why the MOF glass cannot crystallize, i.e., the long-range order cannot be recovered, under accessible laboratory conditions. Therefore, scientists including our group have made considerable effort to answer those questions. In this presentation, we report our recent understanding of MOF glass formation and 'reordering' by characterizing two MOF glass formers: ZIF-4 (Zn(Im)<sub>2</sub>) and ZIF-62 (Zn(Im)<sub>1.75</sub>(bIm)<sub>0.25</sub>). The former shows polyamorphic transitions, ZIF-zni crystal formation and narrow melting transition, whereas the latter exhibits ultrahigh glass forming ability and wider melting range. Upon isothermal treatment in the supercooled region, a drop in potential energy is detected in ZIF-4, but surprisingly the degree of medium-range order is lowered. This might imply that upon heating the link between tetrahedral ZnIm<sub>4</sub> units is more disordered, driven by structural densification of, whereas the ligand rings become less distorted. ZIF-62 glass is extremely stable against crystallization. The ratio between the glass transition temperature ( $T_g$ ) and the melting point ( $T_m$ ) of ZIF-62 is higher than that of any other glass forming systems measured so far. By combining the dynamic data with structure analysis, we present our understanding of the above-mentioned anomalous features of ZIF-4 and -62 glasses. References:

T.D. Bennett, J.C. Tan, Y.Z. Yue, et al., *Nat. Commun.* 6 (2015) 8079.

T.D. Bennett, Y.Z. Yue, P. Li, et al., *J. Am. Chem. Soc.* 138 (2016) 3484.

H.Z. Tao, T.D. Bennett, Y.Z. Yue, *Adv. Mater.* 29 (2017) 1601705.

A. Qiao, T.D. Bennett, H.Z. Tao, et al., *Sci. Adv.* 2018 (in press).

**Keywords:** Metal, organic framework, Glass Formation, Glass, Forming Ability, Reordering

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\*Speaker

# Formation of Metal-Organic Framework Glass via Post-Synthetic Modification

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As a new family of glasses, hybrid glasses - or metal-organic framework (MOF) glasses - have been discovered very recently [1,2]. Unlike the porous and flexible structures of MOFs, MOF glasses have less porous and more rigid structure, and are expected to have potential applications in some fields, such as drug delivery and nuclear waste capture. It is yet far from the understanding of the mechanism of melting and glass formation in MOF glasses. One important issue is that most MOFs decompose and carbonize upon heating before they melt.

It has been suggested that inducing defects in MOFs, such as post-synthetic modification (PSM), may decrease their melting temperature, and thus enable melting upon heating and subsequent quenching to MOF glasses [3]. In the present work, we report the formation of a MOF glass from a MOF-PSM crystal. Although this PSM-MOF crystal is a composite of two MOFs, as manifested by Rietveld refinements of its power X-ray diffraction pattern, calorimetric results indicate the difference between the PSM-MOF crystal and the physically mixed MOFs. Micrographs of the PSM-MOF crystal and its glass suggest that the new crystal has a core-shell structure. This is also supported by the nitrogen absorption and nano-indentation results. The intra-domain connectivity and short range ordering structure of the PSM-MOF glass are confirmed by the nuclear magnetic resonance spectroscopy and pair distribution function measurements. References

T. D. Bennett, J.-C. Tan, Y. Z. Yue et al., *Nat. Commun.* 2015, 6, 8079.

H. Tao, T. D. Bennett, Y. Z. Yue, *Adv. Mater.* 2017, 29, 1601705.

T. D. Bennett, A. K. Cheetham, A. H. Fuchs, F.-X. Coudert, *Nat. Chem.* 2017, 9, 11.

**Keywords:** Hybrid glass, MOF glass, Glass formation

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# Metal-Organic Framework Liquids and Glasses

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Metal-organic frameworks (MOFs) are a family of chemically diverse materials, consisting of inorganic nodes or ions linked by organic ligands. They have applications in a wide range of fields, covering engineering, physics, chemistry, biology and medicine. Until recently, research has focused almost entirely on crystalline structures, with over 60,000 structures now known. However, now a clear trend is emerging, shifting the emphasis onto disordered states, including ‘defective by design’ crystals, as well as amorphous phases such as glasses.

We have recently shown a subset of metal-organic frameworks (MOFs), called zeolitic imidazolate frameworks (ZIFs), to melt, and quenching of the resultant liquids forms a new category of glass.<sup>1</sup> Several structures (e.g. ZIF-4 [Zn(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub>]) melt between 400 and 600 °C, and the glasses obtained upon cooling retain the short-range order (i.e. local bonding under 6 Å) present in their crystalline counterparts.<sup>2</sup>

Here, we introduce the concept of a *liquid metal-organic framework*,<sup>3</sup> and explore the mechanism of melting of ZIF-4, via *in-situ* pair distribution function measurements and associated Reverse Monte-Carlo modelling, coupled with density functional theory based molecular dynamics calculations. We show that melting proceeds with significant structural retention, due to breakage of only part of the metal coordination sphere. The structure of the liquid phase is characterized, as is the mechanism of vitrification upon cooling. The atomic configuration obtained bears striking similarities to that for *a*SiO<sub>2</sub>.

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2. Bennett\* et al, *Nat. Commun.*, **2015**, 6, 8079.

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**Keywords:** Hybrid inorganic, organic, metal, organic framework, porous

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\*Speaker

# STRUCTURE 1



# Local glass structure modification during diffusion views by Raman spectroscopy

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Chemical diffusion in amorphous silicates is a process of paramount interest in many different fields including the geosciences, nuclear and industrial glass melting. Indeed, chemical diffusion plays an important role at all stages of the glass melting and transformation process. Recently, the diffusion description in the glass via the eigenvectors and eigenvalues of the full diffusion matrix starts more and more investigated for the different industrial glass systems [1-3]. The advantage of this approach is a possibility to give the general vision of the diffusion process in the explored domain with a limited number of experiments. This macroscopic method lets interpreted the diffusion as exchange reactions that represent the lowest energy pathways that result in material transport and quantify the rate of exchange by eigenvalues. At the same time, spatially-resolved Raman measurements along the diffusion profile showed that less than 20% of vibrations impacted by the diffusion. In this study, to put in evidence the operating microscopic diffusion pathways the Raman spectra has been decomposed on the partial Raman spectra based on NMF approach [4]. Through the comparison of the eigenvalues with the partial spectra contributions we try to associate each partial Raman spectra to one exchange reactions. The analysis of the vibration bands in the partial Raman spectra and they comparison with the literature used here to identify specific structural entities involved in associated exchange reactions.

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**Keywords:** diffusion Raman spectroscopie

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# The bond valence method applied to glass structure

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Glasses have a structure in which the atoms connect together to form a network that has a random nature. Nevertheless, the short range order in a glass (the bond lengths, coordination numbers and coordination polyhedra) can be as well defined as in an ordered crystal structure. The random nature of the glass structure then arises from variability in the way that the basic structural units connect together. For an understanding of the bonding and structure in a glass it is thus essential to understand in detail the structural units and the connections between them.

The bond valence method has arisen from detailed study of the structure of crystalline materials, and it provides a way of understanding the bond lengths and coordinations that occur between atoms in solids. The application of the method to glass structures will be discussed [1], with examples that include germanate, tellurite and phosphate glasses. Of particular value is the distortion theorem [2], which can be applied to understand the behaviour of the bond lengths in an oxygen bridge in an oxide glass. For example, germanate glasses show a behaviour of the mean Ge-O bond length that is apparently anomalous, in that it is significantly longer for high modifier glasses than for low modifier glasses, even though the structures of both are based mostly on GeO<sub>4</sub> tetrahedra [3]. It will be shown how this behaviour can be understood by application of the bond valence method. The method can also be applied to tellurite glasses, for which the oxygen bridges can be highly asymmetric, and to phosphate glasses which have the unusual feature of terminal oxygens.

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**Keywords:** structure, bonding, coordination number, bond length, germanate, tellurite, phosphate

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\*Speaker

# Raman fitting of the high frequency NBO bands in alkali silicate glasses

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Raman spectra of the SiO<sub>4</sub> symmetric stretch region (800-1200 cm<sup>-1</sup>) for low alkali (M) silicate glasses (5 and 10 mol% M<sub>2</sub>O) yield intense well-resolved Q<sub>3</sub> peaks at ~1100 cm<sup>-1</sup> with mostly Lorentzian character (> 90% at 298K), in contrast to previous Gaussian fits for silicate glasses. Fits to the Q<sub>0</sub> peak of a Li<sub>3</sub>PO<sub>4</sub> melt at 1550K also yields a predominantly Lorentzian peak. The spectra of both Na and Li glasses show an additional Q<sub>3</sub> peak. It results from close approach of alkalis (M) to BO, which alters Raman shifts of the Q species to somewhat lower frequencies. The linewidths (FWHM) of fitted Q<sub>1</sub>, Q<sub>2</sub> and Q<sub>3</sub> species peaks are similar (35-55 cm<sup>-1</sup>) at 298K for all alkali silicate glasses. The Q species FWHM of 5 and 10 mol% Cs<sub>2</sub>O silicate glasses show a T dependence similar to those of crystal silicate spectra: both increase by 35-45 cm<sup>-1</sup> from 298K to 1200K. The T dependence and the Lorentzian lineshapes can be explained on theoretical grounds considering Heisenberg lifetime linewidths and the Balkanski formulation. The 30 mol% K<sub>2</sub>O glass and the 50 mol% Na<sub>2</sub>O spectra are then readily fit with two or three Q<sub>2</sub> or Q<sub>3</sub> peaks of mainly Lorentzian character, which yield reasonable linewidths and separations between peaks. The 50 mol% Na<sub>2</sub>O spectrum shows that Q<sub>3</sub> > Q<sub>1</sub>, and the free oxygen content is 4.5 (±1.5) mol%, in good agreement with previous <sup>29</sup>Si NMR and O 1s XPS results.

**Keywords:** Structure, Raman, fitting, Q species, Lorentzian, Gaussian, NBO

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# Dissolvable Borophosphate Glasses: Unravelling Changes in Short- and Medium-Range Structure with Solid-state NMR Spectroscopy

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The structural integrity, yet dynamic flexibility of regenerative inorganic tissues within living organisms involves a delicate balance that is difficult to reproduce from a materials science perspective. Take for instance the complex rearrangement at the atomic-level for sea urchin teeth, whereby a balance between Mg and Ca calcite is essential to maintain their unique "Rock-Chewing" ability whether for food or for eluding predators. Likewise, the formation of apatite within the body to repair, replace and strengthen mammalian skeletal features is a natural biomineralization process. In the search for new or improved biocompatible materials for dental and medical applications, we will discuss our current research in glass and glass-ceramic materials with targeted applications in ion releasing glasses. A series of borophosphate glasses modified with Ca (or Sr) will be presented revealing distinct local structures and dissolution effects upon exposure to simulated body fluid (SBF). Changes in the boron and phosphate chemical structural (both local- and medium-range structure) will be highlighted pre- and post- SBF treatment using Ca and Sr modifying cations. We will also discuss our recent developments looking at improving commercial dental ceramic veneers and the impact to atomic-level structure due to exposure of variable temperature treatment, highlighting the transition from ceramic to glassy materials through ex-situ variable temperature and multinuclear magnetic resonance spectroscopy. The major challenge in describing disordered structures is their inherent lack of long-range periodic order inhibiting traditional inorganic techniques such as X-ray or neutron diffraction. Solid-state NMR spectroscopy elegantly reveals atomic-level information providing a direct probe into the coordination of boron, phosphate speciation and boron-phosphorous neighbours using one and two-dimensional MAS NMR methods.

**Keywords:** NMR, Borophosphate, Feldspar, Medium range structure, Dissolution

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# 1D/2D NMR investigation of the Pyrex glass

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The structure of the important technological glass Pyrex® was investigated by 1D- and 2D-correlation NMR techniques. The local order was first analysed by 1D <sup>23</sup>Na, <sup>27</sup>Al, <sup>11</sup>B and <sup>29</sup>Si MAS-NMR performed at 9.4 and 18.8 T. In a second step, the medium range order was documented using homo- and, for the first time, hetero- nuclear correlation NMR techniques. The presence and nature of BOB bonds were analysed using 2D <sup>11</sup>B DQ-SQ map; the silicate speciation was probed by 2D <sup>29</sup>Si/X (X=<sup>11</sup>B, <sup>23</sup>Na and <sup>27</sup>Al) D-HMQC maps and the <sup>27</sup>Al/<sup>11</sup>B interactions were studied by TRAPDOR-NMR experiments. Altogether, the set of NMR data was used to extract accurate NMR parameters, to update the different borate site description, to distinguish different Q4 silicate units and to finally document how aluminium ions enter into the Pyrex® network.

**Keywords:** borosilicate, NMR, correlation, structure

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\*Speaker

# STRUCTURE 2

# Evidence of phase separation phenomena in {La<sub>2</sub>O<sub>3</sub> - B<sub>2</sub>O<sub>3</sub>- SiO<sub>2</sub>} system by high resolution NMR spectroscopy

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Rare-earth borosilicate glasses are of great interest for applications in many fields, including optical fibers, amplifiers and laser waveguides. Borosilicate glasses are also used widely to immobilize highly radioactive nuclear waste, because they provide high incorporation rate and good thermal stability. For all technological applications quoted previously, preventing or favoring devitrification is an important factor to produce either glasses or glass-ceramics, depending on the material function. It is therefore important to study structural modifications induced by phase separation in borosilicate networks to be able to control these phenomena.

Structural and microstructural properties of both homogeneous and phase separated lanthanum borosilicate (La<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system) glasses were investigated. SEM, TEM and XRD analyses have been carried on to highlight the microstructure and the presence of crystalline phases for each sample.

High resolution solid state NMR has been used to probe the structural modifications induced by phase separation in borosilicate network. We observe dependence between phase separation and La<sub>2</sub>O<sub>3</sub>/B<sub>2</sub>O<sub>3</sub> molar ratio. Phase separation occurs when this ratio is lower than 1. According to <sup>11</sup>B NMR experiments, apparition of a secondary BO<sub>3</sub> species towards 13 ppm is observed when glasses are phase separated. At the same way, <sup>29</sup>Si NMR MAS spectra show a progressive polymerization of the network with appearance of a new Q<sub>4</sub> species.

For a complete structural description, based on homonuclear NMR correlation experiments IN-EDEQUATE <sup>29</sup>Si and <sup>11</sup>B, and on heteronuclear NMR correlation experiments HMQC probing <sup>29</sup>Si/<sup>11</sup>B vicinity (D-HMQC) or chemical bonding properties (J-HMQC), a description of the chemical environments modifications induced in this system in presence of phase separation will be proposed.

**Keywords:** Glass structure, phase separation, Solid state NMR

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\*Speaker

# Understanding of the reactivity of granulated blast furnace slags by a multi-scale structural characterization

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Granulated blast furnace slag is a by-product of the iron making process. It has been used for many years as a cement constituent (type CEM II and CEM III) or as a concrete addition, replacing Portland cement clinker up to 80% in some niche applications. Above a certain addition level, GGBS-containing binders have superior long term properties but early strengths development is below the ordinary Portland cement (OPC) or cements with lower additions levels. Moreover, as a by-product, slags with different origins show various short and long term effects on the mechanical strength of the concrete. Two reasons for that are different chemistry and glass contents. But in order to understand really the behavior difference of slags with different origins, it is important to consider a complete multi-scale description of the slags, such as the structure of the vitreous matrix (the main phase) as well as the identification of inhomogeneities such as inclusions or nanocrystals. Blast furnace slags are Ca-Si-Mg-Al oxide glasses (in most cases 95 to 100% glass content) containing numerous secondary elements such as Na, K, Fe, Ti, Mn... The homogeneity of the glass matrix was investigated at different scales using both SEM and TEM coupled with EDS analyses evidencing a heterogeneous local dispersion of minor elements in the matrix. Multi-nuclear high resolution solid state NMR was used to describe the vitreous network. <sup>27</sup>Al MAS and <sup>3</sup>Q-MAS NMR experiments evidenced the presence of both tetra- and penta-coordinated aluminum species in slightly different amounts according to the composition of the slag. <sup>29</sup>Si MAS NMR experiments outlined the difference in polymerization of the samples. Finally, the crystalline phases of the slags were appreciated using XRD, SEM and TEM. The different structural organizations are related to the development of the short term strength of the slags.

**Keywords:** blast furnace slag, structure, NMR, TEM

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# Application of multinuclear solid-state NMR to structural analysis of slag and glass

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Silicate and aluminosilicate melts and glasses are major components in many geological processes in the Earth's mantle and crust. They also are important in the steelmaking process as slag in metal extraction from coals and iron ores, and as mold flux in the continuous casting process to slowly cool molten steel. Since macroscopic properties such as viscous flow are considered to be well related with atomic-scale structure and dynamics, detailed structural analysis of the slags is required.

High-resolution solid-state nuclear magnetic resonance (SSNMR) is one of the best methods for analysis of structure and dynamics. SSNMR is useful for probing the atomic environments of disordered materials such as glasses unlike diffraction techniques. Also, characteristic worth of special mention is that NMR provides structural information on the local structure around a specific kind of atom.

We have been applied to SSNMR to slags and related glasses to obtain information on chemical structure (for example, coordination number and structural role) and dynamics. Our targets are not only glass frameworks (e.g. <sup>29</sup>Si, <sup>27</sup>Al and <sup>17</sup>O) but also network-modifying cations such as <sup>43</sup>Ca; some of those nuclei are enriched with isotope to increase NMR sensitivity. In addition, structure and dynamics in molten state of the aluminosilicate system have been investigated using in situ high temperature NMR (~1500 degC).

**Keywords:** aluminosilicate glass and melt, solid state NMR

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\*Speaker

# Structure and hydration of amorphous blast-furnace slag

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Glass alteration is of large interest, from materials to Earth and environmental sciences. Ground Granulated Blast-furnace Slag (GGBS) is a glassy by-product of pig iron and steel manufacturing. This non-crystalline solid is a porous and textured calcium aluminate glass with an unusual silica-poor composition (about 35 wt.% SiO<sub>2</sub>). It acts as a hydraulic binder: the dissolution of the vitreous structure in water leads to the formation of various products including a calcium silicate hydrate (CSH) gel which is responsible for the setting of the material. When the GGBS is mixed with cement or another activator, this alteration takes place within a few days. GGBS has been used in cement for a hundred years as it improves its resistance to chloride and sulfate attacks and contributes to reduce the CO<sub>2</sub> footprint by limiting the use of clinker. Various studies have tried to better understand and predict GGBS reactivity in water. However, the structural control of glassy slag to binder transformation is poorly understood. In particular, the role of the cations in the starting glass and the hydration layer is still unknown. It has also been noticed that above 1 wt.% TiO<sub>2</sub> in the pristine glass, the reactivity of the slag drops drastically but there is no understanding of the structural origin of this variation. We present here the first results on the structure of the pristine glass and the reactivity of amorphous GGBS with a particular focus on the role of titanium during the hydration. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) enabled the visualization of the first stages of this glass hydration, including the release and precipitation of elements of interest. The study also includes X-ray absorption spectroscopy (XAS) at Ca and Ti K-edges and Raman spectroscopy results.

**Keywords:** Inverted glass, Glass structure, Alteration, X ray absorption, Scanning Electron Microscopy (SEM)

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# Direct Probing of Structural Transitions in Amorphous Oxide under Extreme Compression and Friction

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Electronic bonding transitions in amorphous oxides with low-z elements under extreme compression and friction is critical in clarifying the chemical and physical evolution of the Earth. Recent advances in element-specific experimental probes, such as nuclear magnetic resonance spectroscopy and inelastic x-ray Raman scattering (XRS) allowed us to reveal the detailed structural transitions around the low-z elements under extreme compression and friction. Here, we provide an overview of the recent progress that we have made into the bonding transitions in amorphous oxide at high pressure and rapid frictional slip [1,2,3]. Although anomalous melt properties have been attributed to the presence of triply coordinated oxygen ([3]O), the presence of [3]O in covalent amorphous oxides has not been revealed experimentally. We report the <sup>17</sup>O NMR spectrum for amorphous Al<sub>2</sub>O<sub>3</sub> and reveal the presence of [3]O. The detailed NMR characteristics of the oxygen tricluster are distinct from those estimated for the crystalline analogs, thus indicating its unique structure [1]. We also report the detailed structural transitions of oxides under extreme friction, which reveals the atomistic origins of the melting temperature depression of materials during frictional heating [2]. Finally, we showed the structural transition in amorphous oxides under extreme compression above megabar pressures using both experimental and theoretical XRS at high pressure up to ~120 GPa [3]. [1] Lee, S. K. and Ryu, S. B., *Journal of Physical Chemistry Letters* 9, 150-156 (2018); [2] Lee, S. K., Han, R., Kim, E. J., Jeong, G.Y., Khim H., and Hirose, T., *Nature Geoscience*, 10, 436 (2017); [3] Yi, Y. S. and Lee, S. K., *Physical Review B*, 94, 094110 (2016)

**Keywords:** anomalous melt properties, triply coordinated oxygen, NMR, XRS, glasses under extreme compression and friction

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\*Speaker

# Structural study of TeO<sub>2</sub>-MyO<sub>z</sub> glasses by X-ray total scattering and molecular dynamics

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Tellurite materials, especially in their vitreous forms, are of major interest in the field of information and communication technologies due to their remarkable optical properties. Pure tellurium dioxide TeO<sub>2</sub> glass shows important non linear susceptibility and Raman amplification superior to that of silicon-based glasses. However, its thermal stability and its poor mechanical properties make it difficult to use the pure TeO<sub>2</sub> glass as it is. Adding a modifier to compensate for the drawbacks without degrading the optical properties becomes a necessity. In order to understand the evolution of the properties with the addition of a modifier, the structural study of the modified glasses, in comparison with the pure glass, is essential.

This study consists of two sections: an experimental part put in comparison with a simulation of the glasses structures. The modifiers were chosen to be a transition element oxide and an alkali element oxide in order to be able to study the influence of the type of modifier and its quantity on the glass structure.

After the synthesis of pure TeO<sub>2</sub> glass and (100-x)TeO<sub>2</sub>-xMyO<sub>z</sub> (with M the alkali or the transition element) samples, structural studies based on experimental techniques, such as X-ray diffraction and Raman spectroscopy, were led in order to verify the amorphous nature and the homogeneity of the samples. Thermogravimetric analyses were realized to follow the evolution of the thermal stability of the glasses with the addition of modifier. An X-ray total scattering study was completed to determine the changes in the environment of the Te and O atoms in the glasses by comparing the pair distribution functions (PDF) of the different samples.

The simulation of the structure was carried out using the DL\_POLY [1] software using interatomic potentials for Te-O [2] and M-O [3]. PDF were calculated based on the simulated structures and were compared to the experimental ones.

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Jentys and Catlow, Catal. Lett., 22 (3), (1993), p. 251-257.

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\*Speaker

**Keywords:** Tellurite glasses, glass structure, X, ray total scattering, molecular dynamics

# STRUCTURE 3

# Short range order in amorphous germanium tellurides

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Short range order of several amorphous germanium telluride alloys (Ge-Te, Ge-Sb-Te, Ge-Cu-Te, Ge-Ga-Te, Ge-As-Cu-Te, Ge-Ag-I-Te...) has been investigated by diffraction techniques and EXAFS. Large scale structural models have been obtained by fitting experimental data (usually 3-5 datasets for each composition) simultaneously by the reverse Monte Carlo simulation technique.

It has been revealed that the 8-N rule is obeyed in Ge-Te, without any signs of threefold coordination for Te or distorted octahedral coordination of Ge. Introducing further components may alter the environment of Ge and Te as well as the connectivity of Ge-Te host network in different ways. Structural changes induced by various elements are overviewed. Limitations of experimentally available structural information are discussed and experiment-based models are compared with recent theoretical results.

**Keywords:** Ge, Te glasses, short range order, diffraction, EXAFS, modelling

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# Chemical homogeneity and network topology from NMR experiments

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The structure of glasses at the nanometer scale can be assessed from homo- or hetero-nuclear NMR experiments involving ensembles of NMR active nuclei [<sup>11</sup>B, <sup>17</sup>O, <sup>23</sup>Na, <sup>27</sup>Al, <sup>29</sup>Si, <sup>31</sup>P...]. They provide different types of information on the spatial proximities or on the nature of the network of chemical bonds. They thus allow to characterize the structure, chemical homogeneity, or topology of ordered or disordered solid state materials at the molecular level that are closely related to their macroscopic properties.

**Keywords:** Structure, spectroscopy, nmr

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\*Speaker



# Local environment of iron ions in magnesium aluminosilicate glasses from liquid helium temperature to glass transition temperature

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Iron is the key element to affect the coloration of glass in ultraviolet and near-infrared regions. From the energy point of view, the sheet glass, for example, has to be tailored to have optimized optical absorption to improve energy-saving of house and building. Glass coloration has been well known to strongly depend on oxidation and coordination states of iron, and precise understanding of the iron speciation and its correlation with glass structure promote to add new functionality to glass.

This study gives our focus on aluminosilicate glass system, especially magnesium aluminosilicate glass. Since Al<sup>3+</sup> and Mg<sup>2+</sup> have close ionic radius to those of Fe<sup>3+</sup> and Fe<sup>2+</sup>, respectively, site distribution of Fe is of particular interest in this glass system. The purpose of this study is to understand the local environment of Fe ions in magnesium aluminosilicate glasses by measuring the optical absorption spectra as functions of glass composition and temperature.

UV-Visible-NIR absorption spectroscopy (UV-Vis) was applied to the glass samples at the temperature from ~100K to around glass transition temperature. Electron paramagnetic resonance (EPR) spectroscopy was also used to evaluate local environment of Fe<sup>3+</sup>. By combining these approaches, the relations between local structure of Fe (e.g. redox state, site distribution, site distortion) and structural frame work of aluminosilicate glasses are discussed.

**Keywords:** Iron, aluminosilicate glass, structure, optical absorption spectroscopy, electron paramagnetic resonance

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# Structural role of aluminum cation in alkaline-earth aluminosilicate glasses

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One of the most important goal of physical chemistry for molten materials (and their glasses) are to deeply understand how each components are mixed together in their non-crystalline structure, impacting on physical and chemical properties of the disordered materials. Alumina is a common component of silicate melts and glasses, which are important system for earth-science and high-temperature-industries (e.g. metallurgy, glass making). Therefore, the detailed chemical state, i.e. short-range structure, in the neighborhood of aluminum cations in silicate glasses has been studied for a long time. It is well known that the coordination number of aluminum cations varies from 4 to 6 in the melts and glasses where the structural role of 5- and 6-coordinated aluminum cations are still not sufficiently understood while the 4-coordinated aluminum cations acts as a network former. In the present study, the kinds of non-framework cations in aluminosilicate glasses are changed from calcium (Ca) to magnesium (Mg), giving a variation in coordination number of aluminum cations; aluminum-27 magic angle spinning nuclear magnetic resonance (MAS NMR) spectra shows that 5-coordinated aluminum cations ([5]Al) increase with replacing Ca by Mg cations in (30-x)CaO-xMgO-15Al<sub>2</sub>O<sub>3</sub>-55SiO<sub>2</sub> glasses (x = 0, 7.5, 15, 22.5 or 30 mol%). Silicon-29 MAS NMR spectra of these glasses shows that the amount of non-bridging oxygens decreased with increasing the Mg/Ca ratio, indicating non-framework cations are consumed in-part to compensate the negative charge of oxygen between 4-coordinated silicon ([4]Si) and [5]Al cations ([4]Si-O-[5]Al), which has a larger negative charge than that of [4]Si-O-[4]Al. These phenomena indicated that [5]Al cations should behave as a network former. It is also found that the atomic packing density, which is derived from the density of the glasses, increases with increasing the amount of [5]Al cations. These structural change by increasing [5]Al will impact the thermal conductivity of these glasses.

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**Keywords:** aluminosilicate glass, density, MAS NMR

# Impact of Temperature and Pressure on the Structure of Borosilicate Glasses

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The underlying network structure of glasses controls many important and beneficial properties, including their optical, thermal and mechanical attributes. As glasses continue to be developed for increasingly complex uses, these relationships between structure and properties can be further complicated by the glass thermal and pressure histories. Borosilicates are a particular noteworthy example of glasses with significant commercial success, exploiting their beneficial thermal properties in the case of Pyrex®<sup>®</sup>, to current emphasis on mechanical properties for several technological applications. Borosilicate glasses are also especially suited for structural study using NMR spectroscopy, at both short- and intermediate-range length scales, where the former includes boron coordination number and non-bridging oxygen concentrations, and the latter is often comprised of superstructural units involving borate polyhedra. Here we make use of multi-nuclear NMR to investigate how both temperature and pressure impact these structural elements in borosilicate glasses, leading to substantial changes in properties like density and hardness. In particular, boron coordination and superstructural units like the boroxol ring exhibit substantial sensitivity to changes in fictive temperature and high pressure compaction, and are shown to have a pronounced impact on glass properties.

**Keywords:** NMR, borosilicate, structure, compression, hardness

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# STRUCTURE 4

# Structural investigation of glasses in the BaO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system with coupled Raman/Brillouin spectroscopy

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Porous substrates with low permittivity and high electrical resistance could provide opportunity to develop new generation of high frequency devices. By taking advantage of phase separations occurring in borosilicate systems, we might be able to create such new devices after selective etching of the boron-enriched phase.

Since structural data of glasses in the ternary system BaO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (BaBSi) are limited, using a coupled Raman-Brillouin spectrometer (ARABICA) we could directly observe and correlate changes on the elastic properties and structure.

Two series of glasses, in the ternary system were synthesized. The first one has an almost constant SiO<sub>2</sub>/B<sub>2</sub>O<sub>3</sub> molar ratio (~1) and spans perpendicularly to the immiscibility gap. The second glass series has a constant BaO amount (32 mol%), and progress parallel to the decomposition area. The effects of BaO content and SiO<sub>2</sub>/B<sub>2</sub>O<sub>3</sub> molar ratio on both B-coordination and on the global network connectivity were investigated following the vibration modes for Si and B in the Raman spectra.

In the high frequency envelope (1200-1600 cm<sup>-1</sup>), related to boron stretching modes, we can observe the change from BO<sub>3</sub>-BO<sub>4</sub> to BO<sub>3</sub>-BO<sub>3</sub> coordination with increasing boron content. In details, the frequency position of the two main bands slightly increases whereas, the relative intensity of the bands related to 3-fold coordinated boron strongly increases with respect to the 4-fold coordinated one. The Brillouin spectroscopy results show that mechanical properties are related to the extent of the network variations. In decomposed samples we noticed the appearance of two peaks in the Brillouin spectra, which might be related to silica and boron phases. From the results here obtained we will propose a model estimating the changes of B coordination in the BaBSi ternary system and relating them to property changes (such as electrical properties).

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**Keywords:** barium borosilicate glass, Raman/Brillouin spectroscopy, boron coordination

# Combined Solid-State NMR and Molecular Dynamics Study of the Structure of Strontium-Aluminosilicate glasses

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Solid-state NMR has firmly established itself as a method of choice for providing key information for the elucidation of glass atomic-scale structure. Recently, a methodology based on the combination of DFT-NMR calculations with molecular dynamics simulations has emerged as a significant step for the improvement of the detailed interpretation of experimental NMR spectra. Using this approach, we have investigated the structure of aluminosilicate SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-SrO based glass compositions which are largely unexplored systems. Glasses on the compensation line Al<sub>2</sub>O<sub>3</sub> = SrO, were studied with <sup>17</sup>O, <sup>29</sup>Si and <sup>27</sup>Al solid state NMR at high (11.7 T) and very-high (20.0 T) magnetic fields, together with neutron diffraction spectroscopy. Classical and ab-initio molecular dynamics (MD) simulations were performed and combined with calculations of NMR parameters with the DFT-GIPAW method. Computed NMR parameters were linked to local structural features to establish relationships between experimental NMR spectra and the underlying topological disorder (in terms of chemical and geometrical disorder). NMR fingerprints of debated units such as tricoordinated oxygen atoms could be predicted with the aims to assess their existence from experimental data. In agreement with experimental NMR data, MD simulations predict that aluminium is predominantly tetrahedrally coordinated for all the studied compositions with a small fraction of AlO<sub>5</sub> units ranging from 2-5%. Variations of the <sup>29</sup>Si NMR spectra, and to a less extent of <sup>27</sup>Al spectra, could be quantitatively correlated to the Al/Si mixing. In parallel, the Al/Si connectivities were investigated using advanced NMR techniques enabling the resolution of the <sup>29</sup>Si NMR spectrum in terms of Q<sub>n</sub>(mAl) units (i.e., Q<sub>n</sub> connected to m Al units). Simulations of <sup>17</sup>O NMR experiments from our first-principles methodology combined to <sup>17</sup>O-<sup>27</sup>Al correlation experiments allowed extractions of Al-O-Si, Al-O-Al and Si-O-Si peaks which were found to be strongly overlapping in experimental 1D and 2D <sup>17</sup>O MAS NMR spectra.

