

An investigation of the mixed mobile ion effect in glasses

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The ion transport properties of glasses are important for a number of different applications, ranging from glassy electrolytes in batteries and other electrochemical cells, sensors and chemically stable storage materials. However, ionic conduction in glasses is still not completely understood. There are several poorly understood issues, for instance the mixed mobile ion (MMI) effect (i.e. the dramatic conductivity drop when two different types of mobile cations are mixed, see e.g. Ref. [1]). In this study we have tried to understand the MMI effect on a structural basis using neutron and x-ray diffraction experiments and reverse Monte Carlo modelling on the three different glass series $\text{Li}_x\text{Na}_{1-x}\text{PO}_3$ ($x=0,0.5$ and 1), $\text{Li}_x\text{Rb}_{1-x}\text{PO}_3$ ($x=0,0.25,0.5,0.75$ and 1) and $\text{Na}_x\text{Rb}_{1-x}\text{PO}_3$ ($x=0,0.5$ and 1). Conductivity data on the $\text{Li}_x\text{Rb}_{1-x}\text{PO}_3$ system show a conductivity decrease of more than eight orders of magnitude around the $x=0.5$ composition [2], thus the MMI effect is well pronounced in these systems. The neutron diffraction experiments were performed at the liquid and amorphous diffractometer (LAD) at Rutherford Appleton Laboratory, UK, whereas the x-ray diffraction experiments were carried out on the GILDA instrument at the European Synchrotron Radiation Facility (ESRF), Grenoble, France.

In figure 1 we show the experimental static neutron and x-ray structure factors, $S(Q)$, for the three mixed alkali series in comparison with corresponding structure factors computed from the RMC produced models (note the excellent agreement). The overall similarity between the structure factors of each glass system leads us to conclude directly from the experimental data that there are no major structural differences between the mixed and the single alkali glasses. The only significant differences in the neutron data are observed in the low- Q region, indicating a slight difference in the intermediate range order of the investigated glasses. This is expected due to the size difference of the ions, which induces changes in the inter-chain correlations as well as in the conformation within the poly-phosphate chains to account for the coordination of the differently sized ions.

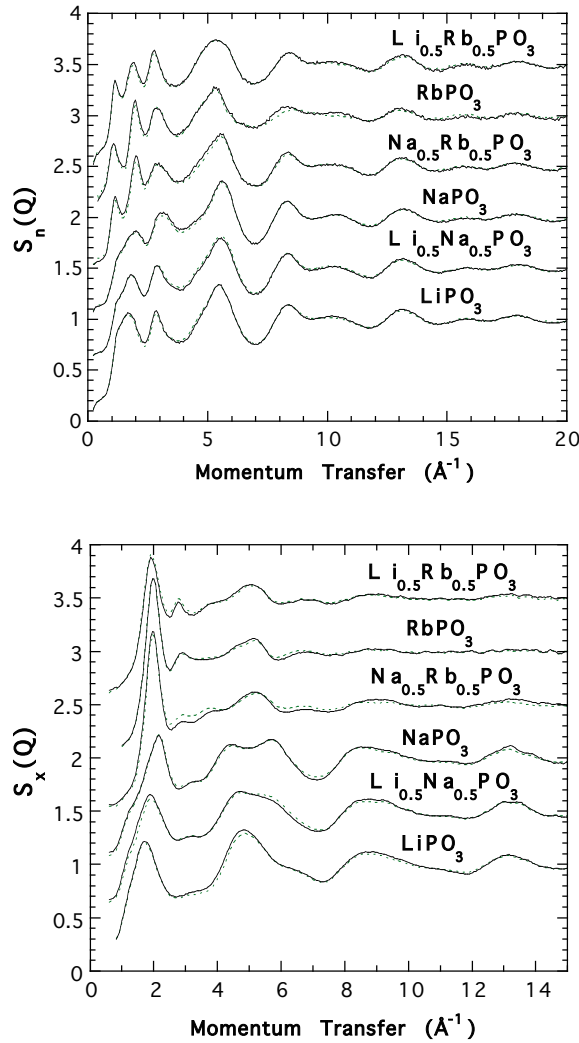


Fig. 1. Experimental neutron (a) and x-ray (b) structure factors (full lines) and computed neutron weighted (a) and x-ray weighted (b) structure factors for the RMC configurations of mixed and single Li, Na and Rb phosphate glasses. Consecutive curves are shifted by 0.5 for clarity.

Turning to the local environment of the alkali ions, we investigate the partial pair correlations that can be extracted from the RMC configuration. Figure 2 shows typical alkali-oxygen partial pair correlation functions, $G_{MO}(r)$, for the $\text{Li}_x\text{Rb}_{1-x}\text{PO}_3$ system. It is evident from the figure that both the Li-O and the Rb-O partials are very similar for the single and mixed alkali glasses. The average bond lengths and coordination numbers for the alkali-oxygen correlations, are summarised for all glasses in table I. From table I it is evident that the nearest neighbour environment of the different ionic species is distinctly different. It is furthermore clear from these data that there is no difference, within the experimental errors, in the local coordination of a mixed alkali glass compared to the single alkali glasses.

