Combining Experimental and Computational Solid State NMR for Structure Oetermination of Oxide Glasses

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Since solid-state NMR allows the observation of local chemical environment of atoms independently of the existence of long range order, it has now become a key tool to resolve the structure of glassy materials. Today, the high level of sophistication of multidimensional magic-angle spinning (MAS) NMR experiments allows structural motifs to be identified both at the short range order (i.e ~2A, such as silicate and borate polyhedra) and at the intermediate range order (2-8 A, connectivity patterns between these polyhedra).

However, despite these achievements, the spectral broadening associated to the structural disorder of glass often limits the detailed interpretation of NMR spectra. In complement to these advances in NMR techniques, the combination of molecular dynamics simulations and first-principles calculations of NMR parameters (GIPAW method) has therefore recently emerged as a valuable tool to significantly improve the assignment, detailed interpretation and processing of NMR spectra. This new approach offers new means to address several fundamental issues (in the context of glassy materials) : i) direct comparison of MD simulations with NMR experiments, ii) linking variations of the local structure (such as bond distances or angles) with NMR signatures ; iii) improving the analysis of the NMR parameter distribution. As will be shown, the last point is essential for accurate processing (fitting) of the experimental data.

All these NMR methodologies will be illustrated through applications to various oxide glasses and in particular borosilicate glasses modeling the French nuclear waste glass. In this context, applications to key issues will be presented: i) elucidation of the incorporation mechanisms of elements such as lanthanum and lead; ii) effects of irradiation on the glass structure; iii) impact of thermal history on chemical durability. Our latest methodological development based on Machine Learning will be presented.

Recent References

T. Charpentier et al., *Self-healing capacity of nuclear glass observed by NMR spectroscopy*, Scientific Reports, **2016**. Scientific Reports 6, 25499.

Y. Ishii et al., *A DFT-Based Aspherical Ion Model for Sodium Aluminosilicate Glasses and Melts*, J. Phys. Chem. C **2016**, 120, 24370-24381.

F. Angeli et al., *Structure and Chemical Durability of Lead Crystal Glass*, Environ. Sci. Technol. **2016**, 50, 11549-11558.

F. Angeli et al., *Effect of thermally induced structural disorder on the chemical durability of International Simple Glass*, npj Materials Degradation 2, 31 (**2018**)

T. Charpentier et al., *Structure of Strontium Aluminosilicate Glasses from Molecular Dynamics Simulation, Neutron Diffraction, and Nuclear Magnetic Resonance Studies*, J. Phys. Chem. B **2018**, 122, 9567-9583.

Z. Chaker et al. *NMR shifts in aluminosilicate glasses via Machine Learning*, in press.