**Keywords:** Aluminosilicate, NMR, MD, DFT, Glass structure

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\*Speaker



# Solubility and role of iodine and xenon in silicate glasses

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Iodine is the heaviest stable halogen element. In spite of its low natural abundance, iodine is interesting in Geosciences, mainly because of its link to xenon. Indeed, most of the iodine isotopes become xenon isotopes by  $\beta$ -radioactive decay and this relationship is helpful in various research fields. In cosmochemistry, the now-extinct  $^{129}\text{I}$ - $^{129}\text{Xe}$  radioactivity is used as a geochronometer to date meteorites and provide information on the formation of planetary atmospheres.  $^{129}\text{I}$  is also of particular concern because it will be a major contributor to the radioactivity released by a geological repository site for nuclear wastes. In the context of the Comprehensive Nuclear-Test-Ban Treaty, the detection of underground nuclear explosions is allowed by seismic, acoustic, and radionuclide techniques. Atmospheric radioxenon analyses provide the only distinctive signature of a nuclear explosion. For all these reasons, it is important to understand the mechanisms related to the solubility of iodine depending on the composition of the glass, the temperature or the pressure and to analyze its solubility, redox state, and distribution in the glass network.

First, a series of glasses with simplified chemical compositions is synthesized. Then, alkali iodate or iodide is added to the glass in a welded platinum capsule. Different conditions of pressure and temperature are tested, and a hot isostatic press is used to experiment the influence of relatively high pressures (until 2000 bar). The redox state of iodine is determined by Raman and X-ray Absorption Spectroscopy.

Our study on alkali borosilicate glasses, wherein iodate ( $\text{IO}_3^-$ ) is incorporated at 1000 bar and 1000°C, shows that iodine can take various redox forms ( $\text{I}^-$ ,  $\text{I}_2$  and  $\text{IO}_3^-$  with degrees of oxidation -I, 0 and +V, respectively) within the same glass. Iodine concentrations are up to 3.3 wt.% in the glass with 20 mol%  $\text{B}_2\text{O}_3$ .

**Keywords:** redox, halogen, borosilicate, Raman, XAS

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# Effect of a third network former on the properties of aluminosilicate glasses

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In this study the properties of metaluminous aluminosilicate glasses have been investigated as well as changes upon the addition of phosphate. Glasses in the system SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub> were prepared with a variation of the P<sub>2</sub>O<sub>5</sub> content (up to 7.5 mol%) and of the SiO<sub>2</sub> content (between 50 and 70 mol%). MAS NMR experiments confirmed that aluminium is present in four-fold coordination mostly as shown in Figure 1. Aluminium is thus charge-balanced by sodium ions and incorporated into the silicate network. Glass density was found to decrease with phosphate addition, possibly owing to reduced cross-linking of the glass network upon phosphate incorporation. Another possibility is an interaction between phosphate groups and [AlO<sub>4</sub>]- tetrahedra, which may lead to formation of non-bridging oxygens by sodium ions, which are no longer needed for charge-compensation. Glass transition temperature showed a trend similar to that of the density for phosphate addition; however, it decreased in glasses with fixed 7.5 mol% phosphate when the silica content was increased. This unexpected trend points towards a complex interplay between the three network formers (Si, Al and P). The two different roles of sodium (network modifying or charge-balancing) may also affect the glass properties. Raman spectra showed changes in band intensities which are in agreement with an observed decrease in hardness with phosphate addition. For some features of the Raman spectra, interestingly, the increase of phosphate content had a similar effect as an increase in silica content. Thus the underlying changes in the glass network may also be similar. In summary, the incorporation of phosphate as a third network former affects the thermal and mechanical properties of aluminosilicate glasses in a way which points at complex, non-linear structural changes.

**Keywords:** aluminosilicate glass, mechanical properties, structure property relationships, three network formers

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# The Complex Raman Response of Cations in Alumino-Silicate Glasses

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Raman scattering of ternary alumino-silicate glasses with alkali and alkaline-earth cations (M=Mg, Ca, Sr, Ba, Na,...) has been performed. The concentrations range from the peralcaline ( $MO/Al_2O_3 > 1$ ) to the peraluminite ( $MO/Al_2O_3 < 1$ ) domain keeping constant the silica content. The vibrational signature of the cations is clearly evidenced at low frequency in the depolarized (VH) spectra. Between one and three bands are identified. They associate to different types of motions depending on the charge carried by the cation (alkali or alkaline-earth atoms). In addition, glasses with magnesium exhibit a very peculiar behavior. Very interestingly, some bands disappear for the tectosilicate glasses ( $MO/Al_2O_3=1$ ) and in the peraluminite domain revealing a clear vibrational contrast between network modifier cations and charge compensator cations [1]. A preliminary experiment in a quaternary alumino-silicate system combining two types of alkali atoms highlights the possibility by simple Raman spectroscopy to define the preferential role of each cation, *i.e.* network modifier or charge compensator, and to make a semi-quantitative treatment as well. [1] B. Hehlen and D. Neuville, *Raman Response of Network Modifier Cations in Alumino-Silicate Glasses*, J. Phys. Chem. B **119**, 4093 (2015).

**Keywords:** Raman, oxide glass, aluminosilicates, vibrations

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# Structure and crystallization in the B2O3-La2O3 binary and focus on the congruent lanthanum metaborate composition (LaB3O6)

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The B2O3-La2O3 binary system contains a narrow glass domain around the La2O3.3B2O3 metaborate composition. This glass domain is of interest in the field of nuclear waste containment glasses, rich in rare-earths and B2O3, and as optical materials. An extensive study of the structure and crystallization properties of these glasses has been undertaken recently<sup>1-3</sup>. In this paper, we focus on the lanthanum metaborate composition, that melts congruently at 1140°C. When undercooled, the crystallization of this melt is characterized by a heavily heterogeneous nucleation and a high activation energy for the crystal growth ( $\sim 800$  kJ.mol<sup>-1</sup>). To understand these peculiar properties, we compare the crystal and the melt structures, using a range of complementary techniques. <sup>11</sup>B and <sup>17</sup>O MAS NMR results do not indicate significant differences regarding the fraction of fourfold coordinated boron and the fraction of non-bridging oxygens in the crystal and in the glass, while Raman (performed on a series of binary glasses around the LaB3O6 composition) reveals a complex borate network with a great variety of superstructural units, dissimilar to that of the crystal. RE sensitive spectroscopic tools such as optical spectroscopies (Nd<sup>3+</sup> and Eu<sup>3+</sup> substituted for La<sup>3+</sup>) and EXAFS pointed out shorter RE<sup>3+</sup>-NBO interactions in the glass. X-ray wide angle (WAXS) and neutron scattering measurements have been carried out to produce the total structure factors and allow the building of structural models for the glass, allowing a deeper insight into the differences and relationships to the crystalline structure.

1 O. Majérus, H. Trégouët, D. Caurant, and D. Pytalev, *J. Non. Cryst. Solids*, vol. 425, pp. 91–102, 2015.

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\*Speaker

2 D. S. Pytalev, D. Caurant, O. Majérus, H. Trégou'et, T. Charpentier, and B. N. Mavrin, *J. Alloys Compd.*, vol. 641, pp. 43–55, 2015. 3 H. Trégou'et, D. Caurant, O. Majérus, T. Charpentier, L. Cormier, and D. Pytalev, *Procedia Mater. Sci.*, vol. 7, pp. 131–137, 2014.

**Keywords:** Borate glasses, rare, earths, glass structure, crystallization

# Structural investigation of M2O-SiO2-B2O3-Al2O3 glasses by Raman spectroscopy and the influence of thermal history.

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Alkali-borosilicate glasses are one of the most used glasses with a high technical and commercial importance. Due to their high chemical and thermo-shock resistance, hardness, fracture toughness and good optical properties, they are suitable for a wide range of different applications such as substrates in electronic devices or as household and laboratory ware. As the macroscopic properties of glasses (i.e. mechanical properties) are directly correlated to their microscopic structure, the understanding of the glass topology is therefore one of the most important key parameter in order to design/optimize glass.

To investigate the effect of the modifier cation size on the boron structure, the Na oxide is substituted by Li and K oxide on the following compositions 74SiO<sub>2</sub>-10B<sub>2</sub>O<sub>3</sub>-16Na<sub>2</sub>O and 74SiO<sub>2</sub>-20.7B<sub>2</sub>O<sub>3</sub>-4.3Na<sub>2</sub>O-1Al<sub>2</sub>O<sub>3</sub>. To analyze also the influence of Al<sub>2</sub>O<sub>3</sub> addition and thermal history on the glass structure, glasses of both series with different amounts of Al<sub>2</sub>O<sub>3</sub> and tempering methods were produced.

The change in the connectivity and sort to medium-range order were observed with the help of Raman spectroscopy, where the influence on the local connectivity can be determined by changes in the vibration bands. Based on the frequency bands between 700-850 cm<sup>-1</sup> (borate and boroxol ring modes), 1000-1200 cm<sup>-1</sup> (silicate, borate and mixed B-O-Si stretching modes) and 1250-1600 cm<sup>-1</sup> (trigonal borate entities) we were able to observe the change in boron and silica coordination. In combination with mechanical testing, i.e. testing of the Vickers hardness, we want to correlate changes in mechanical properties to atomic local structure for different compositions and thermal histories. With this model we want to predict better new mechanical properties.

**Keywords:** Raman, Borosilicates, Ultra, Strong, Glasses

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# STRUCTURE 5

# The structure of bioactive phosphate glasses using diffraction techniques and EPSR modelling

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Neutron and X-ray diffraction, coupled with <sup>23</sup>Na and <sup>31</sup>P NMR, have been used to investigate the structural effects of substituting CaO with SrO in a 40P<sub>2</sub>O<sub>5</sub>·(16-x)CaO·20Na<sub>2</sub>O·24MgO·xSrO glass, where x is 0, 4, 8, 12 and 16 mol%. Binary metaphosphate glasses were also studied using neutron diffraction and the results were used to guide the analysis of the diffraction data obtained for these complex multi-component glasses. Diffraction data was analysed using direct fitting and EPSR modelling to extract information on the phosphorous and modifier environments. The P-O environment was consistent with NMR results. The M-O coordination environments (M= Mg, Ca, Sr, Na) determined by direct fitting of the neutron data yielded broad asymmetric distributions of bond length, with coordination numbers that were smaller, and bond lengths that were shorter, than in corresponding crystals. The Mg-O coordination number was determined as 5.0(2). EPSR models gave very similar results, but showed the local environments of the modifiers to be even more asymmetric, with higher coordination numbers, closer to those found in published simulations of phosphate glass structure. Functional properties, including glass transition temperatures, thermal processing windows, dissolution rates and ion release profiles were also investigated. Dissolution studies showed a decrease in degradation rate with initial addition of 4 mol% SrO, but further addition of SrO showed little change. The ion release profiles followed a similar trend to the degradation rates observed. The limited changes in structure and dissolution rates observed for substitution of Ca with Sr in these fixed 40 mol% P<sub>2</sub>O<sub>5</sub> glasses were attributed to their similarities in terms of ionic size and charge.

**Keywords:** phosphates, diffraction, NMR, Modelling

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# Structural study of sodium borate glasses combining molecular dynamics and nuclear magnetic resonance

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Borate glasses are known to have a large fraction of the boron atoms involved in superstructural units like boroxol or pentaborate rings, in addition to the double coordination of boron atoms (3 and 4). This generates the boron's anomaly, which is a non-linear evolution of properties upon the addition of sodium oxide. For example the glass transition temperature reaches a maximum for alkali content around 25%.

In this study, we used an approach combining Molecular Dynamics (MD) with Nuclear Magnetic Resonance (NMR) to examine the evolution of the glass structure with the increase of alkali content. Structural models were generated by Classical MD (CMD) and ab-initio MD (aiMD) to compare the reliability/performance of both methods to reproduce NMR properties which were computed using the GIPAW method.

Only aiMD permits to generate superstructural units whereas CMD models are free of any 6-membered ring. With those MD-GIPAW data, correlations between NMR parameters could be highlighted, especially between the quadrupolar coupling constant CQ and the isotropic chemical shift  $\delta_{iso}$  for boron and sodium. Accounting for those, the fitting model used for the analysis of experimental 1D and 2D spectra could be significantly improved.

Comparison of MD NMR results with experimental ones shows that boron-11 chemical shifts range obtained on the aiMD models reproduce almost perfectly the experimental one. Our calculations reveal chemical shift variations for BO3 and BO4 when boron atoms are inside or outside a superstructural unit. Moreover, NMR parameters are less distributed for boron inside a ring, as a result of the stronger geometrical constraints inside a superstructural unit.

In addition, correlations between local structural features and NMR parameters were investigated such as the dependence of boron-11 isotropic chemical shift with the average angle B-O-B.

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\*Speaker

**Keywords:** solid state NMR, molecular dynamics, borate glasses, superstructural units

# New tellurite glasses within the TeO<sub>2</sub>-NbO<sub>2.5</sub>-WO<sub>3</sub> system: relevant correlations between structural and optical properties

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Tellurium oxide based glasses have been of attractive scientific and technological interest due to their physical properties such as a high refractive index (around 2.2) high dielectric constants, a wide band infrared transmittance (up to 6  $\mu\text{m}$ ), a low phonon energy (600-700  $\text{cm}^{-1}$ ) and large third order nonlinear optical susceptibilities  $\chi(3)$  (50 times higher than those of silica-based glasses) [1-3].

The glass-forming domain of new glasses within the TeO<sub>2</sub>-NbO<sub>2.5</sub>-WO<sub>3</sub> system was investigated. The structural evolutions upon adding NbO<sub>2.5</sub> and WO<sub>3</sub> were analysed using Raman spectroscopy; the linear and nonlinear optical properties were studied using optical transmission and spectroscopic ellipsometry. Consistent correlations have been revealed between structural and optical properties in these glasses.

Globally, no striking evolutions take place upon adding NbO<sub>2.5</sub> and WO<sub>3</sub>. Adding WO<sub>3</sub> leads to (i) uniformly dispersed WO<sub>6</sub> octahedra throughout the Te–O–Te network (at low WO<sub>3</sub> contents) and (ii) amorphous WO<sub>3</sub>-rich regions (at higher WO<sub>3</sub> contents). Adding NbO<sub>2.5</sub> engenders (i) a weak structural depolymerization of the Te–O–Te network and (ii) occurrence of NbO<sub>2.5</sub>-rich regions. The investigated glasses exhibit high linear refractive indices of 2.13 in average and remarkable nonlinear susceptibilities  $\chi(3)$  of  $5.48 \cdot 10^{-13}$  esu in average, i.e., about 37 times higher than  $\chi(3)$  of silica SiO<sub>2</sub> glass.

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**Keywords:** tellurite glass, glass structure, linear and nonlinear optical properties, Raman spectroscopy

# Stabilization of Silicate Melts through Polymerization Reactions, with Implications for the Redox State of the Mantle and Crust

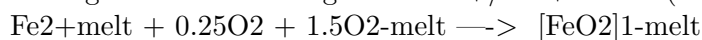
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Melting of forsterite, fayalite, and numerous metasilicate crystals (e.g., pyroxenes, pseudo-wollastonite) produces melts appreciably more polymerized than their precursor crystals. Melting of forsterite, which is composed solely of Q0 species, produces melts in which Q1 and Q2 species dominate. Melting of fayalite also produces melts more polymerized than its precursor crystal and more polymerized than Mg<sub>2</sub>SiO<sub>4</sub> melt. Q2 silicate crystals (e.g., pyroxenes) also produce melts more polymerized than their precursor crystals. The polymerization reactions stabilize the melts by buttressing them against the effects of extreme thermal agitation, by diminishing librational and rotational contributions to their heat capacities. In the absence of polymerization, melting temperatures of the most common silicate minerals would be appreciably greater than observed. Polymerization of Si tetrahedra in crystals and melts proceeds via nucleophilic reactions. Nucleophiles are produced by strong thermal agitation which causes dissociation of the bond between non-bridging oxygen (NBO) and a counter cation (M). Bond scission produces the negatively charged nucleophilic species Si-NBO<sup>-</sup>, which may attack and bond to Si centers of adjacent tetrahedra leading to melts more polymerized than their precursor crystals. All polymerization reactions produce free oxygen (O<sup>2-</sup> or oxide ion). Melting of forsterite, for example, yields a minimum of ~6 mol% O<sup>2-</sup> and still greater amounts of O<sup>2-</sup> are produced during melting of fayalite. Melting of Q2 crystals produces ~1-5 mol% O<sup>2-</sup>, thus melting of olivine and pyroxenes in the mantle should produce O<sup>2-</sup> at the mol% level. This strong base is likely to partition strongly into the melt rather than into the residual crystals. With accumulation in the melt, the chemical state, including redox states, will be affected by driving the melt toward greater Fe<sup>3+</sup>/Fe<sup>2+</sup> values (more oxidized) according to:



**Keywords:** Free oxygen, melting, redox, polymerisation

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# Uranium speciation in binary alkali-borate glasses: a multispectroscopic study

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During centuries, uranium has been used as an efficient coloring agent in glasses. It is also used as a surrogate of transuranic elements in nuclear waste matrices. In glasses and ceramics, U is mainly present in the forms of U(VI) and U(IV), with minor amounts of U(V). Silicate glasses show uranyl sites U(VI) with an original geometry, based on shorter distances between U and equatorial oxygens than in most uranyl complexes found in crystals and aqueous solutions. This intermediate speciation of U(VI) in glasses is also illustrated by their color, which may vary between green to brown, depending on the glass composition. Uranium speciation has been investigated since years in complex technological borosilicate glasses using XANES, EXAFS and neutron/x-ray diffraction data. However, there has been no investigation of the more simple alkali borate glasses, despite they show a large diversity of cation sites as a function of the presence of various structural superunits. Here we report the study of uranium speciation in binary borate glasses using U optical and L3-edge X-ray absorption spectroscopies to determine the valence and local structure of U. Our results show that the alkali content and nature drastically influence uranium speciation: the color change from pale green to deep yellow with increasing alkalinity reflects the change of the redox ratio between co-existing U(IV), U(V) and U(VI). In addition, changes in the 5f-electron localization causes the transformation from uranyl to uranate speciation. The relation between the uranium species and the glass network will be discussed in light of the composition-dependent structural changes of the borate glass.

**Keywords:** uranium, borate, EXAFS, nuclear waste storage

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# Structure, thermodynamic properties and viscosity of silicate melts: development of a model in the Adam and Gibbs theoretical framework

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The rheological and thermodynamic properties of silicate melts played a crucial role in the formation and the evolution of the Earth, as well as in the history of human civilisations. For instance, they determined the geologic evolution of the Earth primordial magma ocean, and, thus, influenced the differentiation of the Earth mantle and crust. Nowadays, silicate melt properties control, for example, the dynamic of volcanic eruptions or glass-making processes in the industry. Therefore, predicting silicate melts properties is critical to understand and to solve various problems in Earth and Material sciences.

The Adam and Gibbs theory offers a thermodynamic framework that allows relating the chemical composition of a melt to its structure and its properties. Within this theoretical framework, viscous flow occurs through the cooperative re-arrangement of molecular sub-regions in the melt. From high temperature Nuclear Magnetic Resonance and Raman spectroscopy data, it actually is known that viscous flow occurs because of the cooperative exchange of oxygen atoms between network former polyhedral units, allowing their motions. Therefore, it appears that such structural knowledge can be linked to the melt entropy, heat capacity and viscosity with using the Adam and Gibbs theory.

In this communication, building on our previous work on Na-K silicate glasses (Le Losq and Neuville, 2017), we will show how this idea can be used for modelling the properties of aluminosilicate melts. First, we will highlight how the distribution of network former tetrahedral units can be calculated from the melt chemical composition. Then, this structural knowledge will be linked to the melt thermodynamic properties, which, in turn, will allow calculating the melt viscosity. Such model opens new pathways in order to gain structural, thermodynamic and rheological information about silicate melts and glasses.

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**Keywords:** viscosity, entropy, structure, glass, melt, aluminosilicate



# 1D/2D NMR investigation of borophosphate glasses

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The local and medium range orders of the borophosphate glass network have been analysed by <sup>11</sup>B/<sup>31</sup>P correlation nuclear magnetic resonance. A high field NMR protocol (18.8 T), including recently developed NMR sequences, has been applied on different borophosphate systems (sodium, lithium, tin -borophosphate) during the last decade. This contribution summarizes how NMR provides new insights onto the nature of the mixed borophosphate species, the distribution of borate units in the glass network, the formation of BOB bonds and the presence of POB3 linkages.

**Keywords:** phosphate glasses, correlation NMR, structure

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\*Speaker

# STRUCTURE 6

# Role of basicity and Al<sub>2</sub>O<sub>3</sub> on the NBO/T in calcium aluminosilicate melts

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The effect of basicity and Al<sub>2</sub>O<sub>3</sub> on the structure of CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> melts has been studied using XPS, Raman and NMR spectroscopy investigation. The content of Al<sub>2</sub>O<sub>3</sub> and basicity (CaO/SiO<sub>2</sub>) were varied to determine the compositional effect on the structure of high temperature ionic melts. The amount of oxygen ions (XO<sub>n</sub>-(n:0,1,2)) in the super-cooled liquids were estimated by deconvolution with PeakFit™ 4.1 of O1s binding energy using X-ray photoelectron spectroscopy (XPS) [1]. The proportion of Q<sub>n</sub> species were analyzed by Raman [2] and MAS NMR spectroscopy [3]. As a result of the quantitative analysis, the experimental-based NBO/T is shown as follow.

$$\text{NBO/T} = [\text{Q}_n * (4-n)] / ([\text{IV}]\text{Al} + [\text{IV}]\text{Si}) \quad (1)$$

NBO/T was shown linear relationships to the basicity (CaO/SiO<sub>2</sub>) including inflection point at CaO/SiO<sub>2</sub>=1.0. It is due to the stability and Q<sub>n</sub> dominant unit of melts change around the wollastonite (CaSiO<sub>3</sub>) congruent point [2]. As Al<sub>2</sub>O<sub>3</sub> increases, the NBO/T converges because of the preference of Q<sub>2</sub> chain structure near the anorthite (CaAl<sub>2</sub>SiO<sub>8</sub>) congruent point [4]. This is due to the change of the dominant polymeric unit into Al-O-Si and Al-O-Al [5]. Also, iso-NBO/T and lines were derived by comparing XPS and Raman spectroscopy results. The comparative evaluation between the viscosity and the sulfide capacity, which is a representative property of the melts, was carried out.

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**Keywords:** NBO/T, XPS, Raman spectroscopy, MAS NMR, Aluminosilicate Slags

# Structure of aluminate liquids and glasses under extreme conditions

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In contrast to pure silica, SiO<sub>2</sub>, liquid alumina Al<sub>2</sub>O<sub>3</sub> does not form a glass. This is in accordance with Zachariasen’s rules, since a significant fraction of aluminium atoms exhibit a coordination number of more than four and share edges. However, the introduction of CaO increases the O:Al ratio, allowing the formation of corner-shared AlO<sub>4</sub> tetrahedra that facilitate glass formation. Liquid calcium aluminates are important components of natural magmas and their glasses have important applications for infrared-transmitting optics. A detailed and accurate description of the structural role of Al and Ca in high temperature CaO-Al<sub>2</sub>O<sub>3</sub> liquids is important for understanding glass-forming mechanisms. Furthermore, pressure-induced structural transformations in calcium-aluminosilicate melts, and associated changes in physical properties (e.g. compressibility and viscosity), have a profound impact for the rheology of natural magmas and geophysical processes, from planetary formation to present-day volcanism. In this communication, I will summarise recent progress in using the containerless high-temperature technique of aerodynamic levitation with CO<sub>2</sub> laser heating, in combination with synchrotron x-ray diffraction, neutron diffraction with isotope substitution, and state-of-the-art molecular dynamics computer simulations, to reveal unique insight into dramatic and unexpected structural transformations on local and intermediate-range length-scales which take place during vitrification of these non-traditional glass-forming liquids [1,2,3]. I will also discuss the results of *in situ* laser-heated diamond anvil cell experiments with synchrotron x-ray diffraction of calcium-aluminate liquids and glasses, which reveal pressure-induced Al-coordination change and the development of short-range topological ordering [4].

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**Keywords:** aluminate glass, extreme conditions, high temperature, high pressure, liquid structure, neutron diffraction, synchrotron Xray diffraction

# Structure and phase separation investigation of Zr containing Na<sub>2</sub>O-CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> glass

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Zirconium is widely used in glass ceramic as a nucleating agent. It can also enter a few specific glass compositions like nuclear waste insulation tank. We know that in MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-ZnO classical parent glass used in glass ceramic, it can generate some nanoscale heterogeneities before crystallization [1]. In that case, some regions are highly concentrated in Zr while the residual glass is Zr-poor. These heterogeneities can act as phase separation and are precursors for the crystallization. During classical SiO<sub>2</sub>-Na<sub>2</sub>O-CaO-Al<sub>2</sub>O<sub>3</sub> industrial forming glass, some Zr can leave the Zr-containing wall of the furnace to enter the glass structure. Zr atoms can segregate into the glass matrix and form a droplet that can modify the final glass properties. These droplets can eventually crystallize to create another kind of defect. A structural study of NCAS glasses with variable amounts of Zr allows understanding how Zr environment impacts the crystallization processes. Various analyses have been obtained (XANES, EXAFS, NMR...) to describe the Zr environment from its first neighbors to the polymerized glass network in order to determine if phase separation also affects crystallization in this system. [1] O.Dargaud, L. Cormier, *Journal of Non-Crystalline Solids* 358 (2012)

**Keywords:** Zirconium, Phase separation, Soda lime glass

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# Europium environment modification by Electron irradiation in metaphosphate and polyphosphate glasses: impact of electron energy

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The rare earth (RE) doped phosphate glasses are attractive materials in optics due to their low transition temperature and a high capacity to dissolve rare earth ions compared to silicate glasses. In this work, we are interested in understanding the mechanisms leading to the structural modification of Zn polyphosphate and metaphosphate glasses under electron irradiation in order to try to control the RE doping ions environment linked to the luminescence properties. In particular, we present here some results on the impact of the electron energy (700 keV and 2.5 MeV) on the RE environment modification. The glass compositions deal with mixing different alkaline and alkali-earth ions (Na, Li, K and Mg) and different polymerization degree of phosphate glasses. After 2.5 MeV or 700 keV irradiation, the Raman spectra traduce a significant depolymerization of the polyphosphate vitreous network from 108 Gy dose opposite to metaphosphate glasses that remain more stable. The modification of the network seems not to strongly affect the local environment of Eu<sup>3+</sup> as demonstrated by the significant increase of the asymmetry ratio (As) of Eu<sup>3+</sup> ions in irradiated metaphosphate glasses compared to polyphosphate glasses. Under 700 keV irradiation, the Eu<sup>3+</sup> As variation can be noticed in a larger volume than the penetration depth of the electrons. Moreover, the variation depends on the alkaline ion type showing a role of alkaline migration on the Eu<sup>3+</sup> environment modification. The shift of the transition associated with a broadening indicates a modification of the Eu<sup>3+</sup> crystal field and larger site distribution of Eu<sup>3+</sup> ions in polyphosphate glasses. To better explain the composition influence, the local environment of Eu<sup>3+</sup> ions will be studied by MD calculations. Finally, the reduction of Eu<sup>3+</sup> into Eu<sup>2+</sup> is more efficient under 700 keV irradiation: four to seven times compared to 2.5 MeV.

**Keywords:** Europium doped phosphate glasses, electron irradiation, europium environment, luminescence

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# Glass structure – crystallization relationships through EPSR modelling of synchrotron X-ray total scattering data of Na, Li, Fe, and B, substituted aluminosilicate glasses

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Advanced diffraction techniques have been applied towards the understanding of the structure of sodium aluminosilicate (NAS) glasses of varying Al/Si addition as far back as the late 1970's - early 1980's. It has been determined previously that despite the similarities among the average local structures of vitreous aluminosilicates, the crystallization behaviors vary significantly among these systems during cooling from the molten state. In the present work, we expand on these previous findings through the compositional substitution of NAS glasses with Li, B, and Fe. Substitution of Al with B and Fe have been found to increase crystallization at low B and Fe fractions and eventually frustrate crystallization. Substitution of Na with Li results in complex crystallization behavior which is likely influenced by the mixed alkali effect. The influence of Al/Si and Fe/Si ratio on crystallization has also been explored and is strongly dependent on the fraction of SiO<sub>2</sub>. The measurement techniques employed in this study include: synchrotron X-ray total scattering, nuclear magnetic resonance, Raman spectroscopy, and X-ray diffraction. Structure models were calculated through Empirical Potential Structure Refinement (EPSR) of the measured X-ray pair distribution functions (xPDFs). Our models of glass structure suggest an influence of alkali coordination number on crystallization propensity and that further crystallization may be promoted by chemical partitioning during crystal growth.

**Keywords:** Silicate glass structure, synchrotron total scattering, structure modelling

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\*Speaker

# Time-resolved structural evolution of supercooled barium disilicate liquid during in-situ crystallization

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The homogeneous and congruent crystallization of the barium disilicate (BaSi<sub>2</sub>O<sub>5</sub>) glass makes it possible to trace the temporal evolution of Raman bands from their positions within the supercooled liquid to those in the crystalline phase. As a result, a detailed structural evolution is revealed during crystallization. The *in-situ* crystallization of supercooled liquid BaSi<sub>2</sub>O<sub>5</sub> at 790°C has been monitored for over 400 minutes revealing a three-stage crystallization process. Stage 1 involves changes in the barium sites toward a bonding environment that is similar to the ninefold site in the low barium disilicate phase, sanbornite. The end of stage 1 is marked by the loss of a Q<sub>4</sub> species vibration at 1170 cm<sup>-1</sup> and the new presence of a vibrational band at 440 cm<sup>-1</sup>, which marks the beginning of stage 2. This behavior may be explained by the degradation of the Q<sub>4</sub> site to form highly distorted bridging oxygen sites producing the 440 cm<sup>-1</sup> band. Stage 2 is also marked by strong shifts in the bridging oxygen modes at 540 and 575 cm<sup>-1</sup> towards their crystal-like positions and relative intensities. This stage is also marked by the transition of the Q<sub>3</sub> peak, at 1060 cm<sup>-1</sup>, from a Gaussian-like to a Lorentzian curve, indicating the formation of well-developed sheet structures. The final stage involves subtle movements of the barium and bridging oxygen sites, and a rapid decrease in the remaining Q<sub>n</sub> species to form Q<sub>3</sub>. These structural changes involve the entire silicate network on the tens of microns scale. The observation that barium atoms drive the initial stages of crystallization provides direct evidence that the short-range order around the network modifier is a critical factor involved in homogeneous crystallization.

