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Random ion distribution model: A structural approach to the mixed-alkali effect in glasses

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We have performed structural studies of a series of mixed-alkali phosphate glasses using diffraction experiments and reverse Monte Carlo simulations. We find that the alkali ions tend to preserve their local structural environment regardless of the glass composition. Furthermore, the distribution of the two types of cations in the structure is predominantly random. We propose that the long debated mixed-alkali effect is a natural consequence of the structural findings; a large energy mismatch for ionic jumps to dissimilar alkali sites resulting in blocking of low-dimensional migration pathways.

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Even though ionic conduction in glasses has been known for over a century there is still no generally accepted theory for the conduction mechanism.[1] One of the biggest challenges for such a theory will be to explain the mixed-alkali effect (MAE). MAE is observed as a drastic decrease in the ionic conductivity when one mobile alkali ion is partially replaced by another alkali ion.[2,3] A minimum in the conductivity, several orders of magnitude lower than that of the single alkali glasses, is reached at some intermediate composition. The nonlinear compositional dependence is also observed in other properties related to ionic transport, such as the viscosity, while properties, such as molar volume, density, or elastic modulus, show only a small or no deviation from Vegards law.[2,3] Furthermore, it has been observed that the MAE is stronger for a large size difference between the mobile ions and that the effect decreases with increasing temperature or frequency of the experiment. The effect is also observed in systems with mobile ions other than alkali, such as Ag^+ and Cu^+, and is also known as the mixed mobile ion effect (MMI). One should also note that the MAE is not unique for glassy ion conductors but is also present in crystalline compounds, such as $(Na,K)\text{-}\beta\text{-}Al_2O_3$.[4]

Through the years several different models have been proposed to explain MAE. Following the classification made by Isard[2] these can be divided into two categories. Either a major structural change is assumed to account for the decrease in conductivity upon the addition of a second mobile ion, or an interaction between dissimilar ions is introduced, so as to create immobile pairs of ions and in this way lower the conductivity. The former models are incompatible with structural studies, where neither larger structural differences nor the presence of clusters of similar ions (a microscopic phase separation) have been observed upon the mixing of ions.[5–9] Regarding the second approach, objections have been raised since a general pairing of dissimilar ions has not been experimentally verified[8–10] and the interaction between the ions is furthermore rather arbitrarily postulated.

In this work we present a comprehensive structural model of the MAE built directly from experimental structural data of mixed alkali metaphosphate glasses. The local environment of the cations as well as the intermediate range order of the glasses were investigated using neutron and x-ray diffraction in combination with reverse Monte Carlo (RMC) simulations.[11] The RMC simulations provide three-dimensional structural models of the glasses, which are in agreement with experimental data and imposed constraints, such as the macroscopic density and minimum atomic sizes. We find no tendency of any particular, or unexpected, structural changes in the mixed-alkali glasses. The alkali ions in the mixed alkali glasses are randomly distributed (or mixed) in essentially one-dimensional pathways and they tend to retain the same local environment, with respect to bond distances and coordination numbers, as in the single alkali glasses. Based on these results we propose that the mixed-alkali effect is mainly due to 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 and an effective blocking of many of the essentially one-dimensional pathways. Our model, based on experimental facts, supports the theoretical approach made by Bunde *et al.* in the dynamic structure model.[12]

Three different glass series have been investigated: $Li_xNa_{1-x}PO_3$ ($x=0$, 0.5, and 1), $Li_xRb_{1-x}PO_3$ ($x=0$, 0.25, 0.5, 0.75, and 1) and $Na_xRb_{1-x}PO_3$ ($x=0$, 0.5, and 1). Recent conductivity data on the $Li_xRb_{1-x}PO_3$ system show a conductivity decrease of more than eight orders of magnitude around the $x=0.5$ composition,[13] thus the MAE is well pronounced in these systems. The neutron-diffraction experiments were performed at the liquid and amorphous diffractometer (LAD)[14] at Rutherford Appleton Laboratory, U.K., whereas the x-ray diffraction experiments were carried out on the GILDA instrument[15] at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. The experimental procedure and data corrections were performed with great care and are described in detail elsewhere.[9,13]

