Structural study of lanthanum aluminoborate glasses combining molecular dynamics, nuclear magnetic resonance and neutron diffraction

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In this work, we investigate the structure and properties of $(1-x)LaB_3O_6$-xAl_2O_3 glasses ($x \leq 0.375$) using solid state NMR and neutron diffraction combined with molecular dynamics simulations. This study aims at understanding the mechanism of aluminium oxide incorporation in lanthanum metaborate glass (LaB_3O_6) [1] and its impact on structural features.

^{11}B and ^{27}Al NMR experiments have been performed to obtain the atomic speciation of boron (BO_3 and BO_4) and aluminium ($AlO_{4,5,6}$). Two samples were enriched with oxygen-17 to obtain the BO, NBO population and advanced 2D through-bond heteronuclear correlation (^{17}O-^{11}B, ^{17}O-^{27}Al) was performed to highlights the distribution of NBO on the BO_x and AlO_x structural units, whereas ^{11}B-^{27}Al 2D NMR revealed their connectivity.

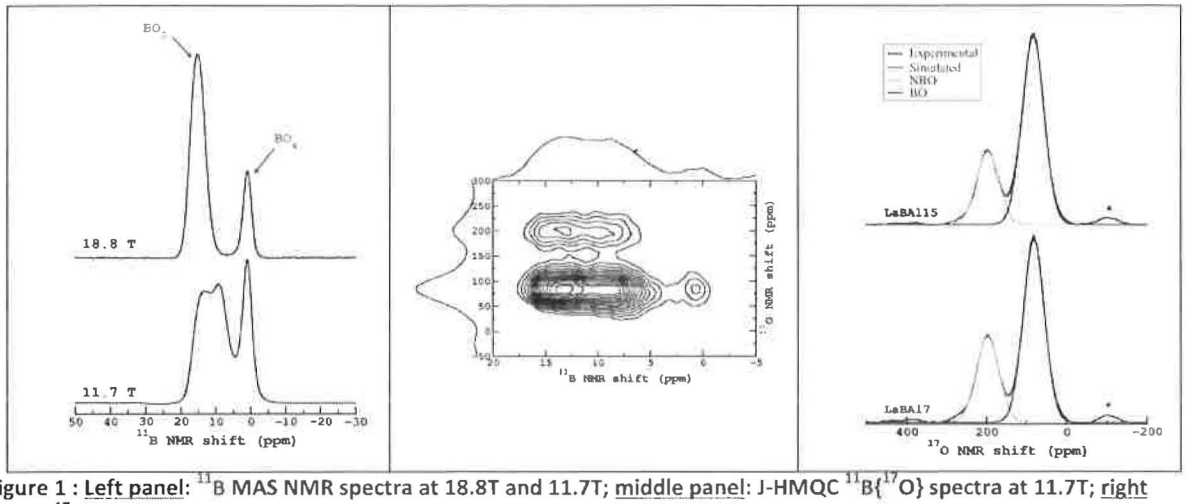

Figure 1 : Left panel: ^{11}B MAS NMR spectra at 18.8T and 11.7T; middle panel: J-HMQC $^{11}B\{^{17}O\}$ spectra at 11.7T; right panel: ^{17}O MAS NMR spectra at 11.7T

However, concerning superstructural units, more precise information are difficult to extract because of broad NMR shift distribution due to the amorphous structure of the glass. We therefore perform Molecular Dynamics (MD) simulations. As shown in previous studies [2], classical MD (based on empirical potential) cannot reproduce superstructural units in contrast to ab-initio MD (aiMD). Nevertheless, aiMD is an expensive computational time method and is therefore limited in the quenching rate so that too much liquid like structures are generated. In order to overcome these limitations, a Hybrid Reverse Monte Carlo modelling approach has been developed accounting for all constraints provided by NMR, in addition to the neutron and X-ray structure factors to converge into stable structures answering to all experimental data.

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