**Keywords:** glass, crystallization, barium disilicate, supercooled liquid, crystal growth, silicate, structure, Raman spectroscopy

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\*Speaker

# Ca and Sr Bonding in Mixed Phosphate Glasses

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Incorporation of Sr to Ca-phosphate bioglasses opened many possibilities for clinical applications. The cation release in physiological conditions is influenced at atomic scale by the interactions with the glass forming groups. To analyze the cation structural preferences in the glass network, two series of mixed polyphosphates glasses were studied: (I) Na-Ca-Sr w Na<sub>2</sub>O (0.57-w-x) SrO x CaO 0.43 P<sub>2</sub>O<sub>5</sub> (0 ≤ w ≤ 0.40, 0 ≤ x ≤ 0.40), and (II) (0.50-x-y) Li<sub>2</sub>O y Cs<sub>2</sub>O x SrO 0.50 P<sub>2</sub>O<sub>5</sub> (0 ≤ x ≤ 0.40, 0 ≤ y ≤ 0.50-x). <sup>31</sup>P, <sup>23</sup>Na, <sup>7</sup>Li and <sup>133</sup>Cs nuclear magnetic resonance techniques were applied to analyze local structure around phosphate groups and cation sites. For polyphosphates with one alkaline earth, transitions in the evolution of properties (molar volume, glass transition temperature, <sup>31</sup>P resonance of chain-end tetrahedra) were detected as a function of the alkaline earth content, which can be interpreted in terms of preferential bonding of the divalent cation to the O in (PO<sub>3.5</sub>)<sup>2-</sup> anions (Q<sub>1</sub>), instead of (PO<sub>3</sub>)<sup>-</sup> (Q<sub>2</sub>). This non-statistical bonding to the available O is only possible up to a maximum concentration of the alkaline earth oxide, calculated as x = 0.28, in good agreement with the observed break in properties in Na-Sr polyphosphate (x = 0.30). A similar behavior seems plausible for Ca<sup>2+</sup> in Na-Ca polyphosphate, but changes in the medium range order and progressive structural distortions induced by the stronger ion cause smooth variations of the molar volume. The systematic variation of the Sr/(Sr+Ca) allowed to observe the transition between these two structural regimes. In series (II), Sr was introduced to perturb the Li-Cs mixed alkali effect. The analysis of the nuclear dipolar couplings shows that both alkalis are randomly dispersed, irrespective of the concentration of Sr. All NMR parameters are scaled by the alkali atom concentration, irrespective of the element (Sr, Li, Cs) used to dilute the alkali, revealing the random mixture of these three species in the metaphosphate matrix.

**Keywords:** phosphate glasses, mixed alkali effect, glass structure, nuclear magnetic resonance

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\*Speaker

# STRUCTURE 7

# Amorphous Ta<sub>2</sub>O<sub>5</sub> and its Relationship with the Liquid State

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Amorphous tantalum films have been used in the successful detection of gravitational waves, where they act as high index layers within the multilayer mirrors of large scale interferometers. From a glass science perspective, a-Ta<sub>2</sub>O<sub>5</sub> is an intriguing material, being composed of an ‘intermediate’ oxide which has not been melt-quenched to form glass, but is typically formed by ion-beam sputtering. Nonetheless, glasses containing large molar amounts of Ta<sub>2</sub>O<sub>5</sub> have been formed from melts of e.g. 50Ta<sub>2</sub>O<sub>5</sub>·50Li<sub>2</sub>O and 46Ta<sub>2</sub>O<sub>5</sub>·54Al<sub>2</sub>O<sub>3</sub> suggesting that Ta may well partake in network formation. Here we use high-energy x-ray and neutron diffraction to study *liquid* Ta<sub>2</sub>O<sub>5</sub> and its putative isomorph – molten Nb<sub>2</sub>O<sub>5</sub>. These measurements are then compared to the x-ray diffraction pattern of a-Ta<sub>2</sub>O<sub>5</sub> obtained in transmission geometry through a 15 μm film, where the silicon substrate has been removed by ion beam milling. Whilst the liquids are dominated by metal cations coordinated by 5 or 6 oxygen, the amorphous solid has a local structure more akin to the crystalline solids built from primarily 6- and 7-fold polyhedra. These results will be discussed in terms of the temperature dependence of the liquid structure and the known structural changes occurring upon annealing and doping of the amorphous films, and glass-formation from heavily modified tantalate melts. Comparison of the diffraction data to molecular dynamics simulations suggests that existing interatomic potentials do not adequately capture the structure of either the melt or the amorphous solid. In particular, the number of edge-sharing motifs is observed to be larger than predicted.

**Keywords:** Amorphous films, High, energy x, ray diffraction, Aerodynamic levitation, EPSR

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\*Speaker

# 95Mo Solid State NMR: Structural study of molybdophosphate glasses

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Molybdenum oxides are often used in phosphate glasses for its ability to act either as network former and as network modifier. Several other properties are improved when molybdenum is added, such as resistance against devitrification, chemical resistance or electrical conductivity. Solid-State Nuclear Magnetic Resonance (SSNMR) is a powerful tool to probe ordered and disordered materials at the atomic scale which makes this technique ideal to explain the relation between structure and properties in molybdenum phosphate glasses. Meanwhile, <sup>95</sup>Mo is an attractive NMR-active isotope with a wide chemical shift range (7000 ppm). Moreover, <sup>95</sup>Mo is a quadrupolar nucleus ( $I=5/2$ ), and as such could provide solid-state NMR spectra dominating by the quadrupolar interaction. This interaction is known to be an invaluable probe to local changes in materials. However, <sup>95</sup>Mo is insensitive to NMR due to its low gyromagnetic ratio and low natural abundance (15.92%). This is the reason why few SSNMR studies are dedicated to this nucleus up to now. However, these limitations can be overcome by using high magnetic fields (*i.e.* 18.8T), fast Magic Angle Spinning (MAS) and different pulse sequences such as Q-CPMG. In order to obtain structural information about glasses, <sup>31</sup>P and <sup>95</sup>Mo NMR experiments are conducted on glassy and crystalline samples. NMR parameters ( $CQ$ ,  $\eta Q$ ) are extracted thanks to DFT calculation. First results show that molybdenum is a better local probe than phosphorus in molybdenum phosphate glasses.

**Keywords:** phosphate glasses, <sup>95</sup>Mo nuclear magnetic resonance, Quantum chemical calculation

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\*Speaker

# Structure and properties of strontium aluminosilicate melts.

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Alkaline-earth aluminosilicates are of both technological and scientific interest. In particular their properties make them attractive for a wide range of industrial applications. In geosciences, they are of fundamental importance as they form a significant fraction of the composition of geological magmas.

Among these systems, strontium aluminosilicates (SAS) are interesting composition for making glass ceramics or transparent ceramics [1]. However, due to their relatively high melting point, only a few structural studies at high temperature exist on this system and the thermophysical properties are almost unknown despite their importance for understanding the glass formation.

In this talk, I will present a structural study of various liquid SAS compositions performed using aerodynamic levitation and laser heating. Results will be also correlated to previous studies [2] and to thermophysical properties determined using the oscillating drop method [3].

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**Keywords:** Strontium aluminosilicates, Melts, Structure, Properties

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# Structure and properties of barium borophosphate glasses modified with molybdenum oxide

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Borophosphate glasses belong among important classes of glassy materials because they offer better thermal stability and chemical durability than phosphate glasses. Doping borophosphate glasses by heavy metal oxides like MoO<sub>3</sub> and WO<sub>3</sub> is interesting due to their semiconducting properties ascribed to the presence of transition metal ions in multivalent states. In this study we prepared glassy samples from the BaO-P<sub>2</sub>O<sub>5</sub>-B<sub>2</sub>O<sub>3</sub>-MoO<sub>3</sub> system in two compositional series (100-x)[0.5PbO-0.4P<sub>2</sub>O<sub>5</sub>-0.1B<sub>2</sub>O<sub>3</sub>]-xMoO<sub>3</sub> and 80[0,5BaO-yB<sub>2</sub>O<sub>3</sub>-(0,5-y)P<sub>2</sub>O<sub>5</sub>]-20MoO<sub>3</sub>. Glasses were prepared from analytical grade BaCO<sub>3</sub>, MoO<sub>3</sub>, H<sub>3</sub>BO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub> using a total batch weight of 30g. The synthesis was carried out in platinum crucibles by heating up to 1000-1200°C. Physical properties of glasses were determined as well as their thermal behavior. For structural studies <sup>31</sup>P and <sup>11</sup>B MAS NMR spectroscopies were applied as well as Raman spectroscopy. <sup>31</sup>P MAS NMR spectra showed on the depolymerization of phosphate chains with increasing MoO<sub>3</sub> content due to the formation of Mo-O-P bonds between octahedral MoO<sub>6</sub> structural units and tetrahedral PO<sub>4</sub> units. <sup>11</sup>B MAS NMR spectroscopy is able to supply information on the boron coordination in the studied glasses because these spectra possess an ability to discriminate between tetrahedral BO<sub>4</sub> boron coordination and trigonal BO<sub>3</sub> coordination due to the different ranges of chemical shift values for BO<sub>4</sub> and BO<sub>3</sub> units. The measurement of <sup>11</sup>B MAS NMR spectra of the studied glasses with the NMR spectrometer with a high resolution (magnetic field 18.8T) revealed the formation of several different BO<sub>4</sub> structural units containing B-O-P, B-O-B and B-O-Mo bonds. The decomposition of these spectra brought relative amounts of individual mixed structural units in these glasses.

**Keywords:** phosphate glasses, glass structure, Raman spectra, NMR spectra

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\*Speaker



# Oxygen environment in lithium borates and silicates: an experimental and theoretical study.

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In crystalline, glassy and liquid oxides, either bridging (BO) or non-bridging (NBO) sites are observed depending on their connectivity to the network. NBOs are defined as oxygen atoms bound to only one framework cation (Si, B, P, ...) and bearing a negative charge. The NBO concentration is an indicator of the network connectivity which influences the physical and chemical properties.

X-Ray Raman Spectroscopy (XRS) has been recently used to carry out investigations on oxygen environment under extreme conditions (pressure / temperature) [1],[2],[3] Recently, a spectral signature of NBOs at the O K-edge spectrum in lithium borates (Fig. 1) has been evidenced and validated by DFT calculations. Such signature can be used as a probe of the polymerization degree of the glass during *in situ* high-pressure / high-temperature experiments. Thanks to the recent implementation of XRS in the module XSpectra of Quantum Espresso, we are now able to understand the fine structures of the edge in terms of oxygen environment in alkali borates and silicates.

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\*Speaker

**Keywords:** lithium borates and silicates, oxygen environment, Xray Raman Spectroscopy

# TELLURITE

# Comparison of TeO<sub>2</sub> and Sb<sub>2</sub>O<sub>3</sub> as Heavy Metal Oxide Glass Formers

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Heavy metal oxide (HMO) glasses are promising materials for new generation opto-electronic applications. Among HMO glasses, TeO<sub>2</sub> and Sb<sub>2</sub>O<sub>3</sub>-based glasses step forward with their unique properties, such as high refractive index, high dielectric constant, relatively low phonon energy, wide optical transparency window, thermal and chemical stability, high devitrification resistance, low glass transition and melting temperature. In this work, a series of HMO glasses from two different ternary systems (WO<sub>3</sub>–MoO<sub>3</sub>–TeO<sub>2</sub> and WO<sub>3</sub>–MoO<sub>3</sub>–Sb<sub>2</sub>O<sub>3</sub>) were prepared by conventional melt quenching technique and the effect of glass formers (TeO<sub>2</sub> and Sb<sub>2</sub>O<sub>3</sub>) on thermal, physical, structural and optical properties of glasses were investigated. Thermal properties were investigated by differential scanning calorimetry (DSC) analysis in terms of glass transition temperature ( $T_g$ ) and crystallization temperature ( $T_c/T_p$ ). Thermal stability against crystallization was evaluated by calculating temperature difference ( $\Delta T$ ) and thermal stability ( $S$ ) values. Density ( $\rho$ ), molar volume ( $VM$ ), oxygen molar volume ( $VO$ ), oxygen packing density ( $OPD$ ), average cross-link density ( $nc$ ), and number of bonds per unit volume ( $nb$ ) values were calculated for the interpretation of physical and structural properties. FTIR spectra of the glasses were discussed in terms of structural transformations in the glass network. For the optical characterizations, transmittance in the visible region and short wavelength absorption edge values were determined by means of UV-Vis spectroscopy analysis. The authors of this study gratefully acknowledge The Scientific & Technological Research Council of Turkey (TUBITAK) for the financial support under the project numbered 116M210.

**Keywords:** Tellurite glasses, antimonate glasses, thermal properties, physical properties, structural properties, optical properties

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\*Speaker

# Thermal, mechanical and structural properties of tellurite glasses

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We present a study of glasses in the systems ZnO-TeO<sub>2</sub> (including pure TeO<sub>2</sub> glass) and R<sub>2</sub>/3O-ZnO-TeO<sub>2</sub> (R=B, Al) where ZnO is replaced by B<sub>2</sub>O<sub>3</sub> or Al<sub>2</sub>O<sub>3</sub>. Glasses were prepared by quenching the melts from Pt crucibles, and their glass transition temperature T<sub>g</sub>, density, mechanical properties and Raman/infrared spectra were measured to correlate glass properties with structure as a function of composition. TeO<sub>2</sub> and ZnO-TeO<sub>2</sub> glasses prepared by melting in Pt crucibles were found to exhibit profound differences in terms of properties and structure when compared to similar glasses melted in alumina crucibles, a method used frequently in the literature. The origin of such differences was traced to doping of the tellurite matrix with Al<sub>2</sub>O<sub>3</sub> leached from the alumina crucible. Raman spectroscopy reveals cross-linking of the tellurite network by Te-O-Al bridges, resulting in the increase of T<sub>g</sub> (by as much as 75 oC for TeO<sub>2</sub> glass), the decrease of density and the strengthening of mechanical properties. Replacement of ZnO by Al<sub>2</sub>O<sub>3</sub> or B<sub>2</sub>O<sub>3</sub> leads to strongly- and weakly-interacting tellurite-aluminate and tellurite-borate structures, respectively. The findings of this study are discussed in relation to the strengths of Te-O, Al-O, B-O and Zn-O bonds. We acknowledge support of this work by the project "Advanced Materials and Devices" (MIS 5002409), implemented under the "Action for the Strategic Development on the Research and Technological Sector", funded by the Operational Programme "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014-2020) and co-financed by Greece and the European Union.

**Keywords:** tellurite glasses, thermal and mechanical properties, structure by Raman and infrared spectroscopy

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# Structural studies of tellurite glass, anti-glass and crystalline phases

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Tellurites are technologically important materials which exist in glass, anti-glass and crystalline phases. Pure TeO<sub>2</sub> forms glass under the condition of high melt-quenching rates; while binary and ternary tellurite systems containing alkali, alkaline-earth, rare-earth, transition and heavy metal oxides form glasses rather easily at normal quenching rates and have wide glass-formation range. Tellurite glasses have a dual Te-O coordination (N<sub>Te-O</sub>) of 3 and 4 with oxygen. N<sub>Te-O</sub> can be determined by Raman and neutron diffraction studies; and it decreases on incorporating metal oxides such as ZnO, Al<sub>2</sub>O<sub>3</sub>, BaO, PbO, WO<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub>, Eu<sub>2</sub>O<sub>3</sub>, Nd<sub>2</sub>O<sub>3</sub> and MoO<sub>3</sub> into the tellurite and borotellurite network. Borotellurite glasses that contain two glass formers i.e. B<sub>2</sub>O<sub>3</sub> and TeO<sub>2</sub> form transparent glasses over B<sub>2</sub>O<sub>3</sub> concentration of 5 to 25-mol%. 11B Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR) and infrared spectroscopy studies confirm that the boron-oxygen co-ordination (N<sub>B-O</sub>) decreases with increase in B<sub>2</sub>O<sub>3</sub> mol% in borotellurite glasses. Pure borotellurite glasses are hygroscopic and absorb atmospheric water vapors to form crystalline precipitates α-TeO<sub>2</sub> in an amorphous matrix. On adding Al<sub>2</sub>O<sub>3</sub> into borotellurites to form alumino-borotellurite glasses, the chemical durability enhances but the glass formation range deteriorates due to decrease in N<sub>B-O</sub>. Bi<sub>2</sub>O<sub>3</sub> and Nb<sub>2</sub>O<sub>5</sub> when added into TeO<sub>2</sub> form highly intriguing anti-glass inclusions of the size of several microns within a glass matrix. An anti-glass is a solid, which has long range order of cations (Te<sup>4+</sup>, Sr<sup>2+</sup>, Bi<sup>3+</sup>, Nb<sup>5+</sup> etc.) but these are statistically distributed at their sites while the anion sites are partially vacant. Consequently the X-ray diffraction patterns of bismuth tellurite and bismuth niobium tellurite anti-glass samples show sharp peaks but the Raman spectra show broad phonon bands. In this talk an overview of structure-property correlation studies of several tellurite systems by X-ray diffraction, neutron diffraction, MAS-NMR and Raman spectroscopy is presented.

**Keywords:** Tellurite glasses, inclusions, structure, diffraction, Raman spectroscopy, microscopy

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\*Speaker

# Developing Structure-Property Relationships in Optical Glasses to Optimise Functional Designs

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An investigation of the structural motifs present in alkaline earth modified Tellurite glasses has been undertaken in order to further elucidate the effects of network connectivity across atomic structural units on higher level material functionality. With desirable optical properties including high refractive indices, third-order non-linear optical coefficients and near infra-red transmittance these glasses are of industrial value across a range of optical devices. Variations in polarizability between [TeO<sub>4</sub>] and [TeO<sub>3</sub>] units mediates these optical responses, with property changes driven by their relative ratio in the glass network. Classical structural techniques including neutron diffraction, X-ray diffraction and Raman scattering have been performed to show the occurrence of decreasing tellurium coordination number with increasing modifier concentration. Further to this, changes to the structural polyhedra as a result of modifier atoms have been observed using empirical potential structural refinement. Consideration has been given to the occurrence of a lone-pair environment for Tellurium through the use of dummy atoms; in this way robust models have been generated providing good agreement with the experimental structure factors. From this further understanding into the mechanisms behind structure-property relationships has been shown, helping to optimise future glass design.

**Keywords:** Tellurite, Structure, Property, Optical, Glass, EPSR, Neutron, Raman, X, ray

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\*Speaker

# Elaboration, structure, nonlinear optical and lasing properties of tellurite based glasses and glass-ceramics.

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Tellurium dioxide-based glasses are currently considered as very promising materials for high-index and nonlinear optical devices because of their high nonlinearities ( $\chi(3)$  hyper-susceptibility far (50 times) exceeding that of glassy SiO<sub>2</sub>), their high Raman gain coefficients (60 times higher than that measured on a reference Corning 7980-2F silicate glass) and their good visible and infrared light transmittance (up to 7 micrometer). Therefore, some substantial literature has been devoted to the studies of such tellurite glasses during the last decade. Many binary and ternary phase diagrams were investigated and the existence of large glass-forming domains was evidenced for most of them. This conference will present a review of the activities developed in the IRCER laboratory of Limoges since about 20 years on these materials in concentrating mainly on the following topics: (i) synthesis of glasses and transparent glass-ceramics and ceramics, (ii) structural characterization using the total scattering technique and atomic scale modelling methods (molecular dynamics or Reverse Monte-Carlo simulations), (iii) modelling of the nonlinear optical properties, (iv) 3rd-order and second harmonic generation, (v) lasing properties. Our challenge was to elaborate the optimal chemical composition of TeO<sub>2</sub>-based glasses that affords a compromise between structural, mechanical and thermal properties on the one hand, and desirable nonlinear optical properties on the other hand. Our results have confirmed the high potentiality of TeO<sub>2</sub>-based materials in the field of nonlinear optics. Especially, the high third-order susceptibilities of glasses have been demonstrated. Second harmonic generation has been evidenced in glasses using either thermal poling or optical poling. All these properties have been clearly related to specific structural characteristics of tellurite phases, i.e; the presence of different structural units and the nature of their linking (as the chain-like polymerization), the presence of the lone pair on tellurium atom. Using *ab initio* calculations we have demonstrated that the mechanism of the nonlinear electronic polarization in tellurite glasses was mainly associated with the electron mobility within the chains formed by polymerized Te-O-Te bridges.

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\*Speaker



Laser emission has been obtained in Nd<sup>3+</sup>-doped tellurite glasses.

**Keywords:** Tellurite glasses, glass structure, X, ray total scattering, atomic scale modeling, nonlinear optical properties

# The formation of liquids, glasses and the anti-glass phase in the system $\text{Bi}_2\text{O}_3\text{-Nb}_2\text{O}_5\text{-TeO}_2$

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Glasses formed in the technologically important system  $\text{Bi}_2\text{O}_3\text{-Nb}_2\text{O}_5\text{-TeO}_2$  show formation of spherulitic inclusions within a glassy matrix upon annealing resulting in textures that are reminiscent of those used to describe "polyamorphism" in the  $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$  system. However, in the tellurite system the inclusions are crystalline and have been identified as an "anti-glass" phase, i.e., a solid with long-range cation order but with a disordered anion sublattice. The similarity of the textures have caused us to investigate the possibility of links between the formation of anti-glass inclusions in tellurites and polyamorphic behaviour in the aluminate system. In this part of our study we report high energy X-ray diffraction data for liquids and glasses formed in the  $\text{Bi}_2\text{O}_3\text{-Nb}_2\text{O}_5\text{-TeO}_2$  system at the compositions known to give rise to anti-glass formation. The data were collected for stable and deeply supercooled liquids to the point of vitrification in order to test for evidence of an underlying liquid-liquid phase transition (LLPT). There is however no evidence from the diffraction data to suggest the presence of an LLPT. The study is being continued using molecular dynamics (MD) simulations to explore the metastable region further and investigate the relative stability of different glassy configurations and clusters that form as the glassy state is approached. We suggest that the apparently contrasting behaviour in the two systems can be understood by considering the kinetics of ordering on the cation and anion sites and that initial glassy forms evolve towards more thermodynamically stable states during annealing. The large cations in the  $\text{Bi}_2\text{O}_3\text{-Nb}_2\text{O}_5\text{-TeO}_2$  glasses can readily adopt a positionally ordered arrangement giving rise to the anti-glass phase, mediated by the more mobile  $\text{O}^{2-}$  anions that form a sublattice with disordered vacancies. In  $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ , the system encounters a

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\*Speaker

polyamorphic transition, revealed by the emergence of spontaneous and random density fluctuations in MD simulations. However, it is worth noting that the  $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$  system also exhibits simultaneous crystallisation of a metastable garnet solid solution that competes with the low density (LDA) glassy form. This could represent the equivalent of the anti-glass formation in the  $\text{Bi}_2\text{O}_3\text{-Nb}_2\text{O}_5\text{-TeO}_2$  system.

**Keywords:** tellurites, polyamorphism, anti, glass, diffraction, molecular dynamics simulation, energy landscapes

# Structural, mechanical and optical properties of glasses within the TeO<sub>2</sub>-TiO<sub>2</sub>-ZnO ternary system

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Tellurium oxide glasses have a lot of scientific and technical interests due to their superior physical and chemical properties such as high refractive index, high dielectric constants, a wide band infrared transmittance, a low phonon energy and large third order non-linear optical susceptibility [1].

This work will focus on TeO<sub>2</sub>-TiO<sub>2</sub>-ZnO ternary glassy system which has been previously studied because both addition of TiO<sub>2</sub> and ZnO is known for given very stable glasses having high polarizability and hyperpolarizability [2] and they are also reported as good candidates for ultra-low loss [3] optical material.

In this communication, we will present a new approach of understanding of medium range order structure of these glasses. In fact, we studied both the structure of the glasses by in situ Raman spectroscopy as a function of temperature and especially around the glass transition temperature (T<sub>g</sub>) and the mechanical properties by Resonance Frequency Data Analysis (RFDA) experiments [4-5]. This work will evidence the link that we can point out from those two complementary approaches and will propose a new point of view on the correlation between mechanical and structural properties around T<sub>g</sub> which could be a key point for the optical fiber shaping. Non-linear optical properties obtained by Z-scan experiment, will also be presented to evidence the huge interest of those glasses [6].

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**Keywords:** Glass, structure, mechanical properties, in situ, Raman spectroscopy

# THERMODYNAMICS

# Is the glass-forming melt in equilibrium state?

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## Is the glass-forming melt in equilibrium state?

The four convenient states of glass-forming substance are "the stable equilibrium liquid (**L**), the metastable supercooled liquid (**SCL**), the unstable nonequilibrium glass (**G**), and the stable crystal (**C**)" [1]. If one considers glass as the *self-organizing* system [2,3] then even glass-forming melt ( $T > T_m$ ) does not correspond to equilibrium state whose properties depend only on temperature at a given pressure. Using a special method for analysis of the viscosity-temperature data [4,5] the dynamical liquid-liquid transitions (DLLT) are demonstrated for both the true melt (**L**) and the supercooled liquid (**SCL**). Each DLLT represents a transition from one viscous pattern to another; there is no a definite pattern  $\eta_i(T)$  at a given temperature range but a set of possible patterns belonging to the attractor characteristic for the substance. Glass (**G**) structure is formed by the thermally activated bond waves [2,3], which are orientated by information fields [6] existing during solidification. Such a self-organized structure not necessarily relaxes into crystal (**C**), and the fate of glass is determined by a competition between the translation-type crystalline long-range order and the orientation-type bond wave one.

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**Keywords:** glass nature, self, organization, chemical bonding, glass transition, liquid, liquid transi-

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\*Speaker

tions



# High temperature viscosity of the vitreous phase into porcelain stoneware bodies

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Porcelain stoneware tiles contain 60% to 75% of vitreous phase. Its viscosity at high temperature is crucial to understand the vitrification path, the viscous flow sintering kinetics and the pyroplastic deformation of tiles. Nevertheless, these behaviours depend on both the viscosity of the liquid phase formed by the melting of feldspars (and other minerals) and the viscosity of the body made up of a suspension of crystals dispersed in the melt. Fundamental theoretical background already exists, along with semi-empirical constitutive laws on the viscous flow sintering, the glass densification, and viscosity of liquids and melts. Since different approaches are needed to measure/estimate the two viscosities, the best model for ceramic tiles has been defined by contrasting experimental data with calculated viscosities. The parameterization is based on both chemical composition of the liquid phase and persistence of crystal phases in the melt. Further variables (such as porosity, particles size and shape) play a significant role that is to some extent modelled. Existing models for high temperature viscosity of glasses and melts take into account a large number of oxides and can be applied to a wide range of composition. However, the maximum concentration of alumina considered by these models is too low compared with the content in the vitreous phase of ceramic systems, thus generating a significant error between the calculated and the measured viscosities. Although based on a lower number of oxides, models used in petrology account for alumina levels matching those of the systems of interest. In this contribution, models set up for glasses are used to predict the viscosity at high temperature of the vitreous phase present in ceramic bodies in order to explain their different sintering behaviours. Examples are provided for porcelain stoneware tiles, compared with vitreous china and porcelain bodies.

**Keywords:** Vitreous Phase, High temperature, Viscosity, Porcelain Stoneware.

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# Origin of empirical Vogel temperature emerging from Molecular dynamics simulations

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Vitreous silica was modelled by Molecular dynamics using BKS potentials and the obtained snapshots of glass structure were transferred into undirected graphs and decomposed into disjoint structural units that are ideally mixed to calculate configuration entropy. A good agreement with experimental heat capacity drop at  $T_g$  is demonstrated. Entropy is related with structural evolution of the obtained units; among them dangling oxygen dominantly effects low-temperature course of entropy that is fitted by two parabolas. The parabola corresponding to lower temperatures introduces temperature  $T^*$ , at which structure is completely frozen. It is proposed  $T^*$  stands as a counterpart of Vogel temperature in VFT equation. AGE model is introduced as the combination of the quadratic dependence of configuration entropy and Adam and Gibbs equation. AGE model not only removes the singularity at Vogel temperature but predicts existence of strong and fragile glasses as two limiting cases. Fragility is associated with quickness of structural response to temperature changes and distance between  $T_g$  and  $T^*$ . The model is tested on viscosity curves of SiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> glasses and compared with VFT equation; fits obtained by AGE are better than or at least as good as those by VFT.

**Keywords:** Molecular dynamics, configuration entropy, Vogel temperature, glass transition

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\*Speaker

# Prediction of the glass transition temperature of sugar rich mixtures

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The prediction of the glass transition temperature (T<sub>g</sub>) of sugar rich foods is of high interest in food science to prevent stability issues. The main solids of fruit juices are sugars and organic acids. The low T<sub>g</sub> values of these components are responsible for the occurring stability issues during drying. In order to gain a better understanding of the T<sub>g</sub> in low molecular weight component mixtures, six commercial fruit juice concentrates and artificial juices on basis of the sugar and organic acid profile were transformed into powders and equilibrated over various saturated salt solutions. The powders were analysed for their T<sub>g</sub> values and compared to the estimated T<sub>g</sub> values using a newly developed prediction method for multicomponent systems. The comparison of the predicted T<sub>g</sub> values and the experimental were in good agreement ( $\pm 3\text{C}$ ), especially for the artificial juices. Additionally, the effect of high molecular weight components on T<sub>g</sub> of low molecular weight mixtures were studied. For this purpose, the polysaccharides inulin DP > 23 and maltodextrin DE 10-13 were mixed with blackcurrant juice concentrate at various ratios (3/7, 1/1, 7/3) and converted into a powder. Identical to the fruit juice study, the T<sub>g</sub> values of the powders were determined at various water activities and correlated against the predicted values, which also corresponded well ( $\pm 5\text{C}$ ). The T<sub>g</sub> values indicate a strong deviation from ideal mixing and slow increase of T<sub>g</sub> with inclusion of polysaccharides. This is accompanied with a broader DSC signal for the T<sub>g</sub> of these mixtures and could be an indicator for unequal distribution of local environments.

**Keywords:** Glass transition temperature, DSC, prediction model, multicomponent systems

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\*Speaker

# Glass transition and fragility of polyionic glasses

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We study the glass transition region of ionic fluoride-phosphate (FPS), and fluoride-sulfophosphate (NAFPS) glass series. Considering these glasses as structures which consist of heterogeneous set of environments, and using differential scanning calorimetry (DSC) we discuss length scale of heterogeneity and dependence of dynamic heterogeneity on the ionic bonding. We also comment on influence of these heterogeneities on relaxation from the glassy state towards equilibrium. In order to understand the relaxation process in these glasses, we comment on fragility index at the glass transition temperature, estimated from the heating rate dependence of the glass transition temperature using non-isothermal DSC measurements. We also comment on relation between fragility index and heterogeneity length scale, as well as correlation between ionic conductivity and heterogeneity length scale. Using low-frequency vibrational spectrum, we are able to estimate the Boson peak frequency, and discuss its relation to fragility index and the size of heterogeneous domains estimated using DSC.

**Keywords:** Glass transition, heterogeneity, fragility

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# Low-temperature glassy anomalies in highly stable glasses

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We have investigated how very deep kinetic and thermodynamic stabilization in glasses can affect their universal properties at low temperatures. In particular, we have studied two different materials which allowed us to access highly-stable glassy states, as well as their corresponding conventional glasses: (i) ancient amber [1], which is a glass which has experienced an extremely long hyperaging process; and (ii) ultrastable thin-film glasses of indomethacin [2], prepared by physical vapor deposition at temperatures around  $0.85 T_g$ . Specifically, we have studied 110-million-year-old amber samples from El Soplao (Spain). Specific heat  $C_p$  measurements of pristine and rejuvenated samples were conducted in the temperature range  $0.07\text{K} < T < 30\text{K}$ , as well as around its glass-transition temperature  $T_g = 423\text{K}$ . A modest increase of the boson-peak height (in  $C_p/T^3$ ) with increasing rejuvenation was observed. The amount of tunnelling two-level systems (TLS) was however found to be exactly the same for the pristine hyperaged amber as for the subsequently rejuvenated samples. On the other hand, we have observed an unexpected suppression of the universal TLS in the ultrastable glass of indomethacin, whereas conventionally prepared thin films of the same material exhibited the usual linear term in  $C_p$  below 1 K, usually ascribed to TLS in glasses.

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**Keywords:** specific heat, low, temperature universal properties of glasses, amber, ultrastable glasses, aging, boson peak, two, level systems

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\*Speaker

# Segmental mobility at the glass transition in glass forming liquids : Comparison of two approaches.

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This work investigates the cooperative molecular dynamics at the glass transition through two different theoretical approaches (the approach proposed by L. Berthier [1] and the extended Donth's approach [2,3]) for different glass-forming liquids in a wide range of frequency and temperature. The experimental investigation has been carried out by means of Modulated Temperature Differential Scanning Calorimetry (MT-DSC) and Broadband Dielectric Spectroscopy (BDS).

The first approach allows estimating  $N_c$  the number of dynamically correlated molecules during the main relaxation process, and the second one allows estimating  $N_a$  the number of structural units in a Cooperative Rearranging Region (CRR). But, does it exist a clear difference between  $N_c$  and  $N_a$  ?

In a first work concerning different fully amorphous polymers with different backbones, the molar mass of the relaxing units seemed having an impact on  $N_c$  and  $N_a$  values, involving differences between these two quantities [4].