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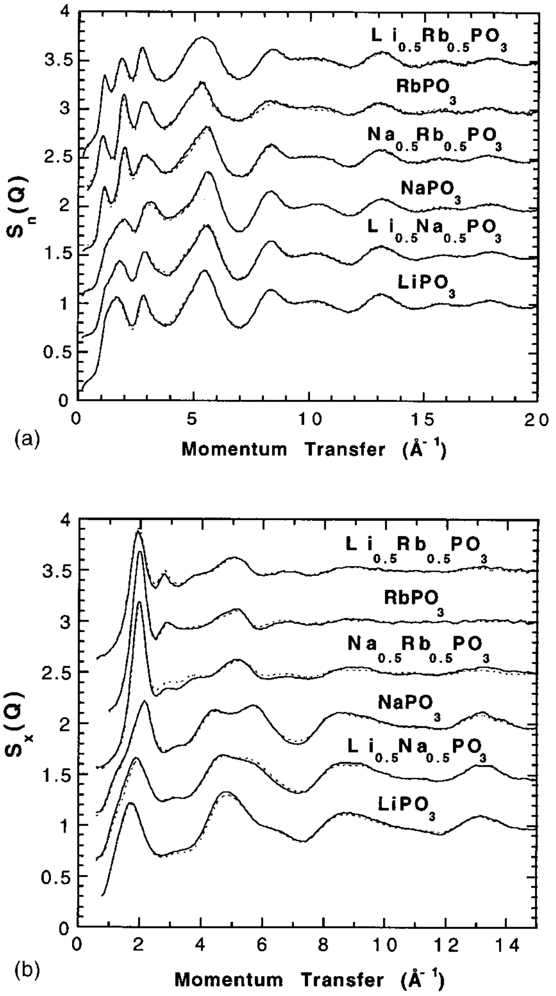

FIG. 1. Experimental neutron (a) and x-ray (b) structure factors (full lines) and computed neutron weighted (a) and x-ray weighted (b) structure factors for the RMC configurations of mixed and single Li, Na, and Rb phosphate glasses. Consecutive curves are shifted by 0.5 for clarity.

The structure of metaphosphate glasses consists of PO_4-tetrahedra sharing two corners and forming polymerlike chains. The alkali-ions coordinate to the nonbridging oxygens of the PO_4 chains and provide weaker ionic links between the strongly bonded covalent chains.[16] In the RMC simulations, each phosphorous atom was thus constrained to be 4 coordinated by oxygen, 1/3 of the oxygen atoms to be two coordinated by phosphorus (bridging oxygens), and 2/3 of the oxygen to be singly coordinated (nonbridging oxygens). In this way phosphate chains with 2 nonbridging oxygens per PO_4 unit were obtained. No coordination constraint was imposed on the alkali ions. Closest approach distances were determined from the experimentally obtained pair correlation functions and tabulated ionic radii. The size of the simulation box, containing 5000 atoms for each glass, was set to satisfy the macroscopic density of the system.

Figure 1 shows 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 interchain correlations as well as in the conformation within the polyphosphate chains to account for the coordination of the differently sized ions.

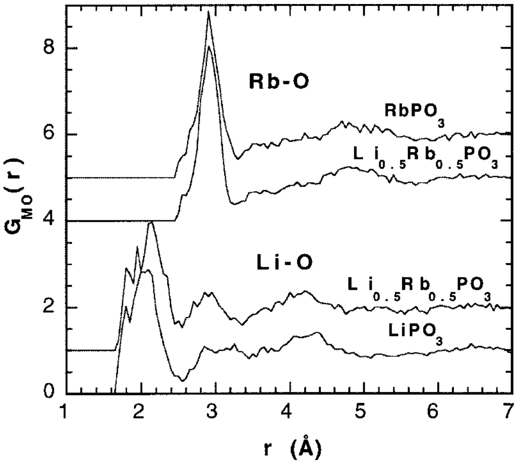

FIG. 2. Alkali ion-oxygen pair correlation functions obtained from the RMC produced models of the $Li_xRb_{1-x}PO_3$ glasses.