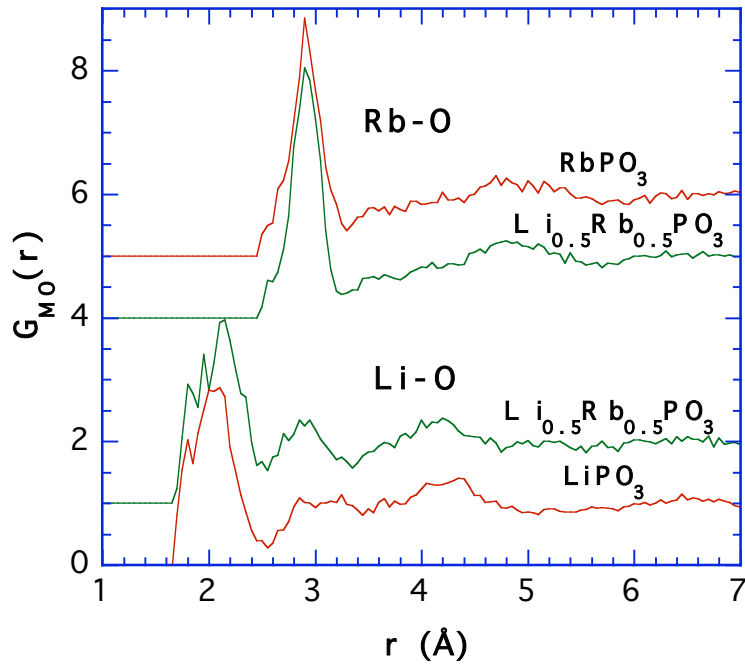


Fig. 2. Alkali ion-oxygen pair correlation functions obtained from the RMC produced models of the $\text{Li}_x\text{Rb}_{1-x}\text{PO}_3$ glasses.

Table I. Average bond distances and coordination numbers for the nearest alkali ion-oxygen distances obtained from the RMC-simulations. The coordination numbers were obtained by integration over the first peak in the corresponding $G_{MO}(r)$ (up to $r=2.5$, 2.8 and 3.4 Å for Li-O, Na-O and Rb-O, respectively).

Glass	r_{M-O}	N_{M-O}
LiPO_3	2.05 ± 0.1	3.8 ± 0.5
NaPO_3	2.50 ± 0.1	3.4 ± 0.5
RbPO_3	2.90 ± 0.1	5.0 ± 0.5
$\text{Li}_{0.5}\text{Na}_{0.5}\text{PO}_3$	2.1 ± 0.1 (Li-O) 2.45 ± 0.1 (Na-O)	4.2 ± 0.8 3.2 ± 0.8
$\text{Na}_{0.5}\text{Rb}_{0.5}\text{PO}_3$	2.50 ± 0.1 (Na-O) 2.90 ± 0.1 (Rb-O)	3.7 ± 0.8 5.0 ± 0.8
$\text{Li}_{0.75}\text{Rb}_{0.25}\text{PO}_3$	2.05 ± 0.1 (Li-O) 2.95 ± 0.2 (Rb-O)	3.5 ± 0.6 5.1 ± 1.2
$\text{Li}_{0.5}\text{Rb}_{0.5}\text{PO}_3$	2.2 ± 0.1 (Li-O) 2.95 ± 0.1 (Rb-O)	3.4 ± 0.8 5.6 ± 0.8
$\text{Li}_{0.25}\text{Rb}_{0.75}\text{PO}_3$	2.15 ± 0.2 (Li-O) 2.95 ± 0.1 (Rb-O)	3.1 ± 1.2 4.9 ± 0.6

From the RMC produced structural models of the mixed alkali glasses it is furthermore clear that the two types of ion are randomly mixed in low dimensional pathways. This fact in combination with the results discussed above suggests that the MMI effect is of

structural origin. Due to the distinctly different local environments of the Li^+ , Na^+ and Rb^+ ions, found in our experiments, we expect a large mismatch between the local potential of site A and the induced potential of ion B, which results in a high activation energy for ionic jumps to dissimilar sites, in accordance to what was proposed in the dynamic structure model [3]. In fact, ab initio molecular-orbital calculations on mixed lithium and sodium silicate glasses have shown that the site mismatch energies are so large that jumps to dissimilar sites are unlikely to occur [4]. Similar findings have also been observed from molecular dynamics (MD) simulations on mixed lithium-potassium silicate glasses [5,6], which furthermore have shown that the large energy mismatch is basically independent of the composition [5]. This result, in combination with our findings that the different kinds of alkali ions are randomly mixed and are located in low-dimensional pathways, implies that the presence of B ions in the pathways of the A ions must result in an effective blocking of many of the energetically most favourable pathways for the A ions, and vice versa. From our structural results we suggest that this blocking effect is the main reason for the MMI effect.

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