In a second work, our motivation was examining  $N_c$  and  $N_a$  with time and temperature variations in amorphous copolymers of poly(ethylene-*co*-vinyl acetate) (EVA) with different vinyl acetate content (VAc): from PVAc (100 wt.% VAc) to EVA50 (50 wt.% VAc). This sample family presented the advantages to have the same backbone, practically the same molar mass, but different number of dipolar pending groups, i.e. different inter-chain dipolar interactions [5,6].

All these investigations will be presented through the presentation.

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**Keywords:** Glass transition, Glass, forming liquids, Dynamic heterogeneity, Cooperative motions, Correlated motions.

# New theoretical model for partition function and configurational entropy in non-equilibrium states

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New model of non-equilibrium thermodynamic states has been investigated. It is well known that once well-defined partition functions are calculated in equilibrium, all the thermodynamic variables can be calculated from them. On the other hand, any standard definition of partition function in non-equilibrium has not established yet, which hinders the derivation of thermodynamic variables from them. To overcome this problem, the concept of temperature is extended in a new style. It is also well known that unique value temperature can be defined for each system only in equilibrium. In contrast, in this paper, configurational temperature apart from kinetic (phonon) temperature is defined as a function of energy fragment. In other words, each fragment decomposed from the whole system has its own configurational temperature. Such definition allows the description of thermodynamic states either in equilibrium or in non-equilibrium. In addition, new formulation of non-canonical partition function, internal energy and entropy are derived on the basis of the new definition of temperature. On the basis of this new model, computational experiments are performed on simple non-interacting systems to investigate the cooling and relaxation effects in terms of the time profile of partition function, internal energy and configurational entropy. It is concluded that the new formulation has gained a foot in applying it to a variety of non-equilibrium systems.

**Keywords:** configurational entropy, thermodynamics, statistical mechanics, computer simulation

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\*Speaker



# THIN FILMS & GLASS SURFACE 1

# Thermal noise in Gravitational Wave mirror coatings: relaxations in SiO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub> films.

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The direct detection of Gravitational Waves has been one of the main discoveries of the century: it finally proved the correctness of the General Relativity and it opened a completely new way to observe the Universe. The main limitation to the detector future developments is given by the thermal noise generated inside the coatings deposited on the optical cavities mirrors of the interferometers.

Such coatings are Bragg reflectors made of glasses with two different refractive indices: SiO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub>. These materials have been selected and optimized for the current detectors considering the optical and mechanical properties. Thermal noise of these materials changes with deposition parameters, annealing or mixing with other oxides and there is no explanation of these behaviours. To understand the origin of thermal noise in glass films a specific investigation has started and developed in collaboration between the vibrational spectroscopy group Soprano at the ILM and the laboratory LMA that delivered the mirrors for all the GW detectors.

In this presentation preliminary results on the correlation between structural properties and thermal noise will be given for the two materials SiO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub>. In particular it will be shown how and why the noise in silica are correlated with the population of the 3-member rings associated with the D2 Raman line and how, in opposite, the tantala structure does not evolve significantly until the onset of crystallization making this glass the true limiting material in the GW detection.

**Keywords:** Relaxations, thermal noise, gravitational waves, films, internal friction, Raman

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# Quartz inversion temperatures of LAS solid solutions of sol-gel derived glasses

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It is well known that the inversion temperature  $T_c$  of quartz, that is the temperature of the reversible high-to-low quartz transformation, is for pure silica at 573 °C, and is for a synthetic solid solutions with less than 80 mol% SiO<sub>2</sub> and equimolar amounts of Al<sub>2</sub>O<sub>3</sub> and Li<sub>2</sub>O at temperatures below ambient. In contrast, the chemical dependence of the inversion temperature of compositions exceeding the impurity level of natural quartz is studied with less depth. To bridge the gap between natural quartz and fully stabilized synthetic high quartz solid solutions, Li<sub>x</sub>Al<sub>x</sub>Si(1-x)O<sub>2</sub> thin films (x in ca. 0.03 steps up to 0.18) were prepared by sol gel-dip coating of seeded silicon wafers. High temperature grazing incidence X-ray diffraction was used to study in situ the inversion process by measuring the diffracted beam intensity of the (102) and (111) reflexes in the 38-40 ° 2theta (CuKalpha) range. Inversion temperatures of the thin Li<sub>x</sub>Al<sub>x</sub>Si(1-x)O<sub>2</sub> films were found to decrease almost linearly with increasing LiAlO<sub>2</sub> content and can be approximated by the equation  $T_c$  (°C) = 573 – 2972x for x less than 0.18.

**Keywords:** quartz, inversion temperature, thin films, sol gel

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# Controlled crystallization of PLD amorphous CZTS thin film for photovoltaic application

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## Abstract

With non-toxic and earth-abundant elements, kesterite-based Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS) semiconductor materials have been extensively explored as an alternative to overcome the large scarcity or toxicity issue of current CuInGaSe<sub>2</sub> and CdTe. The highest power conversion efficiency of solar cells based on CZTS materials has been hovering around 9.2 % which are significantly lower than that of CIGS (22.6%) and CdTe (22.1%), mostly because of low open circuit voltage ( $V_{oc}$ ). Thus, a lot of efforts have been executed to decrease  $V_{oc}$  deficit, especially the controlled crystallization of CZTS amorphous thin film, including the phase formation dynamics during processing, annealing, or re-crystallization. [1]

In this work, we report the thermal induced crystallization and performance of CZTS thin films prepared by pulsed laser deposition (PLD)[2]. Firstly, the flat, compact and uniform amorphous CZTS thin film with stoichiometric can be prepared by our optimized PLD method. Then the influence of post-sulfur annealing temperature on the microstructure, composition, the electrical and optical properties of CZTS thin films has been established. Well-crystallized CZTS films at 600°C showed the compact grains with a bandgap of 1.48eV and a high absorption coefficient of 105 cm<sup>-1</sup> in the visible region. These interesting features have been used in the prototype photovoltaic devices with a conversion efficiency of 4.2 %. These are the first results concerning the use of our optimized PLD CZTS films for photovoltaic application and further improvement of device performance is expected.[3]

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**Keywords:** CZTS thin film, photovoltaic devices, pulsed laser deposition

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# Transient photoinduced optical effects in spin-coated chalcogenide glass thin films

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Spin-coated thin films of chalcogenide glasses are usually obtained through chemical dissolution of bulk glasses in different amine-based solvents with subsequent spin-coating of the liquid onto silica substrate and appropriate one-stage or multi-stage thermal treatment. Such films are relatively stable to the influence of near bandgap irradiation in comparison with their thermally evaporated counterparts. This property can be very useful, especially for the non-linear optical applications which require high transparency in IR spectral region and minimum sensitivity to the visible light. Structure of thermally stabilized spin-coated films can, in general, be considered as a fragments of bulk glass connected through the residual units of organic solvents. However, increase of annealing temperature promotes direct connections between the glass fragments (through chalcogen atom or newly formed appropriate structural units). The decrease in photosensitivity relatively to the evaporated thin films is linked to the lack of excessive concentration of homopolar bonds in the film structure. At the same time, noticeable shift of optical absorption edge (photodarkening or photobleaching depending on composition) is still observed at irradiation of the spin-coated thin films with super band gap UV light. This change significantly depends on intensity of irradiation and usually contains both metastable and transient components. It is shown on the example of As<sub>42</sub>Se<sub>58</sub> spin coated thin films that by changing post-synthesis annealing conditions it is possible considerably decrease the metastable part of the photoinduced shift of optical absorption edge and obtain pure transient switching effects. Kinetics of the transient changes demonstrates significant deviation from the exponential behavior. Mechanisms of the transient effects are proposed based on the obtained fitting parameters. Possible applications of the observed effects are discussed. APSU team acknowledges financial support from NSF grant DMR-1409160.

**Keywords:** Chalcogenide glass, thin films, photoinduced effects, spin coating

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# The long memory of glass surfaces

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What is the structure of a glass surface ? In the same spirit as the glass bulk structures resembles a snapshot of the liquid frozen at the temperature of glass transition  $T_g$ , the structure of a fire polished glass surface resembles a snapshot of the thermal fluctuations of the liquid. The sub-nanometric surface roughness scales as  $(kT_g/\gamma)^{1/2}$  where  $k$  is the Boltzmann constant and  $\gamma$  the interface tension. This results from the superposition of thermal capillary waves frozen at  $T_g$ . We discuss this scenario of freezing of capillary waves in the specific context of glass interfaces produced by fibre drawing. We present recent metrological atomic force microscopy and optical profilometry roughness measurements performed on the silica glass inner interfaces of hollow-core photonic band-gap fibers (HC-PBGFs) and hollow capillaries. The freezing of attenuated out-of-equilibrium capillary waves during the drawing process is shown to result in a reduced surface roughness. The roughness attenuation with respect to the expected thermodynamical limit is determined to vary with the drawing stress following a power law. A striking anisotropic character of the height correlation is observed: glass surfaces thus retain a structural record of the direction of the flow to which the liquid was submitted.

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**Keywords:** surface, interface, roughness, drawing, capillary waves

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\*Speaker

# Structuring of chalcogenide glasses thin layers

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Chalcogenide glasses (ChGs) possess unique properties, e.g. a wide spectral transparency range, low optical losses, high non-linearity of optical properties, which make them very attractive material for applications in optics and optoelectronics [1]. Many of them require ChGs to be structured on micro and/or even nanoscale.

In this paper we give review of techniques suitable for micro and nanostructuring of As and Ge based ChGs thin layers prepared by vacuum evaporation and spin-coating. Due to low rigidity of their structure and low softening temperatures in comparison with oxide glasses their surface can be easily corrugated by direct laser writing method [2] or by embossing [3]. Furthermore ChGs thin layers internal structure can be also easily modified by exposure to suitable radiation (bandgap or UV light, electron or ion beams) [4, 5] resulting in changes of their chemical resistance. Both positive as well as negative high selective etching resulting in thin layers structuring can be achieved by consequent treatment in alkaline solutions. Influence of various parameters (thin layers composition, method of their fabrication, thermal prehistory, alkaline solution composition and concentration) on quality of CHGs thin layers structuring is discussed. Examples of practical application of micro and nanostructuring of CHGs are also given.

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\*Speaker

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**Keywords:** chalcogenide glasses, nanostructuring, microstructuring



# THIN FILMS & GLASS SURFACE 2

# Multicomponent diffusion in industrial glasses and thin films

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Chemical diffusion is an essential transport mechanism in silicate melts and glasses. In magmatic processes, as well as in the glass industry, chemical diffusion at high temperature plays an important role for crystal nucleation and growth, for mineral dissolution and for phase separation. Closer to the glass transition, diffusion controls ionic exchanges for strengthened glasses, and exchanges between glass substrates and thin films.

Multicomponent diffusion models the cooperative nature of species mobility, using a diffusion matrix. The diffusion matrix approach is necessary to account for phenomena such as uphill diffusion, in which a gradient of an initially-constant species arises because of couplings with other species. Diffusion coefficients are obtained as the eigenvalues of the diffusion matrix, while eigenvectors describe couplings between species, in the form of exchange reactions.

In this talk I will focus on multicomponent diffusion in several compositions of industrial interest. I will first explain how to obtain diffusion matrices from experiments. Then I will describe the reaction exchanges evidenced by diffusion eigenvectors and their energetics. Finally I will discuss the consequences of multidiffusion for several situations of industrial importance such as homogenization of melts in furnaces, dissolution of raw materials, refractories corrosion or interaction between glass substrate and thin films.

**Keywords:** chemical diffusion, diffusion matrix, dissolution, thin films

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\*Speaker

# Novel Transrotational Solid State Order Discovered by TEM in Crystallizing Amorphous Films and New Model of Amorphous State Based on Nanocrystals with Curved Lattice

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Exotic thin crystals with unexpected **transrotational** micro-, nanostructures [1] have been discovered by transmission electron microscopy (TEM) for crystal growth in thin (10-100 nm) amorphous films of different chemical nature (oxides, chalcogenides, metals and alloys) prepared by various methods. The unusual phenomenon can be traced *in situ* in TEM column during local e-beam heating, Fig.1a-b, or usual annealing): dislocation independent regular internal bending of crystal lattice planes in a growing crystal. It can take place also during aging like self-organization. Such **transrotation** (unit cell **translation** is complicated by small **rotation** realized round an axis lying in the film plane) can result in strong regular lattice orientation gradients (up to 300 degrees per  $\mu\text{m}$ ) of different geometries: cylindrical, ellipsoidal, toroidal, saddle, etc. Transrotational microcrystal resembles ideal single crystal enclosed in a curved space. Some crystal types have bending of atom/lattice planes similar (but much lower) to that of nanotubes and nanonions. Complex skyrmion-like lattice orientation texture is observed in some spherulite crystals, Fig.1b. Transrotation is strongly increasing as the film gets thinner. Transrotational micro crystals have been eventually recognized by other authors in some vital thin film materials, i.e. PCMs for memory [2-3]. Atomic model and possible mechanism of the phenomenon, Fig.1c, are discussed. New nanocrystalline models of amorphous state are proposed: fine-grained structures with lattice curvature (in particular - transrotation), Fig.1d. Thus the great variety of different transrotational lattice geometries inside fine crystal grains (e.g., complying with different conformal transformations described mathematically for 2D case) in the static model corresponds to different amorphous structures hardly distinguished by usual methods but inevitably resulting in distinct physical properties. Going to 3D clusters of positive or/and negative curvature and dynamics we propose the hypothesis of "dilaton" and "contraction" pulsating or/and circulating in amorphous/glassy solids.

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E. Rimini et al, *J. App. Phys.* **105** (2009), 123502.

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\*Speaker

**Keywords:** Microstructure, thin amorphous films, crystallization, electron diffraction, models, phase change materials, surface

# Investigations of phosphate and silicate glasses and glass-ceramics deposited as nanometric thin films

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Phosphate glasses are investigated as materials for electrolytes in all solid-state batteries, in which they are designed as thin film of thickness not larger than a few tenth of nanometer. Silicate and aluminosilicate thin film glasses have been developed in our group as protective coatings with self-healing behaviour.

Structural studies have been conducted quite extensively on silica, germinate and borate glasses, but none has been reported to our knowledge on phosphate glasses. We will present in this communication a structural analysis of phosphate glasses deposited as thin layers on silicon substrates. The glass compositions are sodium borophosphate and lead phosphate. We used solid-state NMR, which is very suitable for the analysis of the glasses. However, owing to the low sensitivity of NMR and low amount of sample (removed from the support), the sensitivity was first improved by the incorporation of paramagnetic ions (Cu<sup>2+</sup>, Mn<sup>2+</sup>, Gd<sup>3+</sup>), which allows reducing the relaxation delay. We also used Dynamic Nuclear Polarization to enhance the NMR signal. Our results show that some difference in the local structure of the film is observed in comparison with bulk films.

Concerning the aluminosilicate thin films, they were developed to produce glass-ceramics thin films since glass-ceramics have superior mechanical properties than glasses. Hence, we investigated the glass to glass-ceramic transformation of our glass thin films. The composition of the glass is 28BaO-14CaO-10Al<sub>2</sub>O<sub>3</sub>-48SiO<sub>2</sub>. Glass thin films of 150 nm thickness were elaborated and their crystallization was studied *in-situ* by HT-XRD and HT-SEM. For the bulk glass, XRD and <sup>29</sup>Si MAS-NMR indicate that the crystallization leads to the formation of hexacelsian and baryum-calcium metasilicate. For the thin glass layer, baryum-calcium disilicate and hexacelsian are formed, meaning Q<sub>3</sub> and Q<sub>4</sub> sites. The crystallization is thus more constrained in the thin film, leading to less evolution of the Q<sub>n</sub> sites.

**Keywords:** glass thin films, glass, ceramics, phosphate, silicate

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\*Speaker

# Computational and Experimental Investigation of the Atmospheric Pressure Chemical Vapor Deposition of SiO<sub>2</sub> films from TEOS and O<sub>2</sub> and Determination of their Microstructural Characteristics and their Corrosion Resistance in Aggressive Aqueous Media.

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Chemical vapor deposited SiO<sub>2</sub> films from tetraethyl orthosilicate (TEOS) is a key enabling material in numerous applications. Among the several pathways for the CVD of SiO<sub>2</sub> films from TEOS, the poorly investigated medium temperature process involving oxygen ensures a compromise between the high temperature TEOS pyrolysis process and the less uniform ozone assisted pathway. It is a promising route for SiO<sub>2</sub> coatings on complex-in-shape substrates. In this perspective, we investigate the TEOS+O<sub>2</sub> process operating at atmospheric pressure in the temperature range between 350 and 500°C, for the production of SiO<sub>x</sub> barrier coatings against aqueous corrosion in fluorine-containing media.

We develop an original apparent kinetic model involving two intermediate species leading to the deposition of SiO<sub>2</sub>, based on experimentally determined kinetic data and on literature information. The numerical simulation of the process reliably reproduces various experimental

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\*Speaker

deposition profiles. The density, strain and stoichiometry of the obtained SiO<sub>x</sub> films are probed by combining RBS results and FTIR operating under normal and 60° incidence angle, especially through the vibrational modes in the 900-1300 cm<sup>-1</sup> region with well-resolved TO-LO phonon splitting. Complementary density values obtained by ellipsometry allow estimating the porosity of the films. Their corrosion resistance is investigated by the P-Etch test.

It appears that, with increasing process temperature, the corrosion resistance of the films to P-etch aggressive media increases. This improvement is correlated with LO3 pic evolution that highlights an increase of the SiO<sub>x</sub> layer density which can be attributed to a decrease of the porosity. Moreover, two types of silica are distinguished. At process temperature lower than 500°C, SiO<sub>x</sub>H is observed and at temperature higher than 500°C, silanol groups disappear. Silica layers with the lowest abrasive P-etch rate expose hydrogen free structure and very low level of porosity.

**Keywords:** silica film CVD corrosion protection

# Emergence of a substrate-temperature-dependent dielectric process in a prototypical vapor deposited hole-transport glass

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Glasses are object of an intense research due to its importance in industrial applications. In particular, electronic industry has exploited the ease of producing large areas of glassy films with macroscopic homogeneity, extensively using glasses in organic electronic or photovoltaic devices. Vapor deposition, typically used to prepare amorphous organic devices, has recently emerged as a relevant tool to further understand the nature of glasses thanks to the discovery of glasses with unprecedented density levels and tunable molecular orientation, which depends on the deposition conditions. Molecular orientation is, in fact, one crucial parameter in the field of organic electronics, since the charge transport properties of a device or the output efficiency of an OLED can be drastically improved in more ordered structures. Dielectric spectroscopy, on the other hand, is a basic technique to study the properties of glasses at a molecular level, probing the dynamics of dipoles or charge carriers. Here, and for the first time, we explore the dielectric behavior of vapor deposited N,N-Diphenyl-N,N'bis(methylphenyl)-1,1'-biphenyl-4,4'-diamines (TPD), a prototypical hole-transport material, prepared at different deposition temperatures. We report the emergence of a new relaxation process which is not present in the ordinary glass. We associate this process to the Maxwell-Wagner polarization observed in heterogeneous systems, and induced by the enhanced mobility of charge carriers in the more ordered vapor deposited glasses. Furthermore, the associated activation energy establishes a clear distinction between two families of glasses, depending on the selected substrate-temperature range. This finding positions dielectric spectroscopy as a unique tool to investigate the structural and electronic properties of charge transport materials and remarks the importance of controlling the deposition conditions, historically forgotten in the preparation of optoelectronic devices.

**Keywords:** organic glass, ultrastable glass, vapor deposition, molecular orientation, conductivity, organic electronics, dielectric spectroscopy, maxwell, wagner.

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\*Speaker

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# WASTE GLASSES 1

# Radioactive iodine conditioning in silver phosphate glasses

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In France, high level waste generated by nuclear industry is vitrified in aluminoborosilicate glasses at temperatures ranging from 1050°C up to 1300°C. However, radioactive iodine is highly volatile in such conditions. Thus, it can't be efficiently confined by this way. Therefore, in the hypothesis of an iodine management lying on its conditioning, it is necessary to consider other matrices. Particularly, such a matrix development should take into account the constraints of long term storage. Especially, considering the very long half-life of <sup>129</sup>I (more than 15 million years) and its high mobility in geological formations, the chemical durability of these matrices will have to be high.

At the end of the nineties, Japanese teams suggested that silver phosphate glasses could be used as potential conditioning matrices (*Fujihira 1999*), as they can incorporate high amounts of iodine, and can be synthesized at low temperature (between 450 and 650°C). However, their chemical durability could be too low for them to be deemed acceptable matrices for radioactive iodine conditioning. To improve their resistance to alteration in aqueous medium, some recent works showed that crosslinking reagents, such as Al<sub>2</sub>O<sub>3</sub>, could be used (*Lesmesle 2013*). Their role is to create new bonds and thus, to strengthen the glass network. However, alumina was found to have a low solubility in these glasses, leading to a limited enhancement in their chemical durability. Therefore, in the current study, it was decided to investigate new crosslinking reagents, like Nb<sub>2</sub>O<sub>5</sub> and Bi<sub>2</sub>O<sub>3</sub>.

The synthesized glasses were analyzed by NMR spectroscopy. This showed that the insertion of bismuth and niobium in the glass network is responsible for a decrease in the number of Q<sub>20</sub> units, while the number of Q<sub>11</sub> units increases. This betrays a gradual substitution of P-O-P-O-P bonds by P-O-(Nb, Bi)-O-P bonds. Moreover, leaching tests, carried out in pure water at 50 °C far from equilibrium (S/V=0.1 cm<sup>-1</sup>) as well as in near saturation conditions (S/V=80 cm<sup>-1</sup>), showed that this insertion is followed by a significant drop in the dissolution rate for

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\*Speaker

some of these glasses.

**Keywords:** nuclear waste, iodine, silver phosphate glasses, chemical durability

# Rare-Earth solubility limits in simplified borosilicate glass

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The French nuclear waste management strategy is directed towards reprocessing of spent nuclear UOX fuel and conditioning of high level wastes (HLW) in borosilicate glass. In the future, the treatment of different irradiated fuels (PWR, MTR, sodium-cooled fast reactors fuels...) will generate new HLW compositions, especially composed by higher rare earth (RE) and minor actinides amounts and the knowledge of their solubility in the glass is essential to promote this evolution.

Previous studies have shown that a strong RE percentage can lead to the crystallization of apatite-like phases,  $\text{Ca}_2\text{RE}_8(\text{SiO}_4)_6\text{O}_2$ , in the melt or during the cooling process happening within the container.

In this study, the solubility of those elements (particularly La, Ce, Pr, Nd and Gd) was explored in the  $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Na}_2\text{O-CaO-Al}_2\text{O}_3\text{-RE}_2\text{O}_3$  system to better understand the interactions between them afterwards, with a focus on Gd interaction with the other RE, and their role in the formation of apatite structures.

**Keywords:** nuclear waste, glass, rare earth, solubility

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\*Speaker

# Crystallization behavior of iron- and boron-containing nepheline based glasses: Implications for the performance of high level nuclear waste glasses

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The present study focuses on understanding the compositional and environmental dependence of iron redox in nepheline-based simplified, inactive high-level nuclear waste glasses designed in the quinary Na<sub>2</sub>O–Al<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub>–Fe<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system. The impact of composition and different heating environments (air, inert and reducing) on the crystallization behavior and iron redox chemistry of glasses have been investigated using X-ray diffraction, electron microscopy, Mössbauer spectroscopy and vibrating sample magnetometry. The results indicate that while iron coordination changed as a function of glass chemistry, the heating atmosphere exhibited a minimal effect on the redox behavior in the glass-ceramics, thus leading to a minimal impact on the crystalline phase assemblage. However, the heating atmosphere had a significant impact on the microstructural evolution of these glasses as the formation of an iron-rich layer of crystals on the surface of the glass-ceramics was observed when heated in air or inert atmospheres. Details of these results, along with an explanation on the basis of diffusion kinetics of oxygen and network modifiers in glasses, and the plausible implications on the chemical durability of high-level nuclear waste glasses will be discussed in the presentation.

**Keywords:** nepheline, nuclear waste glass, crystallization, iron

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\*Speaker

# Vitrification of Waste Containing High Content of Molybdenum and Sodium

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Sodium carbonate is currently being considered as a wash-out reagent for the removal of the settled solids in the unagitated Highly Active Liquor (HAL) storage tanks at Sellafield. As the settled solids are expected to comprise mainly zirconium molybdate (ZM), this will result in a feed to the Waste Vitrification Plant (WVP) containing high concentrations of both molybdenum and sodium. This feed is expected to be challenging for WVP due to solubility limitations in existing base glass compositions and the operating temperature.

In particular, depending on the wash-out strategy employed, there is the potential to produce high volumes of sodium-containing waste, which will result in large quantities of vitrified HLW containers. Hence, new glass compositions are being investigated as part of a 3-year Innovate UK-funded collaborative project in order to maximise the sodium content of the vitrified product and minimise the number of containers produced. This paper describes the fabrication and characterisation of a number of sodium titanosilicate (NTS) compositions that can potentially contain up to ~15 wt% waste Na<sub>2</sub>O, more than double what is possible using the current UK HLW glass borosilicate composition.

Early results indicated that aluminium-containing NTS compositions met all the product quality requirements, including durability, but were prone to phase separation. Conversely, boron-containing NTS compositions were significantly more stable but generally had very poor durability. Thus, hybrid compositions were investigated in an attempt to optimise the boron and aluminium contents in order to meet both the waste loading and product quality requirements of the final waste form.

**Keywords:** nuclear, waste, vitrification, sodium, molybdenum

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# The Effect of Phosphorus on Molybdenum Solubility in Boroaluminosilicate Glasses

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Despite the widespread acceptance of borosilicate glasses as a matrix for nuclear waste immobilization, the low solubility of certain fission products demands further research into the optimization of these wastefoms. For example, Mo loading above its solubility threshold leads to phase separation of water-soluble molybdates which sequester radioactive alkali and alkaline earth cations like Cs-137 and Sr-90. One promising approach has been to make use of the high cationic field strength of phosphorus as a network former to compete with molybdenum for oxygens. Indeed, phosphate glasses can dissolve high amounts of Mo by incorporation into phosphate chains, however at the expense of chemical durability. We have explored the phospho-silicate system in an attempt to take advantage of both networks to tune the glass properties, with boron and aluminum serving as additional network formers to mitigate the crystallization tendency. The compositions are modeled on SON68 and slow-cooled to mimic industrial nuclear waste processing conditions. The effect of this substitution on the glass structure with and without added Mo is studied using multinuclear magnetic resonance spectroscopy. NMR shows that molybdate and phosphate crystallization are inhibited in P-bearing aluminoborosilicate glasses. The structural origin of these effects appears to be related to increased Mo reticulation at the expense of B and Al connectivity.

**Keywords:** borate, phosphate, aluminosilicate, molybdenum, NMR, nuclear waste

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# Structure of Mixed Anion Salt Glasses from Synchrotron X-Ray Pair Distribution Functions

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This study seeks to understand the melt structure of molten salts in relation to the low temperature reactions and melts that occur during the vitrification of Hanford Low Activity Waste (LAW). Salts (such as nitrates, sulfates, carbonates, halides, etc.) play a key role in these low temperature reactions as they form complex eutectic mixtures during early stage melting. Sulfates are of particular interest as they have limited solubility in the final glass waste form and can be detrimental to its long-term durability as they form a water soluble salt phase on the glass surface. To better understand these low temperature processes, melts of several simple binary and ternary salt systems are studied. In one example, salt melts consisting of varied amounts in the ternary K<sub>2</sub>SO<sub>4</sub>-ZnSO<sub>4</sub>-NaCl were melted and rapidly quenched to retain the amorphous melt structure. Synchrotron x-ray diffraction pair distribution function (PDF) data was obtained for these systems. Empirical Potential Structure Refinement (EPSR) was used to model the PDF. From this model, the individual atom pair distribution functions and coordination numbers were determined. Additional information was determined from infrared absorption spectroscopy and thermal analysis.

**Keywords:** mixed salt, pair distribution function, salt glass

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# WASTE GLASSES 2

# Glass design for the vitrification of high active deposits coming from the Dismantling and Decommissioning of nuclear plant.

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Decommissioning and dismantling of nuclear plants such as UP1, the French reprocessing plant in Marcoule, has revealed the presence of significant amount of high active deposits and sludge in storage tanks. This waste is mainly contaminated by Cs-137 (1 to 10 GBq/g) and contains significant amount of zirconium, phosphorus and molybdenum. Regarding to their high activity level, vitrification of these HL Waste by an In-Can Melting process is a worth conditioning route that minimizes both the waste package volume and the environmental impact in storage conditions. This paper presents the glass formulation studies that have been performed to condition this waste. After selected a reference surrogate waste, borosilicate glass formulations have been proposed that meet both material and process technical requirements. Glass materials, with a simulated waste loading of 10 wt %, have been elaborated in simplified conditions and characterized. Elsewhere, incorporation of higher amount of Zr, P and Mo has been investigated to assess the flexibility of these glass formulations regarding to waste composition variation and uncertainties. By the end, some tests in more representative conditions have been performed to evaluate (i) the reactivity between glass additives and waste surrogate and (ii) the corrosion behavior of the glass canister. The most significant results from these studies are presented.

**Keywords:** vitrification, glass design, nuclear waste

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\*Speaker

# Producing Desired Properties From a Broader Spectrum of Compositions for Nuclear Waste Glass

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The U.S. Department of Energy, Office of River Protection has an extensive research program to develop low-activity waste and high-level waste glass compositions for the balance of mission of the Waste Treatment and Immobilization Plant (WTP). The fundamental data stemming from this program will support development of advanced glass formulations, key process control models, and processing strategies to ensure safe and successful operations for both the Low-Activity Waste and High-Level Waste facilities with an appreciation toward reducing overall mission life.

The Hanford site in Eastern Washington State contains 210,000 m<sup>3</sup> of nuclear waste stored in 177 underground tanks, a result of the production of plutonium from 1943-1987. To immobilize this waste, the Hanford Tank Waste Treatment and Immobilization Plant (WTP) is being constructed onsite. The Department of Energy Office of River Protection has developed an integrated program to increase the waste loading into glass while meeting the melter lifetime, process, regulatory, and product requirements for the WTP.

**Keywords:** Nuclear Waste Glass, glass properties, glass melting, waste treatment using glass

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# Outcomes from the application of the ‘Hazmelt’ thermal treatment technology to a range of simulant LLW and ILW waste-streams.

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‘Hazmelt’ is a thermal treatment technology intended for the vitrification of intermediate and low level nuclear waste, which is derived from novel technology, developed by the main stream glass industry, and specially developed glass compositions. The Hazmelt melter utilises glass melting technology involving the use of submerged thermal elements to allow the treatment of wastes and glasses that would be incompatible with other technologies. This combined with the small volume (~0.15 m<sup>3</sup>) of the melter makes this technology ideal for the thermal treatment of a range of ‘problematic’ intermediate and low level wastes.

The Hazmelt technology has been subject to a series of small scale pilot trials where the technology has been tested through the treatment of three waste simulants; contaminated soil, ‘Magnox’ sludge and IEX resin. Through these trials it was demonstrated that the melting technology has the capability of successfully processing a variety of waste chemistries, including wastes with a high moisture content. However, the trials also established that the novel element technology gave rise to the selective accumulation of some simulant radionuclides within the furnace. This effect along with the other outcomes of these trials are discussed.

The glasses developed for these pilot trials are discussed, including the steps taken in the development of their compositions and the outcomes of durability studies that have been carried out. Details are also provided on how the Hazmelt technology could be incorporated into a waste-treatment plant, taking advantage of the small scale of the melter to produce a small scale waste vitrification plant with the potential for deployment in locations local to waste generation or storage.

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\*Speaker

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**Keywords:** glass, thermal treatment, thermal, vitrification, nuclear, nuclear waste, waste, Hazmelt, melter, melting technology, radioactive, immobilization

# Role of Platinum Group Metals on rheological and electrical properties of nuclear glass

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High level radioactive waste originated from nuclear fuel reprocessing are vitrified in a borosilicate matrix at 1100-1200°C. Some elements from the Platinum Group Metals (PGM) remain insoluble during the vitrification process. This might lead to complex phenomena, such as aggregation and sedimentation of particles, and affect significantly rheological and electrical properties of the glass melt. In order to master the vitrification process, a good understanding of these phenomena is necessary.

Glass electrical conductivity increases strongly when the RuO<sub>2</sub> content is higher than a percolation threshold, explained by a connected network of RuO<sub>2</sub> particles, which are metallic conductors. The formation of these aggregates is favored by particles anisotropy and by some specific process conditions (temperature, mixing,...) and leads to an increase of the glass melt viscosity.