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 $Li_xRb_{1-x}PO_3$ 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 summarized for all glasses in Table I. From Table I it is evident that the nearest-neighbor 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. This fact is also in agreement with earlier EXAFS (Ref. 5) and infrared spectroscopy data.[8]

To investigate the tendency of pairing of similar or dissimilar ions we have calculated the coordination number for $M_i - M_i$ (i.e., like pairs) and $M_i - M_j$ (i.e., dissimilar pairs) as a function of the distance from the ions, see Fig. 3. If there would be a tendency of pairing of similar ions the $M_i - M_i$ coordination number would increase much more rapidly than the $M_i - M_j$ (and the opposite is of course true for a dissimilar pairing). No such tendency is seen in any of the three glass series. The reason for the small differences between the curves in Fig. 3, at 3–6 Å, is that the different kinds of alkali ions have different nearest cation-cation distances and coordination numbers. The nearest Li-Li, Na-Na, and Rb-Rb distances obtained from the RMC models are 2.8±0.2, 3.0

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	$r_{M\text{-}O}$	$N_{M\text{-}O}$
$LiPO_3$	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
$Li_{0.5}Na_{0.5}PO_3$	2.1 ± 0.1 (Li-O)	4.2 ± 0.8
	2.45 ± 0.1 (Na-O)	3.2 ± 0.8
$Na_{0.5}Rb_{0.5}PO_3$	2.50 ± 0.1 (Na-O)	3.7 ± 0.8
	2.90 ± 0.1 (Rb-O)	5.0 ± 0.8
$Li_{0.75}Rb_{0.25}PO_3$	2.05 ± 0.1 (Li-O)	3.5 ± 0.6
	2.95 ± 0.2 (Rb-O)	5.1 ± 1.2
$Li_{0.5}Rb_{0.5}PO_3$	2.2 ± 0.1 (Li-O)	3.4 ± 0.8
	2.95 ± 0.1 (Rb-O)	5.6 ± 0.8
$Li_{0.25}Rb_{0.75}PO_3$	2.15 ± 0.2 (Li-O)	3.1 ± 1.2
	2.95 ± 0.1 (Rb-O)	4.9 ± 0.6

±0.2, and 3.9 ± 0.2 Å, respectively, for all the glasses. Furthermore, the first Rb-Rb coordination sphere of the Rb^+ ion is both larger and more well-defined than in the cases of Li and Na. Thus, the only deviations in Fig. 3 from a totally statistic mixture of the different kinds of alkali ions are caused by the short-range order of the ions, which is different for the different kinds of alkali ions. A random distribution (or, more accurate, mixture) of the ions in mixed alkali glasses is also supported by results from Raman measurements[8,9] and nuclear magnetic resonance measurements.[6,10] The alkali ions are, however, not completely randomly distributed in the glass. From a close inspection of the RMC produced configurations it is evident that the alkali ions are located in essentially one-dimensional pathways, which is further supported by determinations of migration pathways in Ag-based ion conducting glasses, using the bond valence pseudopotential method.[17] These findings are in good agreement with Greaves modified random network structure model.[18]

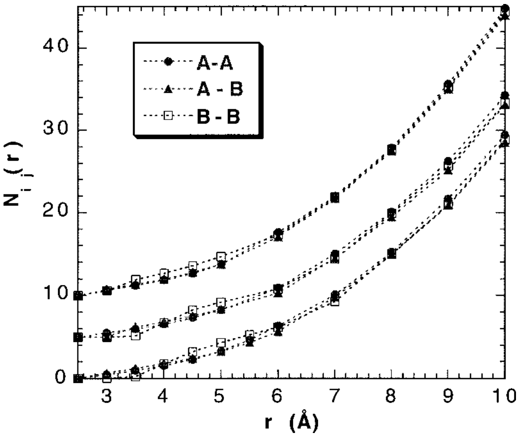

FIG. 3. Alkali ion-alkali ion coordination numbers as a function of distance from a central ion, $N_{ij}(r)$, for the three glass systems that have been studied. The coordination numbers of the $Na_xRb_{1-x}PO_3$ and $Li_xNa_{1-x}PO_3$ glass systems are shifted by 5 and 10, respectively, for clarity.

