Combined Solid-State NMR and Molecular Dynamics Study of the Structure of Strontium-Aluminosilicate glasses

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Abstract

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 SiO2-Al2O3-SrO based glass compositions which are largely unexplored systems. Glasses on the compensation line Al2O3 = SrO, were studied with 17O, 29Si and 27Al 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 AlO5 units ranging from 2-5%. Variations of the 29Si NMR spectra, and to a less extent of 27Al 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 29Si NMR spectrum in terms of Qn(mAl) units (i.e., Qn connected to m Al units). Simulations of 17O NMR experiments from our first-principles methodology combined to 17O-27Al 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 17O MAS NMR spectra.

Keywords: Aluminosilicate, NMR, MD, DFT, Glass structure

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