Electrical and rheological percolation laws are found to be in good agreement, and give a good description of the PGM influence on nuclear glass properties.

**Keywords:** nuclear glasses, rheology, electrical conductivity, noble metals

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\*Speaker

# Conversion of waste feed into glass – cold cap formation

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The cost and schedule of nuclear waste treatment and immobilization is greatly dependent upon the rate of glass production during vitrification. To address this issue, we have developed in recent years a 1D mathematical model of the cold cap, which solves the heat and mass transfer and estimates the rate of melting. However, the one-dimensionality of the model ignores the complex geometry of the cold cap with a central slurry pool from which the slurry periodically overflows to form other boiling pools across the cold cap surface. Thus, this contribution focuses on the understanding of water evaporation on the cold cap top and the interaction of the overflowing slurry with the dry cold cap crust. To simulate the conditions in the cold cap, fast-dried slurry solids were prepared by rapidly evaporating water from feed slurry poured onto a 300°C surface. After water evaporated from the sample, a fresh slurry with 5 wt.%  $3\text{Na}_2\text{WO}_4 \cdot 9\text{WO}_3$  (tracer) was poured onto the dry sample. During the whole experiment, an array of thermocouples recorded the temperatures at various depths in the sample and the water content in the slurry was measured. After the experiment, an X-Ray mCT and XRF were used to investigate the degree of mixing between the incoming slurry and the original sample. We will discuss the implications of the results for the cold cap formation in the melter and for the development of the cold cap mathematical model.

**Keywords:** Waste vitrification, batch melting, cold cap, rheology

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\*Speaker

# Cold crucible induction melting for nuclear waste vitrification: from numerical simulations to industrial operation

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Vitrification of high-level liquid waste is the internationally recognized standard to minimize both the environmental impact resulting from waste disposal and the volume of conditioned waste. In France, high-level liquid waste arising from nuclear fuel reprocessing has been successfully vitrified for more than 40 years with three major objectives: durable containment of the long-lived fission products, minimization of the final waste volume, and suitability for an industrial framework.

In this context, the CEA (French Alternative Energies and Atomic Energy Commission) and AREVA have acquired a unique experience on the Cold Crucible Induction Melter (CCIM) vitrification process through more than three decades of R&D and eight years of industrial operation at La Hague plant. This paper presents the CCIM technology from the numerical simulations development to the industrial operation at La Hague plant.

Numerical modelling of induction heating, fluid mechanism and thermal phenomena have been developed for many years. Induction simulation is coupled to thermal simulation with the Joule power density in the metallic part of the process as well as in the molten glass itself. The flow simulation is also coupled and takes into account the mechanical stirring, gas injection and even Lorentz forces if necessary. The radiative heat transfer and the Marangoni convection are simulated as well. All these phenomena are computed on the full 3D real geometry of the furnace thanks to the use of supercomputing center as the TGCC (Très Grand Centre de Calcul) of the CEA. Developments are under progress to include more chemistry in the simulations, such as a redox model or a digestion feeds model and to improve the accuracy and the predictability of such numerical modelisations.

The simulations have been extensively used in the design of the cold crucible inductive melter (CCIM) commissioned in 2010 at La Hague plant but also to enhance the working knowledge the phenomena occurring in the process. The potential benefits are gains on the reliability, the output capacity and the life time.

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\*Speaker



**Keywords:** cold crucible, nuclear waste glass, numerical simulation

# WASTE GLASSES 3

# New insights on the structure of borosilicate glasses containing zirconium by combining Wide Angle X-ray Scattering and atomistic simulations

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Borosilicate glasses containing zirconium are mostly encountered in the industrial field for high level nuclear waste immobilization. Zr low solubility, its nucleating role and influence on the glass chemical durability during alteration in aqueous conditions, were already tackled by means of XAS, NMR and Raman studies.

However, there are still open questions concerning the medium range order for Zr in relation with the nature and proportion of alkali and alkali-earth species in the glasses. It is therefore our purpose to investigate this issue, by combining Wide Angle X-ray Scattering (WAXS) and Empirical Potential Structure Refinement (EPSR) technique. Atomistic simulations were improved by using several constraints coming from previous 11B NMR experiments and Zr K-edge XANES ones.

Based on a series of five-oxide borosilicate glasses of nuclear interest (with Si, B, Zr, Na and Ca species), where zirconium concentration increases from 0 mol% to 8 mol% (0, 1, 2, 4, 6 and 8 mol%), we investigate Zr environment from the structural point of view. At first sight, the shape and location evolution of the main left peaks appearing in reciprocal space reflects changes in coordinate space for the medium range order. In particular, a right shift of the first peak is visible beyond a Zr concentration of 2 mol%, followed by a splitting of the third peak. An explanation of Zr environment evolution in relation with its second and third neighbours, and with Zr-O-X (X=Si, B, Zr) distribution angles is presented.

Moreover, this structural information is used to improve vibrational bands understanding in both polarized and unpolarized Raman spectra for the overall glasses.

**Keywords:** silicate glass, zirconium, atomistic modelling

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\*Speaker

# Evidence of two layers alteration gel in nuclear glasses containing Zr

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Vitrification of high-level radioactive waste in borosilicate glasses has received a great attention in several countries since decades. Glass leaching by water in geological repository is an important phenomenon that needs to be understood to better constrain the long-term evolution of the glasses used to store these wastes.

We will present structural features of the evolution of nuclear glasses under forcing conditions. During the alteration by water, an amorphous gel is formed at the surface of the glass. The durability of the gel and its properties depend on the structural role played by different elements. New generations of spent fuels require higher content of Zr<sup>4+</sup> in glasses. The modifications of the Zr<sup>4+</sup> environment in the gel has been investigated as a function of increasing ZrO<sub>2</sub> content from 1 to 8 mol% in simplified 5-oxide glass compositions at various pH using Zr L-2, L-3-edge and K-edge XANES and by Zr K-edge EXAFS.

In glasses and alteration gels, Zr may adopt three coordination numbers: [6]Zr, [7]Zr or [8]Zr.

The structural evolution of the gel around Zr<sup>4+</sup> in two distinct layers illustrates the molecular-scale alteration of the glass when in contact with water.

**Keywords:** nuclear glasses, Zirconium, X, ray absorption spectroscopy

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\*Speaker

# Boundary layer approach to heat transfer rate to cold cap

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In an electric glass melter, the heat flux needed to maintain the steady state is a product of the feed to glass conversion rate (the rate of melting) and the conversion heat. On the melt side at the cold cap bottom, the heat flux is a product of heat conductivity of melt and the temperature gradient. On the cold cap side, this heat flux has to be transferred across foam layer to the main reaction layer. The boundary layer approach allows approximating the temperature gradient in the melt as the difference between the melter operating temperature and the cold cap bottom temperature divided by the thermal boundary layer thickness, which is a function of melt viscosity and the bulk velocity. In advanced melters, such as those for nuclear waste vitrification, the melt velocity is enhanced by bubbling gas into the melt pool. Thermal gravimetry, differential scanning calorimetry, evolved gas analysis, and volumetric analysis (the feed expansion test) are the main experimental tools to gauge the melter feed response to heating, including foam formation and collapse. A large variability exists in the foaming response depending on the feed composition and makeup. The boundary layer approach allows combining experimental data and empirical correlations into a simple relationship between the rate of melting and the governing parameters, i.e., melt viscosity, gas bubbling rate, conversion heat, and the foam collapse temperature. Thus, it can serve as a link between the mathematical model of the cold cap and the mathematical model of the momentum, heat, and mass transfer in the glass melt body.

**Keywords:** glass melting, cold cap, heat transfer, boundary layer

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\*Speaker

# Alteration Phases on Hanford LAW Glasses after Long-Term Leaching.

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Long-term leaching experiments using the Product Consistency Test (PCT)-B protocol with glass surface to volume ratio (S/V) of 2000 m<sup>-1</sup> at 90°C, were conducted on 203 different Hanford Low-Activity Waste (LAW) glasses for periods of from one to over 18 years. The glass/leachant reaction is tracked by regular solution sampling and many tests are still on-going. Phases developed on reacted glass samples were characterized using XRD and SEM/EDS. Because LAW wastes contain predominantly sodium, the glasses studied have Na<sub>2</sub>O concentrations ranging from 5 to 25 wt%. That upper soda limit is nearly twice that of high-level waste glasses from West Valley, which were the subject of a similar study [1]; interestingly, however, these two types of glasses are found to behave similarly. In many cases, long running PCTs show resumption of leaching after years of relative inactivity (slow residual rate). Secondary phases formed on the glass surfaces are of two primary mineral types. Large quantities of euhedral zeolites form mostly on samples that have reached resumption. Analcime dominates many of the XRD patterns for the most reacted samples; but SEM revealed much greater numbers of smaller, different morphology zeolite crystals (chabazite, phillipsite, and gmelinite) in many glasses beyond resumption. Phyllosilicates are observed in all LAW PCT samples investigated, regardless of whether resumption is reached or not. Micron to sub-micron smectites crystallize within the altered gel-layer to form layered, textured intergrowths. Beidellite and nontronite were found in samples with compositional variations in Ca, Fe, P, and Ti, with little to no effect on the time to resumption. Glass composition differences were reflected in changes in smectite chemistry. [1] "Characterization of Alteration Phases on HLW Glasses after 15 Years of PCT Leaching," I.S. Muller, S. Ribet, I.L. Pegg, S. Gin, and P. Frugier, *Ceramic Transactions*, Vol. 176 (2005).

**Keywords:** Nuclear Waste Glass, Low Activity Waste, Hanford, Alteration Layers, Zeolite, Phyllosilicate, Morphology

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\*Speaker

# Crystal growth in temperature gradients

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The vitrification of nuclear waste by the cold crucible inductive melter (CCIM) started at La Hague plant in 2010. With this type of melter, the glass melt is heated by direct induction, while the edges of the crucible are cooled by a water circulation system. As a result, in the neighbour of the cooled edges, the glass melt is exposed to a strong temperature gradient (of the order of 1000°C.cm<sup>-1</sup>), going from its liquid state (in the glass melt at 1200°C) to its solid state (near the edge). During the vitrification process, this "frozen" glass layer, called the skull-melter, will be exposed to this temperature gradient for several weeks, what can potentially lead to a partial crystallization. The aim of this work is to determine the impact of this temperature gradient configuration on crystallization properties, as such configuration is known to sometimes lead to an oriented growth of crystals [1, 2].

In a first step, the crystallization properties of a simulated simplified nuclear glass have been studied in isothermal conditions and kinetics growth have been determined, mainly by SEM and XRD analysis. In a second step, a specific equipment has been built to reproduce the skull-melter conditions at laboratory scale, and a 11-weeks experiment has been conducted. The comparison of isothermal and thermal gradient experiments allows to discuss the impact of the temperature gradient conditions on crystallization mechanisms and kinetics.

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**Keywords:** crystallization, kinetics, rare earth silicate, powellite, nuclear glass

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# POSTERS



# Study of Non-Crystalline Structure of Polymer Solid by Utilizing Motion of Impurity Ion

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Investigation of the complex-permittivity dispersion gives us a lot of useful information about the molecular motion of polymers and the structure of polymer aggregates. However, the large dispersion of permittivity at low frequencies due to dc conduction of impurity ions often covers the dispersion originated from polymer motion. In experimental investigation, many researchers have tried to remove the dc conduction experimentally or analytically for a long time. Regarding this problem, our laboratory chose another way of research from the point of view of a reversal in thinking. Namely, the way of this research is to use the impurity ions in the dc conduction as a probe to detect the motion of polymer molecules and to investigate a non-crystalline structure of polymer. In melt-crystallized polymers, free spaces with inhomogeneous size exist in a non-crystalline part among crystallites. This inhomogeneity of free spaces results from a thermal motion of the polymer molecules with amorphous conformation under the spatial restriction made by crystallite morphology. The impurity ions mixed in processing in the crystalline polymers move through these inhomogeneous free spaces. This motion of ions reflects the microstructure of the non-crystalline part. The ionic motion of impurity ions is investigated for several polymers by using the complex permittivity and the complex electric modulus. The polymers under investigation are as follows: low density poly(ethylene) (LDPE), plasticized poly(vinyl chloride) (p-PVC), poly(ethylene terephthalate) (PET), isotactic poly(propylene) (iPP), poly(chlorotrifluoro ethylene) (PCTFE), poly(vinylidene fluoride) (PVDF). Consequently, it was found that there are two group of polymers; one of the group is characterized by small conductivity relaxation time and large permittivity, and another is characterized by large conductivity relaxation time and small permittivity.

**Keywords:** permittivity, electric modulus, conductivity relaxation time, ionic motion, dc conduction, non, crystalline structure

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\*Speaker

# Electronic transport and crystallization kinetics of melt-spun Ni<sub>33.3</sub>Zr<sub>66.7</sub> ribbon studied by electrical resistivity measurements

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In this paper, rapidly quenched Ni<sub>33.3</sub>Zr<sub>66.7</sub> ribbons were successfully prepared by melt spinning technique. The electrical and thermal transport properties of as-spun Ni<sub>33.3</sub>Zr<sub>66.7</sub> alloys were studied in detail by a combination of electrical resistivity and absolute thermoelectric power measurements over a temperature range from 25 °C up to 400 °C. The non-crystalline structure of the samples was fully confirmed by X-ray diffraction (XRD) and scanning electron microscope (SEM). Moreover, the crystallization kinetics of Ni<sub>33.3</sub>Zr<sub>66.7</sub> glassy alloy has been investigated during isochronal and isothermal annealing treatments based on the electrical resistivity measurements. The crystallization activation energy,  $E_x$ , for a series of electrical resistivity measurements at various heating rates, was calculated in the order of 371.4 kJ/mol and 382.2 kJ/mol by means of Kissinger and Ozawa methods, respectively. The Johnson-Mehl-Avrami (JMA) analysis was applied to the isothermal crystallization kinetics, and the local Avrami exponent has been determined in the range from 2.97 to 3.23 with an average value of  $n = 3.1$ , revealing that isothermal crystallization mechanism is diffusion-controlled three-dimensional growth crystallization mechanism, as well as an increasing nucleation rate. In addition, the local activation energy for crystallization,  $E_{\alpha}$ , calculated from the Arrhenius equation decreases at the crystallized volume fraction  $0.2 \leq \alpha \leq 0.8$  and giving an average value of 376.2 kJ/mol.

**Keywords:** Metallic glasses, Electronic transport properties, Thermal stability, Crystallization kinetics, Activation energy

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\*Speaker

# Surface and Volume Crystallization in a SrOCaOB2O3SiO2 glass

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The knowledge of the dominant crystallization mechanism and the corresponding structure of a given glass ceramic is highly required, since most of the applications of those materials depend on these characteristics. In this paper, a CaO-SrO-B2O3-SiO2 glass composition was prepared by melting/quenching. In the next, bulk glass samples were heat-treated in a tubular furnace at temperatures above Tg for different periods of time (Tg " 680oC). The evolution of the crystalline phases formed after crystallization at 850oC for a wide time interval (20h – 382h) was investigated by X-ray diffraction (XRD). Using Raman Confocal Microscopy, the Raman spectra of the partially crystallized glass samples were collected at room temperature, at a wavelength range between 200 and 1200 cm-1. From the SEM micrographs, well-separated crystals were found in the surface (dendritic) as well as in the volume (spherulithic), with well-distinctive crystal growth rates. In addition, as demonstrated by the Raman spectra, these crystals belong to the same crystalline phase.

**Keywords:** glass, crystal growth rates, raman spectra

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\*Speaker

# The Effect of Glass Thickness on Chemical Tempering Efficiency

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Chemically tempered glasses have been widely used in display screens of consumer electronics. They have recently begun to be implemented as automotive windows as a consequence of the weight reduction studies on automobiles. Therefore, the new trend is to reach high strength values with lightweight glasses which is only possible by developing chemically tempered ultra-thin glasses. Chemical tempering which is based on a diffusion reaction between sodium ions in the glass by larger potassium ions in a molten salt bath of KNO<sub>3</sub> improves the mechanical strength of glasses by forming a compressive stress layer on the surface. Up to now, reaction temperature and time on chemical tempering process have been thoroughly investigated. However, the effect of glass thickness on chemical tempering efficiency still remains unknown. The aim of this study is to examine the effect of glass thickness on chemical tempering efficiency in terms of detailed mechanical and optical investigations. For this purpose, aluminosilicate and soda lime silicate glasses in 0.7 and 1.1 mm thicknesses were chemically tempered at 400, 425 and 450 °C for 0 to 24 h. The strength, hardness, scratch and crack behavior, transmittance and roughness values were determined. This study showed that thick glasses exhibit slightly higher compressive stress values compared to thinner glasses. In addition, no significant difference was observed in central tension and depth of layer values.

**Keywords:** chemical tempering, thickness, aluminosilicate glass, soda lime silicate glass, mechanical behavior

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\*Speaker

# Comparison on Chemical Tempering Behavior of Commercial Aluminosilicate and Soda Lime Silicate Glasses

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Mechanical strengthening of glass has recently gained a lot of importance due to the high demand in reducing the thickness of conventional automotive windows without decreasing the effective strength. Accordingly, chemical tempering has begun to be used to improve the mechanical properties of glasses for automotive windows. In chemical tempering, the strength of glass is increased by forming compression stress on the surface of the glass through a sodium and potassium ion-exchange process in a salt bath. In the present study, commercial aluminosilicate and soda lime silicate glasses having different Al<sub>2</sub>O<sub>3</sub> contents were chemically tempered using KNO<sub>3</sub> salt bath at varying temperatures from 400 °C to 450 °C. The effect of Al<sub>2</sub>O<sub>3</sub> content on diffusion behavior in ion-exchange process was investigated to compare the chemical tempering behavior of studied glasses. Surface compression stress measurements and stress depth profiles were studied. The strength of glasses was determined by applying ring-on-ring tests. Scratch depth measurements, hardness tests were conducted. Investigations on concentration depth profile of potassium and sodium ions were performed by scanning electron microscope and energy dispersive X-ray spectroscopy techniques. The changes in optical and morphological properties were examined by spectrophotometer and white light interferometer.

**Keywords:** chemical tempering, aluminosilicate glass, soda lime silicate glass, diffusion behavior

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\*Speaker

# Voltammetry and oxygen activity in SnO<sub>2</sub>-doped alkali free aluminoborosilicate melts

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Voltammetry using platinum crucible is a powerful tool to trace the redox reaction of multivalent element in-situ in melt state electrochemically. In the last three decades a lot of studies on redox behavior of various single multivalent elements in silicate or borosilicate melts was performed by voltammetry from the viewpoint of thermodynamics and kinetics for the reduction of  $M(x+n)^+$  to  $Mx^+$  (This is hereafter designated  $M(x+n)^+/Mx^+$ ). Platinum crucible has a great advantage from the viewpoint of no reaction with melts. But it is sensitive to electric field. In the present work, voltammetry experiments for alkali free aluminoborosilicate melts (E-glass) doped with Sn were performed in a crucible of platinum, silica glass and sintered alumina, respectively. Oxygen activity was also determined in a crucible of sintered alumina and silica glass, respectively. In voltammograms derived from three kinds of crucible, peak potential position due to  $Sn^{4+}/Sn^{2+}$  at constant temperature was compared one another and its reproducibility at each crucible was estimated. Finally the real redox ratio  $[Sn^{2+}]/[Sn^{4+}]$  at some temperatures was calculated from peak potential and oxygen activity.

**Keywords:** Oxygen activity, Voltammetry, Crucible, Melts, Redox ratio

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# Raman spectroscopy and structure of selected Ga<sub>2</sub>O<sub>3</sub>-CaO-P<sub>2</sub>O<sub>5</sub> glasses

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*The structure of  $x\text{Ga}_2\text{O}_3 \cdot (50-x)\text{CaO} \cdot 50\text{P}_2\text{O}_5$  ( $x = 0, 5, 10, 15,$  and  $20$ ) glasses was investigated by  $^{31}\text{P}$  MAS NMR and Raman spectroscopy. With increasing content of  $\text{Ga}_2\text{O}_3$  the shift from metaphosphate (Q2) to pyrophosphate (Q1) Q-units was found by the  $^{31}\text{P}$  MAS NMR. Only small amount (approx. 3%) of orthophosphate Q0 units was observed for  $x = 15,$  and  $20$ . The principal component analysis of experimental Raman spectra identified two independent components. Multivariate Curve Resolution analysis (MCR) of experimental Raman spectra performed for two components resulted in corresponding loadings and scores. Spectral decomposition by the method of Malfait was performed using the molar amount of Q2 and Q1 units as composition data. Such way the partial Raman (PRS) spectra of Q2 and Q1 structural units were obtained. In both cases (i.e. MCR and Malfait decomposition) the experimental spectra were reproduced with excellent accuracy. Moreover the normalized PRS are practically identical with the corresponding normalized loadings obtained by MCR. As far as the scores obtained by MCR are not unique, the method of scores adjustment was proposed. This way the good coincidence between the adjusted scores and molar amounts of considered Q-units (i.e. Q2 and Q1) was obtained. The obtained results confirmed the structural information acquired from  $^{31}\text{P}$  MAS NMR.*

**Keywords:** glass structure, MAS NMR, Raman spectra, phosphate glasses, MCR

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\*Speaker

# Tellurium oxide based glasses: establishing of nonlinear optical properties from *ab initio* calculations

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During the last decades, nonlinear optical materials with high third-order nonlinear optical susceptibility, like tellurium oxide based glasses, have received much attention because they have new photonic device possibilities for applications in optical memory storage, logic and switching. Since the beginning of this century, a substantial amount of researches was devoted to nonlinear optical properties of various tellurium oxide based glasses of various compositions. In a first step, our aim was to reproduce the experimental data by mean of *ab initio* calculations and to gain a better insight into the origin of the remarkable nonlinear optical properties of those materials. For achieving these purposes, we applied a comprehensive *ab initio* calculation program based on several computational methods and selected the most efficient ones on. Our concern is now to develop a tool able to establish the nonlinear optical properties of unstudied systems in order to select the most promising ones in preparation for applications. Among the different potential *ab initio* calculation methods we decided to start with molecular calculations on clusters containing terminal hydrogen atoms (TenOmHp). The addition of another metal (like Ti, Zn, Mg...) was planned as a second step once consistent results are observed for the TenOmHp clusters. Several functional and basis sets were tested and the first results are presented on this poster.

**Keywords:** tellurium oxide, nonlinear optical properties, computer simulations

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# Electrical characterization of thin film chalcogenide glasses for gas sensors

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Among the several applications that chalcogenide glasses have, one of the latest is their use as sensitive materials for the detection of gases. Although many materials have been successfully tested as sensitive membrane for gas sensors, chalcogenide glasses have the advantage of not requiring high temperatures for the detection of gasses. Tellurium based membranes were the subject of many investigations during the last decade [1], but other chalcogenide systems are being studied as well [2,3].

In this work, we studied the electrical properties of GeTe and GeSe<sub>3</sub> thin film glasses deposited by pulsed laser deposition (PLD). We measured the conductivity of the films by DC measurements and AC spectroscopy. We performed the measurements under various temperatures and under vacuum and NO<sub>2</sub> atmospheres. We encountered in both systems that their conductivity changes in the presence of NO<sub>2</sub>, which means that they are both good options for sensing NO<sub>2</sub>. On account of these results, in future work, we will study whether the addition of other elements to the membrane will improve the electrical response of the sensor.

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**Keywords:** gas sensor, conductivity, thin film, particulate, pulsed laser deposition, PLD

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\*Speaker

# Dissolution dynamics of AgGeSe chalcogenide glasses in basic aqueous solutions

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Chalcogenide glasses are amorphous materials used in great variety of applications: infrared optics, chemical sensors, gas sensors, phase change memories, solid-state electrolytes, etc. In previous works, our group has discovered that  $\text{Ag}_x(\text{Ge}_{0,25}\text{Se}_{0,75})_{1-x}$  (at. %) bulk glasses are heterogeneous and consist of two phases: a Ag-rich phase and a Ag-poor phase. In the range of compositions  $0.08 < x < 0.1$ , the glasses suffer a spinodal decomposition upon solidification. Outside this range, a binodal decomposition takes place.

A high resistance to acidic media characterizes these materials but they are corroded by basic solutions. Our group has shown in previous works that the Ag-poor phase is more easily corroded than the Ag-rich phase.

In this work, we studied bulk AgGeSe glasses with  $x = 0$  and  $10$  by immersing them in KOH (0.3M) solutions at various temperatures. We observed the samples by SEM, measured the mass loss as a function of time, and estimated the reaction order and the activation energy.

**Keywords:** dissolution, corrosion, spinodal decomposition

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\*Speaker

# Surface morphology of AgGeSe thin films deposited by PLD

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Pulsed laser deposition (PLD) is a technique for fabricating thin films that, because of its simplicity, offers great experimental versatility. It allows the stoichiometric transfer of mass from the target to the substrate and the physical properties of the films are, in many cases, superior to those obtained by other techniques.

The main limit for the application of PLD in micro/nano-devices is the presence of particulate at the surface of (and sometimes even inside) the films.

For this work, we deposited thin films by PLD of the AgGeSe system on Si wafers. We tested various deposition parameters and studied the films through SEM. We present images of the surface of the films and study the distribution of particulates.

We found that the largest particulates originate from the tips of the cones that form at the target's surface during the ablation.

**Keywords:** thin film, particulate, pulsed laser deposition, PLD

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\*Speaker

# Ag<sup>+</sup> and H<sup>+</sup> emission from sharp-edged glasses under non-vacuum atmosphere

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Ion implantation is one effective method for surface modification of materials, and has been applied for various field including semiconductor industry and bio-technology. For example, proton (H<sup>+</sup>) implantation, so-called proton therapy, has recently used most often in the treatment of cancer, in which accelerated protons are irradiated directly to cancer cells. In general, discharge plasma (gas) or liquid (e.g. liquid gallium) has been utilized for an ion source. However, in these cases, side reactions (generation of radicals or various ions with different mass such as H<sub>2</sub><sup>+</sup> and H<sub>3</sub><sup>+</sup> etc.) are unavoidable. Also, ion (particle) accelerators are huge and expensive. On the other hand, ion emission from solid electrolytes has also been considered. Hosono *et al.* showed that O<sup>-</sup> ions exist inside cages of 12CaO·7Al<sub>2</sub>O<sub>3</sub> (C12A7) crystal, and they successfully observed O<sup>-</sup> ion emission from the C12A7 by applying a high voltage. In the emissions from solid electrolyte, one crucial aspect is its high ion conductivity, and ion emission current increases with increasing ion conductivity of electrolyte. Compared with gas and liquid ion sources, ion emission mechanism of such solid-emitter is simple and almost ~100% of emitted ions are O<sup>-</sup> ion in the case for C12A7. Even through, a high vacuum (10<sup>-5</sup> Pa or less) condition is usually required, and applications of ion implantations are thus still limited.

We have studied high ion conducting glasses and those applications for ion emission gun. One big advantage of glass is its good formability, and we anticipate such ion conducting glasses can be applied for an emitter of ionic gun since the strength of the electric field is concentrated around the tip of the sharp-edged glass emitter. In our method, a palm-sized ion emission gun around 10 cm in length can be successfully obtained. Here we show preparation and emission properties of Ag<sup>+</sup> and H<sup>+</sup> ions. Surprisingly, these ion emissions can be observed even at room temperature and non-vacuum atmosphere. Evidence and mechanism of the Ag<sup>+</sup> and H<sup>+</sup> emission, as well as the effective enhancement of cell adhesion are also presented.

**Keywords:** ion conductivity, emission, proton

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\*Speaker

# Lithium Aluminosilicate Glass-Ceramics Nucleated by Rare-Earth Orthoniobates and Orthotantalates

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We report on development of oxide glass-ceramics with crystals of rare-earth (Y, Eu, Tb, Tm, Yb, Er, Ho) niobates / tantalates with different structure and degree of ordering prepared by secondary heat-treatments of glasses containing oxides of rare-earth ions, niobium and tantalum. Initial glasses were made by conventional melt-quenching technique with subsequent isothermal heat-treatments and were investigated by differential thermal analysis (DTA), X-ray diffraction (XRD) analysis, transmission electron microscopy (TEM), density measurements, Raman and optical spectroscopy. Crystals of rare-earth (Y, Eu, Tb, Tm, Yb, Er, Ho) niobates / tantalates are not only nucleators of bulk crystallization of phases, imparting thermal shock resistance and mechanical strength to transparent material, but also effectively luminescent centers. The luminescent properties of the proposed functional glass-ceramics depend on the structure and degree of ordering of rare-earth niobate / tantalate crystals. The change in the composition of glasses and their secondary heat treatment regimes will make it possible to flexibly control the functional properties of these glass-ceramics. This work was partially supported by the Russian Foundation for Basic Research (grant 16-03-01130).

**Keywords:** glass, ceramics, nucleator, transparency, Raman spectroscopy, X, ray diffraction, luminescence

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# Faraday rotator based on dysprosium ions-doped aluminophosphate glass

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The work is dedicated to the investigation of optical, structural, magnetic and magneto-optical properties of an aluminophosphate glass doped with Dy<sup>3+</sup> ions, having magneto-optical properties, applied as Faraday rotator in the visible domain [1, 2]. The glass is prepared by a non-conventional wet method of processing the starting reagents followed by melting-stirring and annealing of the glass. The vitreous material belongs to the 16Li<sub>2</sub>O-8Al<sub>2</sub>O<sub>3</sub>-6BaO-60P<sub>2</sub>O<sub>5</sub>-10Dy<sub>2</sub>O<sub>3</sub> system. In order to prepare a glass having a high optical homogeneity, the melt batch was mechanical stirred aiming at reducing the gaseous inclusions and striae. The final heat treatment on the glass was directed toward releasing of remnant stress aroused during the molding stage. Optical homogeneity was measured by polariscopic, polarimetry and interferometry methods revealing an optical quality glass. Electrical conductance measurements in dependence on time revealed a high chemical strength of the glass. Optical absorption of the doped glass in the visible domain showed in evidence specific lines to dysprosium ions and structural investigations made by means of FTIR and Raman spectroscopy put in evidence the vitreous network forming role of phosphorous pentoxide. Ellipsometry measurements on the bulk doped glass in the visible domain demonstrated the decrease of absorption coefficient and refractive index values on wavelength. Magnetic and magneto-optical properties revealed paramagnetic features of the doped glass as well as a Verdet constant of about -0.05 min/O<sub>e</sub>cm at 600 nm wavelength.

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\*Speaker

**Keywords:** Rare earth ions, doped glass, phosphate glass, magnetic properties, magneto optical properties

# The Effect of Nb-doping on thermochromic behavior of VO<sub>2</sub>-based thin films for energy-efficient windows

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Most of the energy consumed in the world is lost from the exterior of the buildings and more than half of this energy is lost through windows. Accordingly, smart glasses are being developed for energy saving in buildings. Recently, attention has been focused on VO<sub>2</sub>-based thin films due to their unique thermochromic property for their use in energy-efficient windows. VO<sub>2</sub> exhibits thermochromic behavior with a reversible semiconductor-metal phase transition when it undergoes a structural transformation from monoclinic to tetragonal at around 68°C. Although this critical temperature is fairly high for outdoor applications, VO<sub>2</sub> is still the most suitable candidate for energy-efficient windows. Addition of metallic dopants having larger ionic radius than vanadium can decrease the thermochromic transition temperature of VO<sub>2</sub>. Therefore, in this study, Nb-doped VO<sub>2</sub>-based thin films were deposited on soda-lime glasses via sol-gel dip-coating route using two different precursors: vanadium oxy acetylacetonate and vanadium oxytriisopropoxide. NbCl<sub>5</sub> was used for Nb-doping in different compositions (1, 2.5, 5, 7.5 molar ratio %) and the effect of Nb-doping on thermochromic behavior of VO<sub>2</sub>-based thin films was investigated. Thermochromic transition temperatures were determined using DSC technique. Phase characterizations were performed by thin film and powder XRD techniques. Morphology of the thin films was observed by SEM analysis. Finally, temperature dependent optical properties of thin films were investigated using UV-Vis spectrophotometer with an in-situ temperature attachment to evaluate their use in energy-efficient windows. The authors gratefully acknowledge the Yildiz Technical University Scientific Research Fund for the financial support under contract No. FYL-2017-3132.