Based on the results discussed above we propose that the mixed alkali 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.[12] 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.[19] Similar findings have also been observed from molecular dynamics (MD) simulations on mixed lithium-potassium silicate glasses,[20,21] which furthermore have shown that the large energy mismatch is basically independent of the composition.[20] This result, in combination with our findings that the different kinds of alkali ions are randomly mixed and are located in essentially one-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 favorable pathways for the *A* ions, and vice versa. One should here note that a similar blocking phenomenon occurs in crystalline mixed alkali compounds, where the presence of *B* ions block diffusion paths for *A*-based defects, and vice versa.[4] Thus, the two kinds of alkali ions, in the mixed glasses, have effectively different and independent pathways, and the conductivity of such glasses, e.g., $(Li_2O)_{0.5}-(Rb_2O)_{0.5}-P_2O_5$, will therefore be close to the sum of the conductivity for the corresponding single alkali glasses with the same concentration of each kind of alkali ion as in the mixed glass, i.e., $(Li_2O)_{0.5}-P_2O_5$ and $(Rb_2O)_{0.5}-P_2O_5$. The mixed alkali effect is a natural and expected result from the present structural findings, which is well supported by simulations and theoretical calculations,[12,19–22] and there is no need of introducing a particular interaction between dissimilar ions or any major structural alterations in the mixed alkali glasses.

The structural model for the mixed alkali effect proposed here can as well acount for the temperature and ac-conductivity behavior. At higher temperatures the mismatch energy will be comparable to k_BT and the difference between the different sites in the structure becomes less relevant for the ionic motion and the MAE is decreased.[13] Moreover, above the glass transition temperature the site mismatch energies will be considerably reduced due to the rapidly relaxing surrounding. The frequency behavior on the other hand can be understood in the context of a local motion of the ions and the jump relaxation model.[23] Within the jump-relaxation model several consecutive forward-backward hops are required to occur before a successful jump is completed. While the unsuccessful jumps do not contribute to the long range diffusivity they will give a considerable contribution to the ac conductivity. In our structural model, with a more or less random distribution of the alkali ions, considerable degree of backward forward hopping can be expected due to the large mismatch for ionic jumps to dissimilar sites. In the $Li_xRb_{1-x}PO_3$ glass the decrease in room temperature dc conductivity is almost nine orders of magnitude for the $x=0.5$ composition, and this very pronounced MAE has almost vanished above 1 GHz, where the decrease in ac conductivity is less than one order of magnitude.[13] This is expected, since the blocking of migration pathways, discussed above, will mainly affect the macroscopic diffusion constant and have much less influence on the very local mobility, as also has been shown in MD simulations.[21]

The here proposed model is much in line with what is suggested in the dynamic structure model[12] in the sense that the proposed site mismatch is experimentally confirmed. However, one should note that the here proposed model distinguish from the dynamic structure model[12] in the sense that it does not include any structural relaxation of the ionic sites. Finally, one should note that to obtain the exact curvature of the compositional dependence of the conductivity one has to take interactions between the moving charges into account.[22]

To summarize, in this paper we present a structural model to explain the mixed-alkali effect based on experimental studies of mixed alkali phosphate glasses. Since the ions preserve their local environment from the single glasses also in the mixed glasses, there is a large mismatch between the different ionic sites and there are effectively less sites available for ionic motion through the structure. The long-range migration of the ions is further impeded by the statistical distribution of the ions in the structure, due to the low dimensionality of the conduction pathways in glasses. Furthermore, a qualitative structural model, based upon the above experimental facts, accounts for the temperature and frequency dependence of the MAE.

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