# Investigations of phosphate and silicate glasses and glass-ceramics deposited as nanometric thin films

Lionel Montagne*[1], François Méar[1], Laurent Delevoye[1], Frederique Pourpoint[1], Olivier Lafon[1], Hiroki Nagashima[1], and Thibault Carlier[1]

[1]Unité de Catalyse et de Chimie du Solide - UMR 8181 (UCCS) – Université d'Artois, Université de Lille, Sciences et Technologies, Ecole Centrale de Lille, Ecole Nationale Supérieure de Chimie de Lille, Centre National de la Recherche Scientifique : UMR8181 – Cité Scientifique - Bâtiment C3 59655 Villeneuve dÁscq Cedex, France

**Abstract**

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 form the support), the sensitivity was first improved by the incorporation of paramagnetic ions (Cu2+, Mn2+, Gd3+), 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-10Al2O3-48SiO2. 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 29Si 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 Q3 and Q4 sites. The crystallization is thus more constrained in the thin film, leading to less evolution of the Qn sites.

**Keywords:** glass thin films, glass, ceramics, phosphate, silicate

*Speaker