**Keywords:** VO<sub>2</sub>, Nb, doping, thermochromic thin films, sol, gel, energy, efficient windows

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\*Speaker



# Investigation of Tellurite Glasses for Radiation Applications

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Radiation protection has become a major issue as the use of high energy ionizing radiations (indirectly ionizing e.g. photons, neutrons and directly ionizing e.g. electrons, protons, alpha particles) increases especially in medical applications and nuclear physics. Accordingly, glasses have recently drawn much attention because of their potential to be used in radiation shielding applications as an alternative to ordinary concrete due to their transparency to the visible light and controllable properties with changing composition. Most of the studies realized on use of glasses as potential radiation shields have mainly focused on silicate, borate and phosphate glasses and compared their radiation shielding properties with standard concrete by presenting their superiorities. Recent studies have shown that tellurite glasses offer promising shielding properties that are comparable or better than other glass systems. Therefore, investigating the shielding properties of tellurite glasses and their ability to reduce the intensity of ionizing radiation have become quite important to be able to use these glasses in radiation protection. Therefore, in this work a new series of tellurite-based glasses in the Bi<sub>2</sub>O<sub>3</sub>-PbCl<sub>2</sub>-TeO<sub>2</sub> system have been synthesized using melt quenching technique and thermal, physical and structural properties of these glasses were studied. In addition, the basic radiation shielding quantities, such as mass attenuation coefficient ( $\mu/\rho$ ), half value layer (HVL), mean free path (MFP), effective atomic number ( $Z_{\text{eff}}$ ) and exposure buildup factor (EBF) values were investigated within the energy range 0.015 MeV - 15 MeV using XCOM program and variation of shielding parameters were compared with different glass systems and ordinary concrete to evaluate the suitability of these glasses for radiation shielding applications.

**Keywords:** Tellurite glasses, Radiation shielding, XCOM

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\*Speaker

# Macroscopic and structural effects of electron irradiation on model glasses

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Glass is often exposed to radiation when used in cosmic and nuclear industry; influence of fast electrons on glass properties is of especial interest as all types of irradiation generates secondary electrons. The presented study observed the effect of 50 keV electron beam on model glasses, namely to vitreous silica and two binary alkali-silicate glasses (15K<sub>2</sub>O.85SiO<sub>2</sub> and 15Li<sub>2</sub>O.85SiO<sub>2</sub>), with aim to better understand, evaluate and correlate the observed changes in volume and structure.

Glasses were irradiated with 50 keV electron beams with various doses up to a few decades of kC/m<sup>2</sup>. Atomic Force Microscopy was utilised to monitor volume changes induced by electron bombarding. Volume responses to low-dose electron bombardment were alike for all glasses; the compaction was recorded. However, higher doses showed volume expansion of alkali-silicate glasses while vitreous silica revealed only further compaction. Irradiated spots were observed by confocal Raman spectroscopy to find out structural changes generated by radiation. Irradiation caused a shift and narrowing of Si-O-Si vibration band for silica glass, what means the volume compaction in vitreous silica is given by both the decrease of the average Si-O-Si bond angle and the narrowing of the Si-O-Si angle distribution. It is also shown, compaction at lower doses is strongly correlated with the increase of the D<sub>2</sub> peak, situated at 602 cm<sup>-1</sup>, that is responsible for the increase of the three-membered rings.

Expansion of alkali-silicate glasses is related to migration of alkali ions out of the irradiated volume. Volume relaxation of irradiated glasses was observed by annealing. It resulted in the levelling of the pits created by irradiation, but only for doses below the incubation dose. Annealing of high-dose (above incubation dose) irradiated glass did not lead to full volume recovering as the alkali ions had migrated out of the irradiated volume. Relaxation was accompanied with a decrease of D<sub>2</sub> peak and the reversion of the Si-O-Si vibrations band.

**Keywords:** Vitreous silica, silicate glass, electron irradiation, glass structure

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# New application for geopolymer materials: integration as matrix in Antennas

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Geopolymers have gained tremendous interest as promising materials, environmentally friendly and with good working properties. These mineral binders result from the activation of an aluminosilicate source by an alkaline solution at room temperature. These materials can be used in several applications such as building and construction materials. An innovative use of these materials is their integration in Antennas. The added value of the use of geopolymer material is the possibility to control the dielectric permittivity value of the material, which can be directly poured into the antenna, without exothermic reaction like in case of resin. The objective of this study is to evaluate the suitability of geopolymer material for such application and to improve the formulation in order to obtain the desired dielectric properties. For this purpose, many formulations (dense and porous materials) and synthesis conditions were tested. Then, the evaluation of dielectric permittivity value of the material was performed for many formulations and synthesis conditions. Based on the feasibility tests, it was shown that porous geopolymer materials can be successfully used and leads to sufficient dielectric properties and adhesion to antenna's material which is stainless steel. Moreover, the optimized parameters of the synthesis and the drying process were 70°C and 90°C, respectively. The preparation of the material with the desired dielectric permittivity value and the filling protocol are in the final phase.

**Keywords:** geopolymer, inorganic, binder, amorphous, application, antenna, dielectric properties

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# Up-Conversion emission in Er-Yb doped transparent oxyfluoride nano-glass-ceramics

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Oxyfluoride glass-ceramics have become increasingly important in the last decades because they combine the advantages of glass processing with the good crystalline properties, such as good mechanical, thermal and optical ones. From the pioneering work of Wang and Ohwaki in 1993 [1], concerning the efficient green and red Up-Conversion (UC) emission in Er<sup>3+</sup>-Yb<sup>3+</sup>-doped GCs containing PbxCd1-xF<sub>2</sub> nano-crystals (NCs), many fluoride crystal phases have been studied, showing the possibility to effectively improve the luminescence of Rare-Earth ions (REI) when they are embedded in fluoride NCs. LnF<sub>3</sub> [2] or RLnF<sub>4</sub> [3] (R= K, Na, Li) crystals phases are especially important because the similar size of ions crystals former and the other REI used as dopants allows their incorporation into the crystals phase.

In these work, two oxyfluoride compositions doped with 0.5Er and co-doped with 2 and 4Yb (mol %) have been studied. A structural study, performed by XRD, showed the precipitation of LaF<sub>3</sub> or NaGdF<sub>4</sub> nano-crystals in the glass. HR-TEM and XANES techniques have allowed evidencing the Er<sup>3+</sup> and Yb<sup>3+</sup> enrichment in the nano-crystals and estimating their concentration in the crystal phase.

Optical measurements of Er<sup>3+</sup> singly doped and Yb<sup>3+</sup> co-doped samples showed UC emission (green and red) upon NIR excitation at 980 nm. A notable improve in the UC emission intensity is observed from glasses to GCs and the two-photon origin of the process was proved. Moreover, the green/red ratio of the UC emission changes with the heat treatment of GCs and a possible explication related to the REI concentration is given.

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**Keywords:** transparent glassceramics, fluorides, optical properties

# Thin film crystallization of Y and Er doped sol-gel derived hafnia

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Work is carried out on the effect of Y and Er dopants on the crystal evolution in amorphous sol-gel derived hafnia thin films. While Er doping is of interest to obtain high luminescence intensities, Y has been used to stabilise high temperature crystal phases with higher dielectric constants or ferroelectric properties at room temperature. Er and Y doped HfO<sub>2</sub> thin films were prepared by dip coating technique with varying dopant amount between 0 and 20 mol%. The effect on the crystal structure was evaluated using grazing incidence X-ray diffraction. While monoclinic phase was predominant at low doping concentrations, high concentrations led to the stabilisation of the cubic phase for both dopants, with a mix of both phases appearing at intermediate doping levels.

**Keywords:** hafnia, sol gel, thin film, doping, erbium, yttrium

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# How to determine the cooling rate of a blast furnace slag?

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Granulated blast furnace slag (GBS) is calcium aluminosilicate glass and a by-product of pig iron production in the blast furnace process. In this process, iron ore is reduced to iron at operating temperatures of about 1500 °C generating a residual silicate material which floats on top of the liquid iron. GBS is obtained by tapping off the molten slag and quenching it through a water jet. The GBS process depends on production factors that vary strongly from region to region. In a first step the hyperquenching-annealing-calorimetric scanning (HAC) approach is utilized to determine thermal history-dependent changes in relevant glass properties. HAC results in fictive temperature and cooling rate data of GBS, but also information about the structural heterogeneity of the corresponding liquid at the fictive temperature is obtained.

**Keywords:** Granulated blast furnace slag, fictive temperature, hyperquenching annealing calorimetric scanning

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# The influence of titanium on the structure and some properties of calcium and sodium zinc-phosphate glasses

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The influence of titanium on the structure and some properties of calcium and sodium zinc-phosphate glasses

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Phosphate glasses (PGs) exhibit attractive properties such as low glass transition and melting temperatures, high thermal expansion coefficients and among other also biocompatibility. Recently, PGs are intensively studied as third-generation biomaterials, i.e. as materials capable of specific biological response. Their advantage is that they can be prepared to include ions commonly found in human body as Ca<sup>2+</sup> and Na<sup>+</sup> and the composition can be widely tailored by the addition of other metals (Ti, Ga, Zn ..) to modify their properties.

In this work, bulk glasses of systems TiO<sub>2</sub>-CaO-ZnO-P<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub>-Na<sub>2</sub>O-ZnO-P<sub>2</sub>O<sub>5</sub> were prepared by conventional melting procedure. The Raman spectroscopy and both <sup>31</sup>P and <sup>23</sup>Na MAS NMR spectroscopy were used to obtain information on their short as well as intermediate-range structure. As Ti+IV(d<sub>0</sub> system) was partially reduced to Ti+III(d<sub>1</sub> system) during synthesis, the vicinity of this paramagnetic sites could be also studied by means of electron paramagnetic resonance. The thermal properties of glasses were studied by differential scanning calorimetry and thermomechanical analysis.

Subsequently, prepared glasses were used to form protective coatings on a corundum and b-titanium substrate by spin coating method. Resulted glass ceramic layer was described using XRD, Raman and optical microscopy. The crystalline phase has been found to be titanium diphosphate.

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\*Speaker



The surface of glasses and layers was evaluated by contact angle measurements and microhardness. Being a significant property in medical use, attention was also paid to the study of the glass dissolution kinetics in the physiological solution.

**Keywords:** phosphate glasses, structure, MAS NMR, Raman spectroscopy

# The effect of thermal annealing on structure relaxation and optical properties of Yb<sup>3+</sup> doped Al<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>-SiO<sub>2</sub> glass

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**Abstract:** The ytterbium doped silica fiber is widely used in high power laser facility. However, few reports had been done on the structure relaxation behaviors with temperature in the ytterbium doped silica glass. In this work, we prepared the Yb<sup>3+</sup> doped Al<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>-SiO<sub>2</sub> bulk glass with sol-gel method combining with high temperature sintering. The annealing was done at different temperature on the glass. The density, fictive temperature, refractive index and spectroscopic properties of the annealed Yb<sup>3+</sup> doped Al<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>-SiO<sub>2</sub> glasses have been characterized. The structures of these glasses were tested by NMR and EPR. The physical and optical property change mechanism is explained by local structure change of Yb<sup>3+</sup> and coordination number change of Al<sup>3+</sup> and P<sup>5+</sup> ions in the Yb<sup>3+</sup> doped Al<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>-SiO<sub>2</sub> glass.

**Keywords:** structure relaxation, optical properties, ytterbium doped silica glass

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\*Speaker

# Scratch groove and ionic packing ratio of oxide glasses

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We investigated the composition dependence of scratch resistance within a region of elastic-plastic deformation. A permanent groove eventually associated with the sub-surface lateral cracks was formed on the glass surface by Vickers indenter. The end view of the groove taken with polarized light showed a residual stress concentration at the bottom of the groove. The residual retardation highly depended on the ionic packing ratio and slightly decreased with time. The cross-section profile of the groove showed that residual indentation depth decreased with increasing Young's modulus and pile-up volume was proportional to the ionic packing ratio. These results indicate that the proportional of elastic deformation, plastic flow and densification varies depending on composition.

**Keywords:** scratch, densification, pile up, plastic flow, ionic packing ratio

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# Formation of Hierarchical Nanoporous Layer on glass of various compositions

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Hierarchical Nanoporous Layer (HNL) glass that has nanoscale pores on its surface was developed in recent years. The HNL exhibit a long-life superhydrophilicity and an optical anti-reflection property. That is, the HNL glass maintains the water contact angle less than 10 degree for more than several months and has a very low optical reflectivity around 0.5% at a wide wavelength (400 to 900 nm).

The pores in the HNL gradually changes its size as a function of depth from apparent surface. The HNL is easily formed by alkaline etching treatment of a glass and its thickness can be controlled by the etching conditions. However, the mechanism of HNL formation on glass is still unelucidated. It is inferred that it becomes possible to control the formation and structure of the HNL by clarifying the mechanism.

In this work, we investigated the formability of HNL on various kinds of glass like soda-lime, borosilicate, aluminosilicate and so on by conducting SEM micrography, XPS and so on with changing the glass and etching conditions. The forming speed and the formed structure varied in accordance with the glass composition. We will discuss the HNL forming mechanism from the viewpoint of the composition dependence.

**Keywords:** antireflectivity, superhydrophilicity, nanoporous, etching

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# Characterization of deformation and cracking behavior of high Poisson's ratio oxide glasses with La<sub>2</sub>O<sub>3</sub>

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Poisson's ratio ( $\nu$ ) is the negative of the ratio of the transverse strain to the longitudinal strain for a uniaxial stress state. The adjustment of  $\nu$  is receiving increasing interest as a means of tailoring the ductility of glasses. This has been motivated by the observation of intrinsic ductility in high- $\nu$  (above 0.32) bulk metallic glasses, but it is unknown whether the same relation between ductility and  $\nu$  exists in oxide glasses since all known oxide compositions exhibit  $\nu$ -values below or around 0.32. In this study, we attempt to manufacture high- $\nu$  oxide glasses using two approaches both based on La<sub>2</sub>O<sub>3</sub> incorporation: (i) Known high- $\nu$  glass compositions (La<sub>2</sub>O<sub>3</sub>-containing aluminoborate, aluminogermanate, and aluminosilicate) are first synthesized, and then subjected to hot compression treatment to further increase their atomic packing density and thus likely high  $\nu$ . (ii) ZnO-B<sub>2</sub>O<sub>3</sub> glass composition is doped with increasing amounts of La<sub>2</sub>O<sub>3</sub> to increase  $\nu$ . These glass systems are investigated using various characterization techniques to understand the mechanical response of high- $\nu$  oxide glasses. Elastic moduli including  $\nu$ -values are determined through Brillouin light scattering and ultrasonic echography techniques. Hardness, crack resistance, and cracking patterns of all glasses are investigated using Vicker's microindentation. For selected compositions, annealing-induced volume recovery of indentation imprints is studied to shed light on the deformation mechanisms controlling the response of glass to sharp-contact loading. Finally, micro-Raman spectroscopy is used to acquire Raman spectra in the as-made and the hot compressed glasses, as well as inside the Vicker's indentation imprints of the as-made glasses. The deformation and cracking characteristics are linked with structural features of the investigated glass compositions.

**Keywords:** indentation, poisson's ratio, cracking, deformation

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# Structure and properties of barium tungstate-phosphate glasses

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Tungsten oxide is able to form broad glass forming regions with phosphate glasses. Materials based on WO<sub>3</sub> are known for their electrochromic and photochromic properties, which result in a wide range of applications, such as smart windows, display devices, or sensors. Barium phosphate glasses of the composition (100-x)Ba(PO<sub>3</sub>)<sub>2</sub>-xWO<sub>3</sub> with 0-60 mol% WO<sub>3</sub> were prepared and studied. All glasses reveal very high chemical durability. Thermal studies of the glasses were carried out with DTA, dilatometry and hot-stage microscopy. Glass transition temperature in this glass series increases with increasing WO<sub>3</sub> content from 447°C (x = 0) to 635°C (x = 60). All glasses containing WO<sub>3</sub> crystallize on heating within the range of 650-750°C with the exception of the glass with 20 mol% WO<sub>3</sub>, which is thermally stable. The effect of composition on the properties of these glasses and the relations between composition, structure and properties were evaluated. <sup>31</sup>P MAS NMR studies were devoted namely to the investigation of changes in phosphorous coordination in the dependence on WO<sub>3</sub> content. The gradual shortening of phosphate chains in the direction Q<sub>2</sub>®Q<sub>1</sub>®Q<sub>0</sub> was observed in the studied compositional series. Compositional dependence of the amount of Q<sub>n</sub> units was obtained by the decomposition of the spectra. Changes in the network structure of phosphate glasses can be deduced also from changes in their Raman spectra which confirmed the shortening of phosphate chains by the incorporation of tungstate structural units, most probably in the form of WO<sub>6</sub> octahedra. These octahedra form clusters via W-O-W bonds, the number of which increases with increasing WO<sub>3</sub> content.

**Keywords:** phosphate glasses, MAS NMR, tungsten oxide

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# Redox interaction between Fe and secondary multivalent elements in soda lime silicate glass melts

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Redox interaction between Fe and various multivalent elements in glass and melt have been examined using voltammetry and spectroscopy. Voltammograms of melts doped with Fe exhibited a pronounced peak due to Fe<sup>3+</sup>/Fe<sup>2+</sup>-reduction. The temperature dependence of the Fe<sup>3+</sup>/Fe<sup>2+</sup>-peak potential recorded in voltammograms showed a normal behavior, in other words the corresponding peak potential (E<sub>p</sub>) moves toward the negative direction with a decrease of temperature, indicating that the equilibrium state of Fe redox reaction shifts towards to the oxidation state. However, when S or Sn or Sb or Ce was doped to those melts the Fe<sup>3+</sup>/Fe<sup>2+</sup> peak potential was shifted to negative or positive direction depending on the secondary multivalent ion. For the glasses the depth change in absorption band of Fe<sup>2+</sup> or Fe<sup>3+</sup> in UV-Vis-NIR spectra showed also negative or positive direction under presence of secondary multivalent ion. Comparison of the results in both voltammograms and spectra indicated the same tendency in melts and glasses from the view point of Fe redox: Fe<sup>2+</sup> was favored by presence of S and Sn. But Fe<sup>3+</sup> is a favorite state under doping of Ce or Sb. Thus it confirms that the effect is derived from the melt state. The standard Gibbs free energy for the reduction of each multivalent ion determined in melt doped with redox pair supports strongly the equilibrium state of the suggested interaction reaction. To confirm the foregoing results oxygen activity for the corresponding melts was determined and the actual redox ratio [Fe<sup>2+</sup>]/[Fe<sup>3+</sup>] in each melt was calculated.

**Keywords:** redox interaction, voltammogram, spectroscopy, oxygen activity, redox ratio

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# Mercury thiogermanate HgS-GeS<sub>2</sub> glasses: macroscopic, electric, and structural properties

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Mercury thiogermanate HgS-GeS<sub>2</sub> glasses were synthesized and characterised. Macroscopic property measurement including density, X-ray diffraction (XRD), and differential scanning calorimetry (DSC) were performed. The glass-forming range for  $x\text{HgS} \times (1-x)\text{GeS}_2$  compositions was found to be limited to  $x \leq 0.6$ . As  $x$  increases, the glass transition temperature,  $T_g$ , decreases from 483 °C to 273 °C. The total electrical conductivity, studied using a high resistance meter, shows that the mercury thiogermanate glasses are electronic insulators,  $4.5 \cdot 10^{-15} \text{ S cm}^{-1} \leq \sigma_{298}(x) \leq 4.0 \cdot 10^{-13} \text{ S cm}^{-1}$ , with a non-monotonic electronic behaviour. Raman spectra of the  $(\text{HgS})_x(\text{GeS}_2)_{1-x}$  was also measured over the entire range  $0.0 \leq x \leq 0.6$ . The addition of HgS to the host GeS<sub>2</sub> glass leads to a well-defined feature at  $\sim 320 \text{ cm}^{-1}$  which eventually trespasses in its intensity that of the vibrational modes corresponding to GeS<sub>4</sub> tetrahedra at around 340  $\text{cm}^{-1}$ . Finally, high-energy X-ray diffraction experiments were carried out. The results show that (i) two mercury bonding patterns (HgS<sub>2/2</sub> and HgS<sub>4/4</sub>) are present simultaneously in mercury thiogermanate glasses HgS-GeS<sub>2</sub> and (ii) the population and interconnectivity of chain-like (HgS<sub>2/2</sub>)<sub>n</sub> and tetrahedral (HgS<sub>4/4</sub>)<sub>n</sub> dimorphous forms determine both the structural features and fundamental glass properties (thermal, electronic, etc.).

**Keywords:** Chalcogenide glasses, Electric conductivity, thermal properties, Raman, High energy X ray diffraction

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\*Speaker



# Immobilization of heavy metal oxides by sintering of mixture of LCD waste glass and MSW incinerator fly ash

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Due to the drastic growth of the liquid crystal display industry in the last decade, lots of waste glass is being produced. Especially, end-of-life LCD waste glasses (hereafter designated EOL-LWG) derived from end-of-life LCD devices is contaminated considerably and shows inhomogeneous composition. Furthermore EOL-LWG derived from the glasses produced before 2011 contains some toxic components such as As<sub>2</sub>O<sub>5</sub> and Sb<sub>2</sub>O<sub>5</sub>. Therefore, its effective recycling is limited.

In this study, several mixed batches of EOL-LWG, soda lime silicate waste glasses (SLS-WG) and municipal solid waste incinerator fly ash (MSWI-FA) were prepared to examine the immobilization possibility of wastes with toxic components by sintering. Here as EOL-LWG some LCD glasses produced before 2011 was used. The mixture of three different wastes with some ratio was pressed to disc form and sintered in the range of 830~880 under the consideration of temperature dependence of glass viscosity. Some properties such as bulk density and water absorption for the sintered specimens were determined. Additionally a chemical stability of resulting sintered specimens was estimated by the toxicity characteristic leaching procedure (TCLP) method of the U.S. Environmental Protection Agency (EPA). To examine surface corrosion state, microstructures before TCLP and after TCLP were analyzed, respectively.

**Keywords:** LCD waste glass, waste immobilization, sintering, leaching

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# Temperature and illumination dependent mass transport during the surface relief formation in As-S(Se) amorphous chalcogenides

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Investigations of amplitude-phase optical and geometrical relief formations at room temperatures, rather well known for a-Se and selected compositions from As-Se system [1,2], were extended towards wide temperature range from 77 K up to softening temperatures of given materials. Besides the holographic recording of periodical 1D or 2D surface relief structures experimental techniques were developed and used for in-situ or afterwards measurements of complementary changes in optical transmission and surface relieves. It was shown that changes of optical density and surface relieves can be detected at temperatures down to liquid nitrogen and up to softening temperatures of the given glass compositions. The rate of the processes increases with temperature following Arrhenius law with rather small activation energies, but at temperatures close to the softening temperature thermal erasing prevails. The possible role of diffusion, related to different components of glass and viscosity in these light and temperature stimulated mass transport processes was analyzed. This way the interrelations between composition, recording conditions and efficiency, erasing processes and stability were established for samples from the given system of materials.

## Acknowledgement

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\*Speaker

**Keywords:** chalcogenide glass, surface reliefs, recording, erasing, mechanism

# Features of the silver nanoparticles formation in the bulk and on the surface of the fluoride phosphate glasses.

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Noble metal nanoparticles exhibit unique optical properties, such as resonant absorption and scattering of light, not found in bulk metal. Collective coherent excitations of the free electrons in the conduction band, also known as Surface Plasmon Resonance (SPR), are responsible for the strong absorption and scattering of light by the particles. These resonant properties have been employed in surface enhanced Raman spectroscopy, bio sensing, fluorescence enhancement, catalysis, photovoltaics and optoelectronic. The present work aims to study the formation of the Ag- structures in fluoride phosphate glasses. Nanoscale silver molecular clusters and metal nanoparticles embedded in fluoride phosphate glass were produced by Na $\leftrightarrow$ Ag ion exchange and subsequent heat treatment in an air atmosphere. We report on photoluminescence, optical absorption and transmission electron microscopy of fluoride phosphate glass after the ion-exchange process and heat treatment. It was deduced that during ion-exchange first stage of the particle formation could be identified: (i) reduction of ionic silver by reduced atmosphere of the glass (ii) formation of the small molecular clusters Ag<sub>n</sub> n=2-4 with high luminescence and (iii) formation of the large molecular clusters Ag<sub>n</sub> n=11-70 with blue shifted plasmonic band ( $\lambda$ =325-340 nm). Heat treatment at temperatures near and below glass transition temperature resulted in two SPR bands belonged to large molecular clusters and metal nanoparticles ( $\lambda$  =405 nm). Electron microscopy investigation revealed the completion of silver particles in near-surface regions with high silver concentration induced by thermally assisted diffusion: (i) formation of single-crystalline particles with sizes 1-5 nm in the interior of the glass and some number of the large NP- agglomerates of the small NPs on the surface. The aim of this study is to get a knowledge of the influence of the heat treatment on the optical properties of silver centers, introduced by silver ion exchange into the fluoride phosphate glass synthesized in the strong reduced conditions.

**Keywords:** Optical properties, silver nanoparticles, fluoride phosphate glass

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\*Speaker

# Research Tools and Methodology for Waste Vitrification Process Development

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Since the 1960s, the French Alternative Energies and Atomic Energy Commission (CEA) carried out R&D to develop vitrification processes for high-level and long-lived intermediate-level wastes conditioning. These Researches have led to promote and push forward the French industrial vitrification technologies (increasing of waste loading, production rates and process robustness). Within the CEA, the main goals of the Vitrification Process Development Laboratory (LDPV) are to develop vitrification technologies and processes, to qualify equipments and processes and to support industrial vitrification plant. To achieve these objectives, LDPV has been developing several prototypes at different scale and different TRL (Technology Readiness Level) supported by 3D magneto-thermal-hydraulic models. In this paper, the approach of LDPV needed to develop technologies and processes as well as associated R&D tools is presented. Illustrations of small test rigs used to support the conception of new processes and to describe physico-chemical mechanisms will be showed. Moreover, full scale non-radioactive prototypes allow to qualify technological innovations and to support industrial facilities will be described. Then, numerical simulation of fluid flow, heat transfer and electromagnetic of glass melting used to design furnace prototype and to support industrial vitrification activities will be presented.

**Keywords:** Vitrification, prototype, modeling

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\*Speaker

# Role of Poisson's ratio mismatch on the crack path in glass matrix particulate composites

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The way the mechanical properties of glass matrix particulate composites can be improved by playing on the stiffness, the size, the shape, and the volume fraction of the particles has been quite extensively studied in the past 40 years. Emphasis is mostly put on the influence of mismatches of the elastic moduli and coefficient of thermal expansion, which are known to govern the occurrence of residual stresses upon cooling. However, little attention was paid to Poisson's ratio ( $\nu$ ) so far, although we show in this study that it has a major influence on the stress field in the vicinity of the particles, and thus on the fine details of the crack extension path. Crack front pinning and bridging phenomena are predicted in the case of adhesive particles with  $\nu$  smaller than the matrix. Nevertheless, when located close to the surface, such particles might be detrimental to the strength. Glass offers a unique opportunity to vary composition and properties in a continuous manner, hence opening a new realm of possibilities for tuning Poisson's ratio to improve the apparent fracture toughness of the composite material.

**Keywords:** Glass, Particulate composite, Poisson's ratio, Toughness, Fracture mechanics

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\*Speaker

# Fictive temperature approach: a valuable tool for silica glass photonics

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For many applications, silica glass is the preferred material because of its physical chemistry properties: high transparency from IR to UV, low thermal expansion, high chemical and mechanical resistance and longevity. For all these reasons, silica constitutes an unquestionable choice for photonics applications and particularly in optical fiber technology, glass laser processing for telecommunications and sensors in extreme environment.

It is well known that a fictive temperature  $T_f$  characterizes the structural disorder of a glass. Such a parameter can play a similar role than the thermodynamical ones for fixing, refractive index or Rayleigh scattering. In addition  $T_f$  of silica glasses can be determined by FTIR or Raman spectroscopy. In these methods, scientists use an empirical relation existing between the wavenumber or the intensity of silica structural bands and  $T_f$ . Even if this concept has some limitations, fictive temperature approach is a valuable tool for glass photonics as we review here. The intrinsic loss mechanism limiting SiO<sub>2</sub> transparency is the Rayleigh scattering from frozen-in density fluctuations. In the literature, two approaches have been used to reduce Rayleigh scattering loss in fibers via a reduction of  $T_f$ , namely optimizing the core/cladding chemical compositions and/or optimizing the thermal conditions for fiber drawing. Fictive temperature approach has been also exploited in glass laser processing. Here the main objective is to imprint permanent changes in the optical properties that can be exploited to create devices like waveguides or Bragg gratings sensors for high temperature. For example,  $T_f$  increase within the femtosecond laser-affected zone scales with repetition rate and reaches values up to 1700°C. Consequently, the silica glass network tends to densify resulting in highly stable refractive index changes. For harsh ionizing environment applications there are strong efforts to produce radiation resistant optical fibers, which includes reduction of defects precursors by tailoring glass fictive temperature.

**Keywords:** silica, photonics, fictive temperature, Rayleigh scattering, radiation hardening

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\*Speaker

# Reversible EPR signature of Self-Trapped Holes in fictive temperature-treated irradiated silica

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For a few decades, silica glasses and silica optical fibers have been extensively studied for their use in technological applications like telecommunications and semiconductor industry but the resistance of their functionality is still a challenging issue in various extreme environments. In particular the radiation-induced point defects are still studied for improving the radiation hardening of optical fibers especially for spacecraft and nuclear application. The most commonly studied radiation induced defects in silica optical fibers are namely: self-trapped hole centers (STHs), peroxy radicals (Si-O-O•), non-bridging oxygen hole centers ( $\neq$ Si-O•) and SiE'γ. However, self-trapped hole centers do not exist until the material is irradiated. Because they are the major source of RIA (Radiation Induced Attenuation) in the Visible and near-IR range, they are the most important fundamental radiation-induced color centers arising in pure silica fibers, thin films or bulk.

In this work, post-mortem electron paramagnetic resonance spectroscopy experiments have been carried out between room temperature and 20K to examine the radiation-induced defects in fictive temperature (Tf) treated Heraeus F300 silica (0.1ppm OH, 1500ppm Cl2). In particular, we focus our attention on the strain-assisted formation of Self-Trapped Hole centers detected in various Tf-treated samples irradiated at room temperature by gamma rays at 6kGy. By repeating annealing cycles between 77 and 300K on the same samples, we observed that the EPR signal attributed to STH decreases as the temperature increases but in a reversible manner. We evidenced a deviation from the Curie law for  $T > 70K$  and suggest an interpretation based on the decrease of the so-called "strain-assisted STH" population by reversible excitation of the trapped hole to a delocalized state with activation energy of 7.8 meV. This also means that the precursors of hole trapping sites (a local strain atomic configuration) remain stable until 300K at least.

**Keywords:** radiation effects, defects centers, silica, fictive temperature, self, trapedd, holes

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\*Speaker



# Plasma-chemical etching of 2D-poled glasses

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It is shown that plasma-etching of 2D-poled glasses opens a new route to dry lithography for producing glassy structures for diffractive optics, integrated optics, microfluidics, plasmonics, etc. Poling of alkaline silicate glasses with structured anodic electrodes (that is, electrodes with surface relief pattern) results in the 2-D modulation of composition on the glass surface, with this modulation replicating the anodic relief pattern. Modulation of glass composition, in its turn, results in the modulation of chemical reactivity of the glass surface. Due to the difference in the dissolution rates of modified and unmodified surface regions, plasma-chemical etching of the 2-D poled glasses was expected to produce on the glass surface an exact relief replica of the electrode pattern, that is, above-mentioned glassy structures. Possibility of the proposed technique has been demonstrated via producing a high spatial resolution relief structure (that is, relief surface pattern of 0.5  $\mu\text{m}$  in depth) on the glass surface. It should be noted that both glass poling and plasma-chemical etching are dry processes, and it looks like rather serious advantage as compared to the traditional photolithographic techniques for production such structures and based on the use of wet chemicals. The study has been supported by Russian Science Foundation grant No. 16-12-10044.

**Keywords:** sodalime glass, poling, plasma etching, lithography

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\*Speaker

# Simulation of bubbles dynamics in beer tumblers

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Tumblers for the brewery market represent a growing part of volumes produced by ARC. We propose our customers not only aesthetic articles thanks to continuously innovative designs and outstanding quality decoration but also a real functionality through bubble nucleation. Brewers attach more and more importance to bubbles movement in the glass and foam creation, as one of our customers says "you drink with your eyes". That's why, in addition to the experimental research approach conducted by ARC, we decided develop a new numerical approach to improve our knowledge concerning the way to control effervescence and bubble nucleation. Indeed, even if the dynamics of bubbles are now well understood, there is a lack of data in the study of induced flow patterns in carbonated beverages. It was demonstrated that ascending bubbles generated at chosen nucleation locations act like many swirling motion generators in glasses. Because there is strong relationship between fluid mixing phenomena and aromas exhalation process, the knowledge of the liquid phase hydrodynamic behavior seems to be a key parameter in the beer science. It is the reason why a numerical Lagrangian-Eulerian modeling of flow dynamics induced by the effervescence in a glass of beer has been carried out for the first time using the finite volume method by CFD (Computational Fluid Dynamics). In order to define source terms for flow regime and to reproduce accurately the nucleation process at the origin of effervescence, specific subroutines for the gaseous phase have been added to the main numerical model. These subroutines allow the modeling of bubbles behavior based on semi-empirical formulas relating to bubble diameter and velocity or mass transfer evolutions. Numerical results show how the beer glass shapes and also location and density of nucleation sites can affect the flow patterns and vortical structures induced by the columns of ascending bubbles.

**Keywords:** Tumblers, Flow simulations, Bubbles

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<sup>†</sup>Speaker

# Understanding nineteenth century glass deterioration through artificial accelerated aging

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The Parisian clock-maker, Claude Laurent, fabricated glass flutes in the early nineteenth century. With 189 flutes known worldwide, 20 of them are housed in the Dayton C. Miller Collection at the Library of Congress. Some of the flutes show significant deterioration noted by a fogginess referred to as "crizzling," which raised questions concerning the stability of the glass. The flutes were originally believed to be made from a stable lead-based glass "flûte en cristal" but most were later analyzed to be potash glass.

In order to investigate the relationship between the glass compositions and observed state of deterioration, a series of five model glasses were fabricated, based on the results from elemental analyses. The model glass samples were increased incrementally in K<sub>2</sub>O content from 16.5 wt% to 20.5 wt% with SiO<sub>2</sub> progressively lowered and fixed 2.4 wt% CaO.

Each model glass was artificially aged by three separate methods to simulate the deterioration observed on the Laurent glass flutes: i) steady state environmental aging at 90°C and 90% relative humidity (RH), ii) aging at 90°C and cycling RH and iii) modified vapor hydration testing at 200°C and 75% RH. Various stages of deterioration were seen as the glass reached certain points of aging, as documented by light microscopy and cross sectional SEM-EDS analysis. The vapor hydration testing was found to be too aggressive for modeling the glass flute deterioration whereas the environmentally aged model glasses closely mimicked the observed progression of glass deterioration seen on the potash glass flutes.

Another high-potassium composition (19 wt% K<sub>2</sub>O) found in nineteenth century photographic plate glass was similarly fabricated and leach tests are ongoing to identify the role of the 9 wt% CaO in this formulation. Optimizing the accelerated aging methods will help to understand mechanisms/kinetics of glass deterioration of historical objects.

**Keywords:** Heritage, Glass stability

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# Investigation of boson peak of densified silica glass by terahertz time-domain spectroscopy

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We performed terahertz time-domain spectroscopy on densified silica glasses to investigate the boson peak (BP) dynamics. BP is a low energy excitation universally observed in the THz region of the glass material. In the spectra of  $\alpha(\omega)/2$  [ $\alpha(\omega)$  is the absorption coefficient], BP were observed. Infrared light-vibration coupling coefficient  $CIR(\omega)$  was determined using the  $\alpha(\omega)$  and vibrational density of states  $g(\omega)$  obtained from the low-temperature specific heat measurement, and the charge fluctuations of the densified silica glasses were quantitatively evaluated by Taraskin's model [S.N. Taraskin *et al.*, Phys. Rev. Lett. **97**, 055504 (2006)].

**Keywords:** Boson peak, terahertz time domain spectroscopy, low temperature specific heat, silica glass

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# A catalogue of cation coordination polyhedra in glasses and disordered solids

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The structures of solids  $AmX_n$  with ionic bonding are generally comprised of packed arrays of anions X with smaller cations A occupying interstitial sites. The cation coordination polyhedra AXN have vertices which are defined by the N nearest neighbour anions to which the cation is ionically bonded. Here we report a comprehensive catalogue of 41 convex polyhedra with N less than or equal to 12. One way to distinguish different polyhedra having the same N is by comparing the values of their rotational invariants QL (where L can be thought of as the order of "nodal" symmetry) [ref. 1]. We illustrate the use of rotational invariants to classify cation coordination polyhedra in glasses. For example, in BaF<sub>2</sub>-ZrF<sub>4</sub> glasses Zr has an average N equal to approximately 7.5. Comparison of rotational invariants indicates that ZrF<sub>7</sub> and ZrF<sub>8</sub> polyhedra (respectively) are similar to singly and doubly capped trigonal prisms. Further examples are given by classifying the coordination polyhedra of other cations (La, Al, Na, and Eu) in zirconium fluoride glasses. [1] D. Scott and G. Mountjoy (2014) *J. Non-Cryst. Solids* **401** SI 54-59.

**Keywords:** cation coordination, fluoride glasses, short range order

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\*Speaker

# Probing the degree of polymerization in iron-bearing calcium silicate glasses: A view from high-resolution solid-state Nuclear Magnetic Resonance

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Unveiling the atomic structure of iron-bearing silicate glasses is one of the fundamental unsolved problems in glass sciences and high-temperature geochemistry. Whereas solid-state NMR has been effective in probing the local structures of iron-free oxide glasses, its application to the study of iron-bearing glasses has been limited due to the considerable peak broadening and signal loss stemming from paramagnetic effect. Nevertheless, a recent NMR study demonstrated the utility of solid-state NMR techniques, such as 2-dimensional MQMAS (multiple-quantum magic-angle spinning) for the study of structure of iron-bearing Na-silicate glasses [1]. While this progress holds strong promise for study of hidden structural details in diverse iron-bearing oxide glasses, the previous analyses are rather qualitative and the quantification of the degree of melt polymerization in the iron-bearing glasses has remained to be performed. Here, we report the extent of polymerization in iron-bearing calcium silicate glasses (CaO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>) with varying XFe<sub>2</sub>O<sub>3</sub> [=Fe<sub>2</sub>O<sub>3</sub>/(CaO + Fe<sub>2</sub>O<sub>3</sub>)], up to 12.9 wt% Fe<sub>2</sub>O<sub>3</sub>). The <sup>29</sup>Si NMR spectra show an apparent increase in highly polymerized Q species with increasing XFe<sub>2</sub>O<sub>3</sub>, suggesting an increase in the degree of polymerization. <sup>17</sup>O 1D MAS NMR spectra presented the well-resolved bridging oxygen (BO, Si-O-Si) and non-bridging oxygen (NBO) peaks. The latter decreases with increasing XFe<sub>2</sub>O<sub>3</sub>, consistent with the <sup>29</sup>Si NMR results. Despite the severe peak broadening, the iron-induced changes in the structurally-relevant NMR parameters, such as isotropic chemical shift ( $\delta_{iso}$ ) and quadrupolar coupling constant (Cq) were estimated from <sup>17</sup>O 2D 3QMAS NMR spectra for the iron-bearing Ca-silicate glasses. The results reveal that the paramagnetic effect results in a more pronounced dispersion of  $\delta_{iso}$ , while its effect on Cq is effectively suppressed. Together with our earlier NMR studies of iron-bearing Na- and Mg silicate glasses [1,2], we established the systematic effects of paramagnetic elements and cation field strength of non-framework cations on NMR peak shift and broadening.

H.-I. Kim, J.C. Sur, and S.K. Lee, *GEOCHIM. COSMOCHIM. AC.*,173 160-180 (2016)

H.-I. Kim, and S.K. Lee, Structure and disorder in (Mg,Fe)SiO<sub>3</sub> glasses and melts: Insights from high-resolution <sup>29</sup>Si and <sup>17</sup>O solid-state NMR, under review (2017)

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**Keywords:** iron bearing silicate glass, solid state NMR, paramagnetic effect, degree of polymerization

# Thermal properties and crystallization mechanism of undoped and Nd<sup>3+</sup>-doped calcium aluminosilicate glasses

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In the preparation of glass-ceramics, with specific micro-structure and properties, the knowledge about nucleation rate and crystal growth is of great relevance, since can enable controlled crystallization. A well-established method that uses differential thermal analysis (DTA) to determine the nucleation-rate-like curves in glasses has been proposed by Ray and Day<sup>1</sup>. In this regard, DTA measurements can be used as a rapid method for determining the temperature where the nucleation rate in a glass is a maximum. The scope of this work had two main strands. The first was focused on the role of crystallization mechanism in the synthesis of calcium aluminosilicate glasses doped with Nd<sup>3+</sup>. The second strand of research was the obtaining of transparent glass-ceramics through controlled crystallization of the precursor glasses. Accordingly, this study demonstrates the effect of composition on the crystallization kinetic of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO-MgO-Nd<sub>2</sub>O<sub>3</sub>-doped glasses. Two matrices with quite distinct compositions and degree of polymerization were synthesized. The melting was performed under vacuum atmosphere at 1600C. In rare-earth doped glasses, this vacuum synthesis provides ions in reduced oxidation states and with minimal, or absent, presence of OH<sup>-</sup> in their structures. These OH<sup>-</sup>-free glasses, prepared under vacuum atmosphere, present potential application as solid state lasers and white light (WL) generation devices. Differential thermal analysis was used to evaluate the crystallization kinetic parameters, such as the glass transition temperature (T<sub>g</sub>) and the activity energy of glass transition (E<sub>t</sub>) were also measured with different methods. Glass stability was evaluated by means of the characteristic temperatures of thermal events in the DTA measurements. Non-isothermal methods of Kissinger and Ozawa were used to obtain the apparent activation energy. The results showed that in this system surface crystallization was more favorable than bulk. By confocal Raman microscopy it was estimated that the crystallized region was 20-30 microns from surface to center of sample. The structural characterization, carried out by X-ray diffraction (XRD), revealed calcium aluminum oxide the as the marjorite phase.

**Keywords:** Transparent glass ceramics, rare earth, Crystallization kinetic parameters

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# Effect of the Na/K ratio on the viscosity and the structure of iron-bearing aluminosilicates lavas

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Le Losq and Neuville (2013) have shown that the viscosity and the structure of Na/K aluminosilicate glasses and melts do not follow ideal mixing rules, which that suggest usually imply a decrease of the melt viscosity with upon Na/-K mixing as proposed by the classic alkali mixing model. Instead, polymerised aluminosilicate melt viscosity increases non-linearly when K<sup>++</sup> ions substitute Na<sup>+</sup> ions. This effect can have important consequences for eruptions of volcanoes like the Toba (Indonesia), Mont Dore or the Yellowstone (U.S.A.), which erupted magma with compositions are close to rhyolites (e.g. 83 mol%SiO<sub>2</sub>— 8 mol%Al<sub>2</sub>O<sub>3</sub>-3.7 mol%K<sub>2</sub>O-3.4 mol%Na<sub>2</sub>O) during cataclysmal explosive events. The aim of this work is to test the mixing effect of Na/K on SiO<sub>2</sub>-poorer compositions, such as those of the Yasur (Vanuatu) or the Nyiracongo (Democratic Republic of Congo) lavas, that which are also rich in iron and alkaline-earth elements.

The first viscosity measurements performed on the Yasur lavas, free from crystals and volatiles, show that Na/K ratio the viscosity variations result in viscosity variations that depending on chemical composition cannot be reproduced using an ideal mixing model of the configurational entropy. Consequently, it appears that Na and K elements do not mix randomly in the studied depolymerised iron-bearing aluminosilicate melts. During this communication, we plan to will present and discuss new viscosity, Raman and Fe K-edge Xanes X-Ray Absorption Near the Edge Structure at the Fe K-edge data, and try to establish some links between the melt structure and properties in order to better understand magmatic processes.

Reference: Losq C. and Neuville D.R. (2013) Effect of K/Na mixing on the structure and rheology of tectosilicate silica-rich melts. *Chemical Geology*, 346, 57-71.

**Keywords:** aluminosilicate glasses, redox, lava, viscosity.

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# The role of Pb in silicate glasses and melts

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Lead silicate glasses are important materials from different points of view, societal, environmental and in material science. Indeed these glasses are known for a long time for their very high performance, they also play an important role in the management of lead as a waste. Lead silicate glasses and melts have been already investigated and display an important decrease in viscosity and T<sub>g</sub> when PbO is added to SiO<sub>2</sub>, whereas a large depolymerisation is observed by Raman spectroscopy where the Q species decrease from Q<sub>4</sub> to Q<sub>0</sub> when the PbO content varies from 2 up to 80% [1].

In order to better understand the role of Pb in silicate glasses, we have decided to substitute Pb by Ca or Al. We have synthesized different glasses with simple compositions in the systems (PbO-CaO-SiO<sub>2</sub>) and (PbO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>).

All new and previous glasses are investigated by XANES at the Pb LIII-edges, and reveal that Pb keeps its Pb<sup>2+</sup> form in all compositions.

We present some new viscosity measurements and Raman spectroscopy results, and discuss them by using the Adam and Gibbs theory which gives the configurational entropy which can be discussed in terms of Q species as already shown by Le Losq et al. (2014) [2].

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C. Le Losq, D.R. Neuville, P. Florian, G.S. Henderson, D. Massiot (2014) *Geochim. Cosmochim. Acta*, 126, 495-517.

**Keywords:** glass lead aluminium calcium silicates properties

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\*Speaker

# IR-Investigation of Glass Transition in Thin Films of CF<sub>3</sub>-CFH<sub>2</sub> Cryodeposites

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In the course of our recent studies of the formation processes and properties of thin films of Freon 134a (CF<sub>3</sub>-CFH<sub>2</sub>) cryovacuum condensates, was observed, that in the temperature range from 70 K to 90 K, the sample undergoes a number of structural transformations. This is reflected both in the change of the absorption character and in absorption bands position of the IR spectra for practically all vibration modes of the CF<sub>3</sub>-CFH<sub>2</sub> molecule. This paper is a continuation of these studies and aimed get answer to the question of whether we are observing a glass transition in solid Freon 134a and what is the value of T<sub>g</sub> in this case. For this purpose, measurements at different cryodeposition temperatures of samples in the vicinity of presumed glass transition temperature were taken. On the basis presented results, and our previous obtained data the assumption of presence of structural transformations in cryofilms is made: at a temperature in the vicinity of 72 K, a classical transition takes place the glass state-supercooled liquid (G-SCL). We believe that the value of the temperature of this glass transition is approximately T<sub>g</sub>= 72 K. The temperature range from 75 to 78 K is the area of the quasi-stable SCL existence. At a temperature of about 78 K, crystallization of SCL into the state of an orientationally disordered plastic crystal-OG orientation glass begins. At a temperature T<sub>trans</sub>=80 K, a quasi-glass transition occurs from the state of the OG orientation glass to a plastic crystal with an ordered rotational subsystem of the PC. In the temperature range 83-85 K, a plastic crystal - monoclinic crystal.

**Keywords:** Freon134a, cryovacuum condensates, IR spectrometry, Glass transition

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# Highly coherent mid-infrared supercontinuum generation by chalcogenide optical fiber

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Recent years have seen a rapid growth in interest in mid-infrared (MIR) light source for many applications, such as optical coherence tomography, metrology, and bio-photonics diagnostics. For these applications, a spatially coherent light source is suitable to realize high spatial resolution imaging because it can be focused to a diffraction limited spot size. To realize the high spatial coherent light source, supercontinuum (SC) generation in an optical fiber has been receiving an attention. In this decade, researchers have developed various type of fiber such as photonic crystal fiber, microstructured optical fiber, and rib-waveguide to obtain the MIR SC spectrum. However, intrinsic transmission window of fused silica restrains the SC expansion beyond 3  $\mu\text{m}$ . To extend the SC spectrum beyond 3  $\mu\text{m}$ , alternative materials have been proposed, such as tellurite and fluoride glasses. These glasses have large advantages because of their wide transmittance window, and high nonlinearity. To obtain the SC further into the MIR region, chalcogenide glasses with a wide transmission window beyond 10  $\mu\text{m}$  are attractive. Mostly, broadband SC has been generated by pumping in the anomalous group velocity dispersion regime close to the zero-dispersion wavelength (ZDW). Typical SC light generated by this scheme has a complex temporal profile, are sensitive to input pulse fluctuation and pump laser shot noise. To avoid this effect, SC generation in the normal dispersion regime has been studied recently. In this study, we use chalcogenide double clad fiber (Ch-DCF) to obtain the MIR SC spectrum in the normal dispersion regime as the first step towards the highly coherent MIR SC generation. We experimentally demonstrated the **highly coherent** MIR SC extending from 2 to 14  $\mu\text{m}$  in 2.8 cm-long Ch-DCF. **The result** indicates that the Ch-DCF is a promising candidate to generate the highly coherent MIR SC generation.

**Keywords:** Chalcogenide fibers, Nonlinear optics, Supercontinuum generation

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\*Speaker

# All-solid tellurite photonic bandgap fiber fabrication for dynamic photonic bandgap control

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Photonic bandgap (PBG) control in photonic bandgap fibers (PBGFs) enables a variety of applications ranging from tunable bandpass filters to nonlinear optical devices. The common technique for PBG control in PBGFs is to change the fibers' refractive index by adjusting the glass material composition or change the periodic structure in the cladding. Optical Kerr effect (OKE) is a third-order nonlinear phenomenon which refers to a change in the refractive index induced by an applied electric field through a nonlinear polarization generated in the optical fibers. It can lead to the intensity dependence of the refractive index profile and the generation of all-optical dynamic PBG control. For tellurite optical fibers, the nonlinear refractive index coefficient ( $n_2$ ) is  $5.9 \times 10^{-19}$  m<sup>2</sup>/W, which is almost two orders of magnitude larger than that of silica optical fibers (10-20 m<sup>2</sup>/W). All-solid tellurite PBGFs with high nonlinear refractive index coefficients can lead to significant OKE. Based on it, all-optical dynamic PBG control can be achieved, which could be applied to all-optical switch system. In this paper, all-optical dynamic PBG control by OKE was investigated in an all-solid double-clad tellurite PBGF which was fabricated based on TeO<sub>2</sub>-Li<sub>2</sub>O-WO<sub>3</sub>-MoO<sub>3</sub>-Nb<sub>2</sub>O<sub>5</sub> (TLWMN, high-index rod) glass, TeO<sub>2</sub>-ZnO-Na<sub>2</sub>O-La<sub>2</sub>O<sub>3</sub> (TZNL, inner cladding) glass and TeO<sub>2</sub>-ZnO-Li<sub>2</sub>O-K<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> (TZLKAP, outer cladding) glass. The PBGF was fabricated by the stack-and-draw technique. The all-solid double-clad tellurite PBGF with  $d=5.4$  mm and  $L=9.0$  mm was obtained. At the pump peak power of 200 kW, the signal of 1570 nm, dynamic PBG control was achieved in this all-solid double-clad tellurite PBGF both numerically and experimentally. This is the first demonstration of all-optical dynamic PBG control in optical fibers.

**Keywords:** Kerr effect, Nonlinear optics, Tellurite glass fiber, Photonic band gap

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\*Speaker

# ARTISTIC AND MANUFACTURING GLASS HERITAGE IN THE CENTRE-VAL DE LOIRE REGION IN FRANCE

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The *Centre-Val de Loire* region (France) has a rich glass heritage thanks to abundant artistic and manufacturing activities. We can quote the Henri de Navarre (1895-1971) workshop of *Saint-Benoît-sur-Loire* (Loiret - France), glass workshops in Vierzon (Cher – France) from 1861 to 1951, the glassworks of the Loing valley established from 1752 (historic glasswork of *Bagneaux-sur-Loing* and then Corning workshops), the glasswork society of *la Chapelle-Saint-Mesmin* from 1927.

The many museums of this region testify of this past. For example, the *Vierzon* museum with its large collection of whimsies, the Museum of Fine Arts in *Orléans*, and the Museum of Fine Arts in *Chartres*.

This study presents a transversal approach on glass research with physicochemical, technical, sociological and artistic points of view. Selected museum glass pieces are analyzed in composition, and according to the technical processes thanks to the collaboration of the *Verrerie d'Art d'Amboise Patrick Lepage*. Similar glasses are duplicated to study the durability properties in various atmospheric conditions. A second approach is to integrate the cultural and sociological dimension around the traditional and contemporary glass work thanks to records research and their analysis. Artistic dimension is included to this work in a creative and transversal approach art/science/heritage.

**Keywords:** Glass durability Glass structure Heritage

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\*Speaker

# Modification of spin-coated thin chalcogenide films composition by source solution doping

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Chalcogenide glasses are promising materials for fabrication of optical (micro)elements due to high values of refractive index and wide transmission window in IR. Chalcogenide glasses are frequently used in a thin film form, most commonly deposited by vacuum thermal evaporation, but other techniques based on their solubility in volatile organic bases are recently gaining attention (e.g. spin-coating, spiral-bar coating, etc.). Main advantage of solution based thin films lies in the simplicity and thus low cost of used deposition techniques. Research in this field is mostly focused on glasses of As-S system. Nevertheless, thin films of non-toxic glass compositions (e.g. Ge-S, Ge-Sb-S systems) have been successfully deposited in optical quality using these techniques as well.

The standard procedure of the thin film preparation via solution way requires synthesis of the source bulk glass of the desired composition by standard melt-quenching method, dissolving in organic amine followed by deposition by chosen technique. The composition of prepared thin films corresponds to the composition of the source bulk glass.

In presented work we demonstrate the possibility to modify the thin film composition by changing the composition of source glass solution. Glass solution was prepared using As<sub>40</sub>S<sub>60</sub> bulk glass and the 5N sulfur targeting As<sub>30</sub>S<sub>70</sub> composition. Thin films in specular optical quality were obtained using spin-coating method. Optical properties, thickness, chemical resistance, structure and elemental composition of the thin films were studied in dependence on the annealing temperature. Results were compared with properties of thin films of the same As<sub>30</sub>S<sub>70</sub> composition prepared by standard procedure from As<sub>30</sub>S<sub>70</sub> bulk glass. Different thermo-induced structural transformations were observed in both sets of samples resulting in As<sub>30</sub>S<sub>70</sub> thin films of very similar properties. The possibility to alter the thin film composition by modifying the composition of the glass solution significantly simplifies the tailoring of the materials properties. Authors appreciate financial support from projects and grants No. 16-13876S (GACR), LM2015082 and ED4.100/11.0251 (MEYS Czech Republic) and CZ.02.1.01/0.0/0.0/16.013/0001829 (European Regional Development Fund-Project).

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\*Speaker

**Keywords:** chalcogenide glasses, thin films, spin, coating



# Compositional effects on the rheology of glass particle suspensions

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Vitreous enamel slips are characterized by the mixture of two or more solid phases – usually composed by glass frits, clays and additives – in an aqueous solution. The aim of this study is to shed light on the ionic interaction between clay and glass particles, which are assumed to govern the rheological properties of the slip. Therefore a series of aqueous suspensions using glasses of the composition  $x\text{Na}_2\text{O} \ y\text{CaO} \ (100-x-y)\text{SiO}_2$  with  $x = 0\text{--}26$  and  $y = 0\text{--}10$  are prepared. Oscillating rheometry at ambient temperature is used to investigate the viscoelastic behaviour of the slips. In particular, amplitude and frequency sweeps are performed to determine the time-dependent storage-to-loss modulus ratio from which the stability of the suspension is derived.

**Keywords:** rheology, suspension, enamel, slip, viscoelasticity, glass particles

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# Physico-chemistry of chromia in silicate melts

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Glass industry requires metallic devices in contact with molten silicates. When platinum and ceramic cannot be used, chromia-forming superalloys are generally used. The passivation of the alloy is ensured by the growth of a chromia Cr<sub>2</sub>O<sub>3</sub> layer by oxidation of the alloy. The passive state depends on the stability of the protective layer of Cr<sub>2</sub>O<sub>3</sub> in molten silicates. The limitation of the dissolution of Cr<sub>2</sub>O<sub>3</sub> into the glass solvent leads to a lower corrosion rate of the alloy. Thermodynamic data of chromium in melts (e.g. the solubility limit, the speciation, the diffusion in melts) are necessary to estimate the lifetime of the protective layer. The chemical equilibria are modified by the temperature, the basicity, the oxygen fugacity and the viscosity. To evaluate the influence of these parameters, simplified compositions have been chosen in the following systems: Na<sub>2</sub>O-SiO<sub>2</sub>, Na<sub>2</sub>O-CaO-SiO<sub>2</sub> and Na<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. Equilibration of Cr<sub>2</sub>O<sub>3</sub>-rich melts has been reached through the use of a specific device allowing the independent control of glass composition, temperature and oxygen fugacity. These samples have then been characterized by SEM observation, EPMA measurements and UV-visible spectroscopy. Electrochemical measurements were performed in Cr<sub>2</sub>O<sub>3</sub>-rich melts in order to determine diffusion coefficient of Cr in the medium.

**Keywords:** chromia, molten silicates, dissolution

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\*Speaker

# Impact of Chirality on the Glass Forming Ability and the Crystallization from the Amorphous State of 5-ethyl-5-methylhydantoin, a Chiral Poor Glass Former

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The investigation of the glassy state of 5-ethyl-5methylhydantoin (*i.e.* 12H, a chiral active pharmaceutical ingredient) was attempted by Differential Scanning Calorimetry (DSC) and Fast Scanning Calorimetry (FSC). This compound exhibits a high crystallization propensity for every enantiomeric composition. Nevertheless, glassy states of pure enantiomer or mixtures between enantiomers were successfully reached by FSC at cooling rates of: 1000°C/s and 300 °C/s respectively, even though limitations on the sampling reproducibility were evidenced due to FSC sample size. The Glass Forming Ability (GFA) was proven to increase with the counter-enantiomer content. From the glassy state, pure enantiomer displayed a more pronounced crystallogenic character (with a crystallization occurring 36°C below T<sub>g</sub> during ageing) than that of the mixture between enantiomers. Ageing of amorphous 12H promotes a strong nucleation behavior in both samples but enantiopure 12H crystallizes upon ageing while scalemic 12H evolves towards the metastable equilibrium. Finally, potential new phase equilibria (previously not reported) in the enantiomeric phase diagram could have been highlighted by FSC by recrystallization from the amorphous state.

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**Keywords:** Fast Scanning Calorimetry, Glass Forming Ability, Chirality, Glassy state, Physical ageing

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# Study of point defects associated with phosphorus by theoretical and experimental spectroscopic coupling

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We characterize phosphorus-related defects in glasses by experimental and theoretical approaches. The original approach is to incorporate hypotheses obtained from experimental measurements on irradiated phosphate glasses into the modeling of the structure of P-point defects in order to be able to reproduce by calculations the spectroscopic signatures of unknown defects. The strength of the proposed theoretical-experimental approach is to be able to provide responses on dopant-related defect precursors by characterizing them via ab initio calculation of their optical absorption spectroscopic and EPR signatures while simulating their formation mechanism (precursor nature).

**Keywords:** phosphate glasses, point defects, EPR

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# Polyfunctional photo-thermo-refractive glass: combining photo-thermo-induced crystallization, chemical etching and ion exchange technologies

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Nowadays, commercially available photoetchable materials are Foturan (Schott, Germany) and PEG3 (Hoya, Japan) that are used for fabrication of microreactors, various sensors, "lab-on-a-chip" devices. However, these materials possess low optical characteristics, which limits their applications in optics, photonics, and plasmonics. On the other hand, photo-thermo-refractive (PTR) glass is well-known material for recording Bragg gratings with diffraction efficiency up to 99%. PTR glass is a multicomponent one that changes its refractive index after an exposure to the near UV radiation and the subsequent heat treatment that leads to the formation of silver nanoparticles and NaF nanocrystals in the glass host.

We present the results of studies on ion-exchangeable and photoetchable properties of PTR glass. PTR glass based on Na<sub>2</sub>O–ZnO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–F–Br system doped with CeO<sub>2</sub>, Sb<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, and Ag<sub>2</sub>O was synthesized for further investigation. Irradiation of the samples were carried out by either high-pressure mercury lamp or pulsed fs Ti:Sapphire laser (790 nm).

The rate of chemical etching PTR glass ceramics in the HF solution greatly exceeds that for the glass. It can be explained by a good solubility of NaF crystals in hydrofluoric acid and nanoscale effect. Hollow 3D channels were formed in the bulk of PTR glass with fs laser irradiation, subsequent heat treatment and chemical etching. Such hollow structures can be used for developing various sensors and "lab-on-a-chip" devices based on PTR glass.

The presence of sodium in PTR glass composition allows one to focus on the ion exchange technology widely used for formation of silver nanostructures. Moreover, silver ions in the ion-exchanged layers of PTR glass can be transformed into either luminescent silver molecular clusters or plasmonic silver nanoparticles by adjusting temperature of subsequent heat treatment. Such structures can be used for developing integrated microfluidic-plasmonic sensors.

Thus, combining photo-thermo-induced crystallization, chemical etching, and ion exchange technologies in the glass opens up new prospects for developing "lab-on-a-chip" devices with luminescent and plasmonic nanostructures formed directly in 3D hollow channels.

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\*Speaker

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**Keywords:** photothermorefractive glass, chemical etching, ion exchange.

# Phase function for anomalous scattering of light in nanostructured glasses

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Glass-ceramics and phase-separated glasses frequently demonstrate the so-called anomalous light scattering: wavelength dependence of the scattering coefficient in visible light spectral range is described by the power law with the constant exponent ( $-p$ ), where  $p$  is appreciably greater than the Rayleigh value 4. Earlier we used a simple model to express the phase function and asymmetry parameter for scattering of non-polarized incident light in terms of experimental value of  $p$  ( $p > 4$ ) (M.P. Shepilov, Opt. Lett. 42 (21) (2017) 4513-4516). In this work, we use the same approach and obtain the phase functions of scattered light for linearly polarized incident light. The results are compared with the results of classical experiments carried out by Kolyadin in the mid-1950s for phase-separated glass. I express my gratitude to the Russian Foundation for Basic Research (16-03-01130).

**Keywords:** glass, ceramics, phase, separated glasses, light scattering, phase function, structure factor

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\*Speaker

# Application of several structural models to description of light scattering by nanostructured glasses

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For most glass-ceramics and phase-separated glasses, wavelength dependence of scattering coefficient in some spectral range comparable to visible light spectral range is described by the power law with the constant exponent ( $-p$ ). The exponent  $p$  can take the values up to 9 and frequently is markedly greater than the Rayleigh value  $p = 4$ . This phenomenon is caused by interference effects and is known as anomalous light scattering. To explain the phenomena, we consider a nanostructured glass as a system of identical spherical particles (scatterers) distributed in homogeneous matrix, use several models of their mutual arrangement and examine interparticle interference effects. The model of independent scatterers and the model of hard spheres in the Percus-Yevick approximation cannot explain the anomalous scattering because ordering in the arrangement of spheres in these models is low. To increase ordering in the system, the Percus-Yevick approximation is applied to exclusion zones surrounding particles, and anomalous light scattering is demonstrated for small volume fraction of particles ( $< 0.1$ ); however, the pair correlation function of particles in this case contradicts experimental data and qualitative considerations. And finally, we have concluded that the model where particles interact through a screened Coulomb potential is most suitable for description of anomalous light scattering. For this model, an analytical structure factor derived in the literature in the (rescaled) mean spherical approximation well describes ordering and interference effects. Earlier the model was applied to interpretation of small angle neutron scattering by glass-ceramics. Variation of the parameters of the model allows one to describe the peculiarities of anomalous light scattering. I express my gratitude to the Russian Foundation for Basic Research (16-03-01130).

**Keywords:** glass, ceramics, phase, separated glasses, light scattering, interparticle interference, structure factor, ordering effects

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\*Speaker



# Investigation of vapor cryodeposited glasses and glass transition of tetrachloromethane films

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Establishing a connection between the molecules structure and their cryodeposited conditions on the one hand, and the glass properties formed at low temperatures, such as the degree of kinetic stability, on the other hand, it is an important and hitherto completely unsolved problem of physical-chemistry condensed matter. The organic molecules in combination with the method of their gas-phase cryocondensation provide wide experimental possibilities for studying the glasses and their thermally stimulated transformations, including glass transitions [1, 2]. The object of investigation is tetrachloromethane. In the process of studying the effect of molecules anisotropy on the kinetic characteristics of glasses formed at low temperatures [3]. The results of IR-spectrometric studies of CCl<sub>4</sub> cryovacuum condensates thin films formed on a metal substrate in the temperature range from 16 to 100 K and gas phase pressures P=10-5 Torr are demonstrated. The thermograms of the absorption band position changing are analyzed, which are a consequence of thermostimulated transformations in the CCl<sub>4</sub> cryofilm.

(Figures)

The left figure shows fragments of absorption spectra of CCl<sub>4</sub> cryogenic film 2.5 μm thick, obtained at these heating temperatures. The right figure shows the corresponding thermogram obtained at the observation frequency = 799 cm<sup>-1</sup>. The thermogram behavior features correspond to the temperature intervals of the structural transformations shown in the figure in the sample.

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**Keywords:** tetrachloromethane, glass transitions, cryofilm

# Development of REE-doped chalcogenide fibers for active mid-IR optics

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Experimental results of the development of high-purity undoped and rare-earth doped chalcogenide glasses and optical fibers for mid-IR sensing and active fiber optics were presented. Research was carried out in the following directions: 1) search of optimum glass compositions for active and passive mid-IR optics, 2) development of purification methods of components and glasses, 3) development of optical fibers capable to withstand the high power of the laser pumping and having specified luminescence characteristics in the spectral range 2-6  $\mu\text{m}$  [1,2]. Methods for the synthesis of high-purity Ge-S(Se)-Ga, Ge-As-Se-Ga(In), Ge-Sb-Se-Ga(In) glasses, host and doped with 0.05-0.2 at.% Pr(3+) and Dy(3+) ions, have been developed. Glasses with a low tendency to crystallization, a high glass transition temperature, and a high luminescence yield in the mid-IR were produced. Optical fibers were obtained; their optical losses and emission characteristics were studied. The influences of the laser pump power at the wavelengths of 1.55 and 1.97  $\mu\text{m}$  on the emission intensity for the REE-doped glass fibers were studied. For the first time, the emission properties of REE-doped glass fibers with lengths corresponding to values for requirements of the laser generation model developed in [3] have been experimentally characterized. For the first time, the capabilities of optical fibers to withstand the high power of the laser pumping (up to 1.5 W) were demonstrated.

Prepared fibers were used in the experimental optical scheme as a broadband radiation source for the analysis of liquid media having absorption bands in the spectral range of 2.2-2.7 and 3.5-5.5  $\mu\text{m}$ . Experimental modeling of the sensor geometry for increasing of the analytical sensitivity have been carried out.

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**Keywords:** chalcogenide glasses, REE, preparation, fibers, luminescence, middle IR FEWS

# Spin-coated As<sub>30</sub>Se<sub>70</sub> chalcogenide glass thin films – novel approach for solvent formulation

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Chalcogenide glasses (ChGs) are semiconducting materials with high refractive index and wide IR transmission window. Due to their unique properties, they have found many applications in optics, optoelectronics and photonics. ChGs can be used in a form of bulk material, fibers or as a thin film deposited on appropriate substrate. The thin films are frequently deposited by physical vapor deposition techniques (e.g. thermal evaporation, laser ablation, etc.) but solution based techniques (e.g. spin-coating, dip-coating, spiral bar-coating, etc. [1]) which exploit solubility of ChGs in volatile alkaline amines are also gaining attention. The main advantage of solution based deposition techniques lies in low cost instrumentation, simplicity of thin films deposition and ability to use flexible substrates. However, poor solubility of selenide ChGs in volatile amine solvents limits the variety of glass compositions suitable for solution processing. Previously, the arsenic-selenide thin films were deposited from ethylenediamine [2] or ethanolamine [3] solutions but their optical quality, roughness or targeted composition were highly affected. Also, the high boiling points and low volatility of used solvents dampened the possibility of successful organic residuals removal from deposited thin films.

In this work, we present the study of volatile amine-based solvent formulation and its influence on As<sub>30</sub>Se<sub>70</sub> ChG solubility and dissolution mechanism. The stable solutions of quantitatively dissolved selenide ChG were used for spin-coating of thin films in specular optical quality. The post-deposition thermal treatment proved to have high impact on thickness, optical properties and structure of studied thin films. The content of organic residuals was also significantly reduced. The proper solvent formulation and thermal stabilization process yielded the thin film with high refractive index, very low surface roughness and composition close to the source bulk glass.

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**Keywords:** Chalcogenide Glasses, Thin films, Spin coating, Solution Processing

# Producing bulk ZIF-62 glasses by optimizing melt-quenching process

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Zeolitic Imidazolate Framework (ZIF) glasses are a newly emerged family of melt-quenched (MQ) glasses [1-3]. ZIFs are a subset of metal-organic frameworks (MOFs). Very recently, ZIF-62 has been found to be an outstanding glass former [4], which has a chemical formula of  $\text{Zn}(\text{Im})_{1.75}(\text{bIm})_{0.25}$ , where Im and bIm refer to imidazole ( $\text{C}_3\text{H}_3\text{N}_2$ ) and benzimidazole ( $\text{C}_5\text{H}_7\text{N}_2$ ), respectively. MQ ZIF-62 glass exhibits a number of interesting features such as ultrahigh Poisson's ratio and high transparency [3]. However, producing a bulk sample from ZIF-62 is a challenge, mainly because of a limited amount of reactants accessible to an optimum reaction and of high oxidation probability of the sample during heating-quenching protocol. The latter factor leads to degradation of the framework during the melt-quenching process.

In this work, we optimize the production process of ZIF-62 glass to get large-sized bulk samples by adjusting various parameters such as melting temperature, time and gas used in an electric furnace. Samples of around 200 mg were produced, by heating to 460C and varying the dwell time. With extension of melting time, an interplay between homogenization of the sample and decomposition caused by remnant oxygen has been observed. Final glass samples were characterized by measuring density and by taking scanning electron microscopy from cross-sections of the sample. Glass transition temperature was determined by performing differential scanning calorimetry and thermogravimetry measurements. Hardness measurements were also conducted in order to initially assess the influence of dwell time at 460C on mechanical properties and cracking behavior of bulk ZIF-62 glasses. Finally, we have obtained homogeneous glasses of diameter of about 1 cm. This work provides some information that is useful for upscaling of MOF glass production.

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\*Speaker

**Keywords:** Melt Quenched Zeolitic Imidazolate Framework Glasses, Structure of glasses, Glass properties, Glass formation, Glass production



# Corrosion of Ni-30Cr alloy in silicate melts: electrochemical measurements

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Contact between a metal and a molten silicate occurs in many industrial applications. For example, soda-lime silicates can be encountered in the glass fibering industry and boro-silicates are used in the vitrification process of nuclear wastes. Chromia-forming Ni-based superalloys are often used in these applications as they exhibit good mechanical properties and a high resistance to corrosion by molten silicates.

Considering the ionic conductivity of molten silicates, electrochemical methods are perfectly adapted for:

- the characterization of the medium (electroactive domain, potential measurements)
- the determination of physico-chemical properties of multivalent species (diffusion coefficient, standard potential)
- the study of corrosion of metal (active or passive state)

In this work, simplified systems are investigated to evaluate the influence of several parameters (e.g. basicity, viscosity) of the medium on the corrosion of materials. These systems are binary soda silicates Na<sub>2</sub>O-SiO<sub>2</sub>, ternary soda-lime silicates Na<sub>2</sub>O-CaO-SiO<sub>2</sub> and boro silicates Na<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>.

A classical three electrodes design has been adapted to high temperature conditions. The reference electrode is made of Yttria-Stabilized-Zirconia (YSZ), and the counter electrode is a platinum plate. Two kinds of working electrodes can be used: (i) the characterization of the properties of the silicate melt and of the dissolved species requires a platinum working electrode, and (ii) corrosion studies require a working electrode consisting of the considered alloy. With the latter type of electrode, I vs. E plots can highlight the existence of a passive domain of the alloy, and thus give access to the passivation current. Consequently, the active or passive state of the alloy can be given by a simple potential measurement, which can thus evidence the depassivation of the alloy vs. temperature or time.

**Keywords:** corrosion, electrochemistry, nickel base alloys, molten silicates

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\*Speaker

# Blurring behavior of a fingerprint on Hierarchical Nanoporous Layer glass.

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Hierarchical Nanoporous Layer (HNL) glass is a functional material which has nanoporous structure on its surface. The HNL is simply formed by alkaline etching of a silicate glass. Optical low-reflectivity and long-life super-hydrophilicity which results in anti-fogging, anti-fouling and so on characterize the HNL glass. Furthermore, we have recently found a phenomenon that fingerprint attached on a HNL glass gradually gets indistinct. In order to elucidate the mechanism of the phenomenon, we conducted an IR absorption spectroscopy and an optical micrograph analysis.

The IR measurement was performed for a centimeter-size spot on HNL glass with and without fingerprints, that provides an averaged value for the relatively large area in comparison with a fingerprint pattern. The obtained spectrum for a fingerprint-attached HNL glass was different from unattached one and did not change even after the fingerprint got indistinct. This indicates the total amount of organic substance in the fingerprint was unchanged. The fingerprint was not decomposed and indicated to rapidly diffuse on the HNL.

We then analyzed optical micrographs to evaluate the speed of the blurring and the diffusion constant. The environmental dependence like humidity will also be discussed.

**Keywords:** fingerprint, surface diffusion, porous structure

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# Viscosity of TeO<sub>2</sub>-based glasses

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Glasses based on tellurium oxide are of particular interest due mainly to their relatively low melting temperature, high refractive index and high third-order non-linear susceptibility [1]. Because of their exceptional properties tellurite glasses are promising materials for a broad range of technological applications. To our knowledge, there are limited studies on the viscosity of tellurite glasses. In this work, we present results of a viscosity study of binary and ternary TeO<sub>2</sub>-based glasses including the systems: ZnO-TeO<sub>2</sub> as a function of ZnO content and R<sub>2</sub>/3O-ZnO-TeO<sub>2</sub> (R=B, Al) where ZnO is replaced by B<sub>2</sub>O<sub>3</sub> or Al<sub>2</sub>O<sub>3</sub>. All glasses were prepared by melting in Pt crucibles, the structure of glasses was characterized by Raman and infrared spectroscopy and was correlated with the viscosity-temperature behavior of glasses.

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We acknowledge support of this work by the project "Advanced Materials and Devices" (MIS 5002409), implemented under the "Action for the Strategic Development on the Research and Technological Sector", funded by the Operational Programme "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014-2020) and co-financed by Greece and the European Union.

**Keywords:** Tellurite glasses, viscosity

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\*Speaker

# Synthesis, thermal, structural and linear optical properties of new glasses within the TeO<sub>2</sub>-TiO<sub>2</sub>-WO<sub>3</sub> system

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The glass-forming domain and physical properties, namely, the density, thermal, structural and linear optical properties of new glasses within the TeO<sub>2</sub>-TiO<sub>2</sub>-WO<sub>3</sub> system have been investigated. By means of micro-Raman spectroscopy, the structure of these glasses was examined based on a full-scale spectral decomposition. The optical transmission and refractive index dispersion were measured by UV-Vis-NIR spectroscopy and spectroscopic ellipsometry respectively. Consistent correlations were established between the structural and linear optical properties. Only minor structural modifications of the original TeO<sub>2</sub>-rich network are taking place upon adding TiO<sub>2</sub> or WO<sub>3</sub>, suggesting the absence of Te–O–Te bond network depolymerization. Our results also suggest that, upon increasing TiO<sub>2</sub> content, a phase separation occurs between amorphous TeO<sub>2</sub>-rich and amorphous TiO<sub>2</sub>-rich regions. We also argue that the structural trends upon adding WO<sub>3</sub> evolve from uniformly dispersed WO<sub>6</sub> octahedra (at low WO<sub>3</sub> content) to amorphous WO<sub>3</sub>-like regions (at higher WO<sub>3</sub> content) before the crystallization of  $\gamma$ -WO<sub>3</sub> at 30 mol.% of WO<sub>3</sub>. The compositional dependence of the refractive index and several optical constants (Urbach EU and dispersion Ed energies, oxide ion polarizabilities) is highlighted. These glasses collectively exhibit high refractive indices in the order of  $\sim 2.2$ .

**Keywords:** Tellurite glasses, glass structure, Raman spectroscopy, linear optical properties

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# Strain rate sensitivity of germanium-selenium glasses

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Chalcogenide glasses are widely used in optical applications either as information carrier or as sensors due to their optical transparency in the mid-infrared window (8-15  $\mu\text{m}$ ), high refractive index and non linearity. Glasses from the GexSe1-x system have been extensively studied over the last decades because some of their physical properties do show an anomalous behaviour (Tg, density, band gap, indentation fracture toughness) at certain specific compositions for instance at x=20% also called the percolation threshold. In this work we studied the indentation behaviour of GexSe(1-x) ( $0 \leq x \leq 30$ ) under constant strain rate conditions. Instrumented Berkovich micro indentation were performed at different strain rates (from  $10^{-3}$  to  $10^{-1} \text{ s}^{-1}$ ) at ambiante temperature, indentation residual imprints were image by atomic force microscopy. Energies at stake during indentation, strain rate sensitivity (computed from Norton's law) as well as indentation imprints shape and volumes are discussed as a function of the litterature and glass structure. Experimental results are in good agreement with a similar study based on pure Se glass. From AFM pictures a transition behaviour is identified near the percolation threshold.

**Keywords:** Indentation, chalcogenide, strain rate, berkovich, atomic force microscopy, glass

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\*Speaker

# Crack velocity, fracture surface energy and fracture toughness of BaO-TiO<sub>2</sub>-SiO<sub>2</sub>

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The ternary BaO-TiO<sub>2</sub>-SiO<sub>2</sub> glass system has been potentially applied daily. Some mechanical properties of this system have been studied and most properties show a good agreement with the increase of the TiO<sub>2</sub> ratio. However, the relationship between the crack velocity ( $v_c$ ) and the stress intensity factor (KI) has not been shown elsewhere, especially with help of the SEPB method. In this study, with the relative humidity of about 60 %, the  $v_c$ -KI relationship of four different compositions varying by the increase of TiO<sub>2</sub> and the decrease of SiO<sub>2</sub> has been studied. The cross-head speed of 0.02  $\mu\text{m/s}$  has been used to obtain the stable test as shown in figure 1. Moreover, with this stable test, the work of fracture has been calculated, which leads to the calculation of fracture surface energy as well as the fracture toughness of these four glass composition in the system. A decrease of  $K_{Ic}$  is observed as the TiO<sub>2</sub> content is increased or as the SiO<sub>2</sub> content is decreased, while Young's modulus, Poisson's ratio and the atomic packing density are increased. This observation may find its source in the structural similarity between the fresnoite crystal and the glass structure[1].

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**Keywords:** Crack velocity, Fracture surface energy, Fracture toughness

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# Scintillation characteristics of borosilicate glass doped with Tb<sup>3+</sup>/ Ce<sup>3+</sup> ions

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The oxide glass doped with rare-earth ions (REI) are widely used as active media in optoelectronics, scintillation materials, UV-Vis radiation converters. Simplicity of synthesis of glassy materials, the ability to manufacture optical elements of any shape and size, relatively low cost, possibility to incorporate impurities, opportunity to change the host composition and high optical homogeneity makes them an alternative to single crystals.

The development of new materials with specific optical properties requires an understanding of the luminescence mechanisms in different systems, processes for electronic excitations between the luminescence centers and the glass host, the interaction of activated ions between them. All of this purposes directed to improving of luminescent characteristics and light yield for different applications.

In this work, we developed Tb<sup>3+</sup>/Ce<sup>3+</sup> doped Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-BaCO<sub>3</sub>-Gd<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> scintillating glasses by a melt quenching method. The luminescent properties were studied by the transmittance, photoluminescence, cathodoluminescence spectra and decay curves.

In nanosecond time range the strong "blue" emission (4f-5d transition) due to radiation of Ce<sup>3+</sup> ions under selective and non-selective excitation was recorded. The results are shown that the Ce<sup>3+</sup> ions sensitized the luminescence of the Tb<sup>3+</sup> ions by energy transfer process from Ce<sup>3+</sup> to Tb<sup>3+</sup> ions under UV and electron beam excitation.

The luminescence in "blue-green" region spectra for all investigated samples is occurred. The radiative transitions occur from the excited states 5D<sub>3</sub>, 5D<sub>4</sub> to the ground state 7F<sub>j</sub> in terbium ions.

The luminescence decay kinetics of glass excited by electron beams and pulse laser excitation was studied in detail. The mechanism of energy transfer between Tb<sup>3+</sup> and Ce<sup>3+</sup> ions are discussed.

**Keywords:** scintillating glass, luminescence decay kinetics, electron excitation

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\*Speaker

# Energy level of Ce<sup>3+</sup> at energy higher than 2000 cm<sup>-1</sup> in silica

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Among rare-earth ions, cerium is widely used in laser technology, fast scintillators and white emitting LEDs thanks to its ability to emit in the UV-visible. This emission band is due to the transition of an electron from the 5d energy levels to the 4f ones. As a consequence, the position of its emission wavelength depends strongly on the environment. It spans from UV in fluoride to red in nitride. Electrons on the two 4f levels (2F<sub>5/2</sub> and 2F<sub>7/2</sub>) are shielded from the external field by the 5s<sup>2</sup> and 5p<sup>6</sup> electrons. Then, the two 4f levels are usually known to be separated by  $\sim 2000$  cm<sup>-1</sup> whatever the change of the environment. However, it has been reported recently that a higher 4f energy level does exist in crystals, located at 3639 cm<sup>-1</sup> in Gd<sub>3</sub>Ga<sub>5</sub>O<sub>12</sub> [1] and  $\sim 4000$  cm<sup>-1</sup> in Lu<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> [2]. In cerium-doped silica glasses prepared by sol-gel, we have measured absorption spectra in the 4f energy levels domain. An absorption band at  $\sim 5300$  cm<sup>-1</sup> has been observed. During this presentation, we shall discuss on the origin of this absorption band, based on results obtained both in silica and silicates (silica containing aluminum or sodium) glasses prepared by sol-gel, melt-quenching and phase vapor (MCVD process).

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**Keywords:** Silicate, Cerium, 4f transition

# Development of PSS-free PEDOT transparent conductive film on Hierarchical Nanoporous Layer glass

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Transparent conductive films are widely used in electrical products such as touch panel devices. Indium tin oxide (ITO) is a typical material for it because it has a good balance between its conductivity and optical transparency though containing a rare metal and being vulnerable to bending. Therefore, a conductive polymer without any rare metals and with excellent flexibility attracts attention as a substitute material for ITO.

Poly (ethylene-3,4-dioxythiophene) / poly (styrenesulfonic acid) (PEDOT/PSS) is one of the most featured conductive polymers with excellent in conductivity, transparency and chemical stability. PSS in the PEDOT/PSS composite not only solubilizes PEDOT in aqueous solution but also supplies conductive carriers to PEDOT. PSS, however, can reduce the conductivity of the composite because PSS molecule itself is not conductive.

In this work, we tried to develop a PSS-free PEDOT film in combination with a hierarchical nanoporous layer (HNL) glass as a substrate. PEDOT was polymerized in the HNL pores with a polymerization initiator of iron chloride (III) and a carrier dopant of benzenesulfonic acid. The obtained PSS-free PEDOT film on HNL glass exhibited high sheet conductivity with high optical transparency.

**Keywords:** conductive polymer, hierarchical nanoporous layer glass, transparent, PEDOT/PSS

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# Investigations of Medium-Range Structure of Bioactive Borophosphosilicate Glasses by Solid-State NMR Experiments

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Borophosphosilicate (BPS) glasses are promising materials for bone tissue engineering [1]. Such glasses are termed bioactive, because when exposed to body fluids, they bond to bone/tooth by forming a layer of hydroxy-carbonate apatite (HCA) that features a similar composition as bone mineral. Compared with the B-free phosphosilicate counterparts, bioactive BPS glasses exhibit a faster degradation in aqueous solutions and a more complete transformation to HCA [1].

The bone-boding properties of BPS glasses depend on their short-range and medium-range structures. Our previous study on the short-range structures shows that BPS glasses consist primarily of BO<sub>3</sub>, BO<sub>4</sub>, and SiO<sub>4</sub> units, while P, as a minor component, exists mainly as readily leached orthophosphate groups, with the remaining forming one P–O–Si or P–O–B bridge (*Q1*) [2]. Here we will present results from studies of the medium-range arrangements of the BPS glasses, which were probed by an array of dipolar-coupling-based NMR techniques:

- (1) The intermixing of BO<sub>3</sub>/BO<sub>4</sub> units, as revealed by the <sup>11</sup>B homonuclear correlation experiments [3].
- (2) The distributions of BO<sub>3</sub>/BO<sub>4</sub> units around the orthophosphate groups, and their relative preferences for bonding to *Q1* units, probed by <sup>11</sup>B/<sup>31</sup>P heteronuclear 2D correlation and REDOR dephasing NMR experiments.
- (3) The relative contents of P–O–Si and P–O–B bridges, deduced from <sup>31</sup>P/<sup>11</sup>B heteronuclear dephasing experiments, and revealing a slight preference for P to bond to BO<sub>4</sub> [3].
- (4) The distributions of Na<sup>+</sup> cations around BO<sub>3</sub>/BO<sub>4</sub> units and the implications of its roles as network modifiers/charge-compensators, as investigated by the <sup>11</sup>B/<sup>23</sup>Na heteronuclear dephasing experiments compared with the molecular dynamic simulations.

We will also present results on the HCA formation from BPS glasses when subjected to a simulated body fluid (SBF), thereby evaluating the dependence of the *in vitro* bioactivity on the relative amounts of B, Si, and P in the glass matrix.

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**Keywords:** bioactive glasses, solid state NMR, borophosphosilicate, apatite formation

# Elucidating the Local Structure and the Mechanism for Hole Conductivity in Cu-As-Te Thermoelectric Glasses by XANES spectroscopy and Quantum Simulations

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Thermoelectricity (TE), efficiently converting wasted heat into electricity, can be considered a viable route to solid-state cooling and power generation. The main paradigm in the present researches on TE is focused on the "phonon glass electron crystal" model [1], which proposes an offbeat combination of glass-like low-thermal conductivity ( $k$ ) and crystal-like high-electrical conductivity ( $\sigma$ ). More recently, semi-conducting chalcogenide glasses, which are known to inherently possess high Seebeck coefficient ( $S$ ) and low  $k$ , are looked upon as potential TE materials [2]. The main limiting factor in these glasses is their mediocre  $\sigma$ . Recently it was found that doping glasses with Cu leads to a huge enhancement in  $\sigma$  [3]. 20% Cu-doping in arsenic telluride shows an increase in  $\sigma$  by almost 5 orders of magnitude ( $\sim 6$  S/m) compared to the pristine arsenic telluride glass ( $\sim 10^{-4}$  S/m), without dismantling its amorphous structure and its characteristic high  $S$  and low  $k$ . These Cu-As-Te glasses have been analyzed by X-ray Absorption Spectroscopy, both near-edge (XANES) and in the extended region (EXAFS), in order to shed light on the mechanism for the huge increase of conductivity that was found with Cu doping. Experimental data have been modeled by means of multiple-scattering calculations. Our model suggests that the experimental results can be interpreted in terms of a small charge-transfer from Te to Cu, leading to an unexpected positive valence for Te. On the basis of these findings, a global picture explaining the enhancement of electrical conductivity with Cu doping has been proposed: electrical conductivity is determined by the holes created in non-bonding Te

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5p orbitals (lone pair) by Cu acceptors [4]. The critical parameter to increase  $\sigma$  is the number of Cu-Te bonds that are formed and not simply the number of Cu atoms.

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**Keywords:** Chalcogenide glass, Thermoelectrics, Hole conductivity, XANES, Quantum calculations

# Controlled crystallization of amorphous ZnSb film for thermoelectric properties applications

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Thermoelectric materials show great promise for applications in many fields, including direct conversion of waste heat to generate electricity and application as solid state Peltier coolers [1]. Zinc antimonide (ZnSb) binary system is one of the promising P-type thermoelectric materials [2-3]. Generally, ZnSb based films prepared at room temperature are amorphous with poor electrical performance and appropriate heat-treatment is essential to improve its performance. In this work, Zn-Sb thin film was deposited by ion beam sputtering deposition method through a multiple target which combined by periodic the Zn and Sb strips. The experimental results show that the as-deposited zinc antimonide thin film has very high resistivity with amorphous structure. It has been found that the electrical resistivity of the film shows three distinguished steps during the heating process, which can be attributed to the crystallization fraction of the amorphous thin film at different temperatures. The amorphous film has an electrical resistivity of 4750 Wm, which dramatically decreases to 2.3'10<sup>-4</sup> Wm at 500 K thanks to generation of ZnSb crystals. Although the amorphous film has a larger Seebeck coefficient value of 1500 mVK<sup>-1</sup>, which decreases to 250 mVK<sup>-1</sup> after heating to 500 K, the power factor of the amorphous film is very low and it is greatly enhanced to 0.3 mWm<sup>-1</sup>K<sup>-2</sup> after crystallization.

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# Structural characterization of thin film chalcogenide glasses used in Ovonic Threshold Switches

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Chalcogenide materials exhibit a unique portfolio of properties which has led to their wide use for non-volatile memory applications such as optical data storage or more recently Phase-Change Random Access Memory. Chalcogenide glasses (CGs) exhibit a high transparency window in the IR range and large optical nonlinearities offering unique opportunities for elaboration of innovative mid-IR components. Besides, a huge nonlinear behavior of conductivity is observed in some CGs under electrical field application. Such CGs, mainly Se-based, are considered as promising materials to be used as Ovonic Threshold Switching (OTS) selector elements in 3D resistive memory arrays. The OTS mechanism consists in a switch between a high resistive (OFF state) and a low resistive state (ON state) when the voltage applied on the CG exceeds a critical voltage. When the current is reduced below the holding current density  $J_h$  the selector recovers its high resistive state. However, the underlying physical mechanism is still under debate with, up to now, two main classes of models involving a pure electronic effects or invoking a local structural change under field application. In that context, we investigated the origin of the OTS effect by means of a structural analysis of some prototypical and state-of-the-art GexSbySe(1-x)-based OTS glasses. The structure of selected thin films, differing significantly by the amplitude of the OTS effect and the performance of OTS devices, has been studied by means of Fourier Transform Infrared (FTIR) and Raman spectroscopy as well as X-Ray Absorption Spectroscopy. As a result, we elucidate how Sb and N doping change the structure of Ge30Se70 glass leading to improved OTS selector performance. Finally, from such a careful structural analysis of our prototypical OTS CGs compounds coupled with ab initio simulations, one will investigate the origin of the OTS mechanism in such state-of-the-art CGs.

**Keywords:** Chalcogenide Glasses, Nonvolatile Memories, Ovonic Threshold Switching

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# Kinetics Study of Non isothermal crystallization in SeX chalcogenide glasses

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Glass chalcogenide have become the subject of intensive research because of their potential applications in technologies. Several studies have developed to understand their properties; the thermal properties are very important which are based on thermoanalytical techniques such as differential thermal analysis DTA, or differential scanning calorimetry DSC. In general the chalcogenide glasses are based on three chalcogen elements Se,Te,S in conjunction with more electropositive elements as As, Sb and Bi. A study of kinetics of non isothermal crystallization process of SeX system was reported and interpreted in this work by different models based on JMA equation. From the differential scanning calorimetry DSC traces obtained under dynamic conditions, the energy of glass transition was determined by Lasocka relation, the activation energy of growth process and the value of n and m which are numerical factors depending on crystallization mechanisms are evaluated.

**Keywords:** Chalcogenide glass, glass transition, thermal parameter

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# Physico-chemistry of ZrO<sub>2</sub> in molten silicates: influence of the melt composition

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Due to its refractory properties and to its well-known low solubility in molten silicates, zirconia ZrO<sub>2</sub> is often used as a component in refractory bricks and crucibles in high temperatures applications involving contact with molten glass. This work proposes to study the interactions between zirconia and a multi-component soda-lime glass at temperatures comprised between 1200°C and 1400°C for times up to 100 h. SEM observation allowed to control the oversaturation of the samples and led to highlight phenomena as coalescence and phase precipitation. In the first minutes of contact, precipitation of zircon ZrSiO<sub>4</sub> was detected. Consequently, a similar study was performed on zircon directly in contact with the melt. The zirconium solubility was measured by EPMA (WDS), leading to dissolution kinetics. After a rapid increase, a stabilization of zirconium concentration is observed. Then, the precipitation of more stable zircon leads to a solubility decrease. Long term experiments have shown significant decrease of the solubility, attributed here to the volatilization of sodium from the melt, which consequently implies a change in its composition. Limits of solubility could thus be determined by choosing a compromised time of 2 hours. The influence of the main glass components on zirconium dissolution at 1200°C was also evaluated via enrichment of the basic composition with 5 and 10 wt.% of network modifiers (*i.e.* Na<sub>2</sub>O and CaO), a network former (*i.e.* B<sub>2</sub>O<sub>3</sub>) and an intermediate (*i.e.* Al<sub>2</sub>O<sub>3</sub>). Additions of Na<sub>2</sub>O and CaO led to the precipitation of new phases in equilibrium with the melt which were Na<sub>2</sub>ZrSi<sub>2</sub>O<sub>7</sub> and Ca<sub>2</sub>ZrSi<sub>4</sub>O<sub>12</sub> respectively. No phase precipitation was observed when B<sub>2</sub>O<sub>3</sub> or Al<sub>2</sub>O<sub>3</sub> were added. Addition of network former B<sub>2</sub>O<sub>3</sub> did not seem to influence zirconium solubility. However, zirconium solubility decreases significantly in the case of Al<sub>2</sub>O<sub>3</sub> addition, as network forming aluminates [AlO<sub>4</sub>]<sup>-</sup> requires charge compensation by Na<sup>+</sup> cations.

**Keywords:** zirconia, molten silicates, dissolution

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\*Speaker

# Optical Characterization of large glazing samples

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Optical evaluation of architectural and automotive glazing commonly involves the measurement of reflectance and transmittance of small sample up to 10 x 10 cm in a spectrophotometer that covers at least the entire solar energy range. There are samples however, that cannot be cut into smaller ones, like for instance tempered glass. Also square metre sized switchable glazing or complete car windshields and rooftop windows which are too expensive or difficult to take smaller sample from, pose a problem for commercial available optical instrumentation. Over the recent years, the authors have developed a number of accessories for commercial spectrophotometers that allows the glazing industry and building institutes to evaluate large samples. This paper gives an overview of the possibilities

**Keywords:** transmittance, reflectance, large sample, windscreen

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\*Speaker

# Effect of Alkali Phosphate Content on Foaming of CRT Panel Glass Using Mn<sub>3</sub>O<sub>4</sub> and Carbon as Foaming Agents

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Phosphates play a role in different foaming processes. In slag foaming, the phosphate can lower the surface tension and increase the foam life time. In the sintering–foaming process, sodium phosphates are added as "foam stabilizers". Although phosphates show some effect on slag foaming, their effect on the sintering–foaming process still needs to be clarified. Here, we investigate the influence of alkali phosphates (Li<sub>3</sub>PO<sub>4</sub>, Na<sub>3</sub>PO<sub>4</sub>, and K<sub>3</sub>PO<sub>4</sub>) on the glass foaming process, foam density, and glass transition temperature ( $T_g$ ) of waste cathode ray tube (CRT) panel glass foamed using Mn<sub>3</sub>O<sub>4</sub> and carbon. The results show that the  $T_g$  of foam glasses decreases with increasing the alkali phosphate content, and with decreasing the alkali ion radius. Furthermore, the foaming temperature is affected by the alkali phosphate, especially by Li<sub>3</sub>PO<sub>4</sub>. Thus, alkali phosphates can be used to decrease the heat-treatment temperature. However, only K<sub>3</sub>PO<sub>4</sub> and Na<sub>3</sub>PO<sub>4</sub> prove to be promising candidates for producing low density foam glasses. In addition, the foam glasses prepared from K<sub>3</sub>PO<sub>4</sub> prove to have a higher degree of closed pores.

**Keywords:** Cathode ray tube panel glass, Foaming, Closed porosity, Alkali phosphate

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