Mixed Mobile Ion Effect and Cooperative Motions in Silver-Sodium Phosphate Glasses

Andreas Hall and Jan Swenson
Department of Applied Physics, Chalmers University of Technology, 412 96 Göteborg, Sweden

Stefan Adams
Department of Materials Science and Engineering, National University of Singapore, Singapore 117574

Carlo Meneghini
Dipartimento di Fisica, Universitá di Roma Tre, Via della Vasca Navale 84, I-00146 Roma, Italy
and OGG-GILDA, c/o ESRF, Grenoble, France

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The conduction pathways and the extraordinary weak mixed mobile ion effect (MMIE) in $\mathrm{Ag}_x\mathrm{Na}_{1-x}\mathrm{PO}_3$ glasses have been investigated by bond-valence analysis of reverse Monte Carlo produced structural models. We find that the MMIE is suppressed in this system due to a common cooperative hopping process, where both Ag and Na participate. This finding is in strong contrast to glass systems exhibiting a pronounced MMIE, where the two types of mobile ions have distinctly different conduction pathways and the M ions tend to block the pathways for the N ions and vice versa.

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Solid state ionic conductors are of great interest, not only for their possible applications but also from a purely scientific standpoint. In these materials, that from a macroscopic view may seem nearly frozen, ionic transport may be present that rivals that of common liquid electrolytes. One of the challenges in trying to fully understand the transport properties of these materials is the mixed mobile ion effect (MMIE) where a partial exchange of the mobile ion in a material to another type of mobile ion results in a drastic drop in ionic mobility, even at small exchange ratios [1,2]. The MMIE has through experimental studies been found to increase with an increasing difference in size of the mobile ions, while decreasing with increasing temperature and frequency of the experiment.

In recent years, computational techniques have provided more insight into the MMIE than is available through experimental techniques alone, showing energy penalties for an ion to jump into a site adapted for a dissimilar ion [3–6] and blocking effects, where one type of mobile ion slows the dynamics of another [7–9]. Studies of the MMIE are usually restricted to those systems that exhibit a strong nonlinearity with respect to composition, but it is of course also of interest to explain why other systems, such as $\mathrm{Ag}_x\mathrm{Na}_{1-x}\mathrm{PO}_3$ [10], show a very small MMIE. The interdiffusion properties of Ag-Na ion exchange in aluminosilicate-based glasses have earlier been studied for production of, e.g., micro-optics and waveguides, and the weak MMIE is found also there [11]. A previous neutron diffraction and reverse Monte Carlo (RMC) study of the $\mathrm{Ag}_x\mathrm{Na}_{1-x}\mathrm{PO}_3$ system [10] revealed that no significant change occurred in the PO network with the exchange of mobile metal ions. In addition, the two ion types are randomly distributed along channels in the glass and their local oxygen environments were shown to be very similar, suggesting that the energy penalty for an Ag ion to jump into an Na site is small. We will here investigate the diffusion pathways of this system by means of bond-valence (BV) analysis of RMC produced structural models, to gain further insight into the MMIE and compare the result to our earlier findings in the mixed $\mathrm{Li}_x\mathrm{Rb}_{1-x}\mathrm{PO}_3$ glass system [8], which exhibits a particularly large MMIE with a drop in conductivity of about 8 orders of magnitude for $x = 0.5$.

Structural models of $\mathrm{Ag}_x\mathrm{Na}_{1-x}\mathrm{PO}_3$ glasses ($x = 0, 0.25,$ 0.5 0.75, and 1) were produced in quantitative agreement with neutron diffraction data using the RMC method [12] as described in Ref. [10]. For this Letter, the structures were further refined by including x-ray diffraction data collected at the GILDA beam line [13] at ESRF (Grenoble, France). The raw data were integrated to 2θ format using FIT2D [14] and subsequently corrected for background and inelastic events using in-house software. For the single ion glasses we used previously presented data, described in Refs. [15,16]. The refined structural models are, as can be seen in Fig. 1, in good agreement with experimental structure factors of both neutron and x-ray data.

Within these structural models, diffusion pathways of both Ag and Na were computed using the bond-valence method [17–19]. The total valence V of a cation M, coordinating to anions X, may be expressed as

$$V = \sum_X s_{M-X}, \qquad s_{M-X} = \exp\left[\frac{R_0 - R_{M-X}}{b}\right], \tag{1}$$

where s_{M-X} is the valence contribution from a single anion. The bond-valence parameter R_0 relates to the preferred bond length and coordination number of $M - X$,

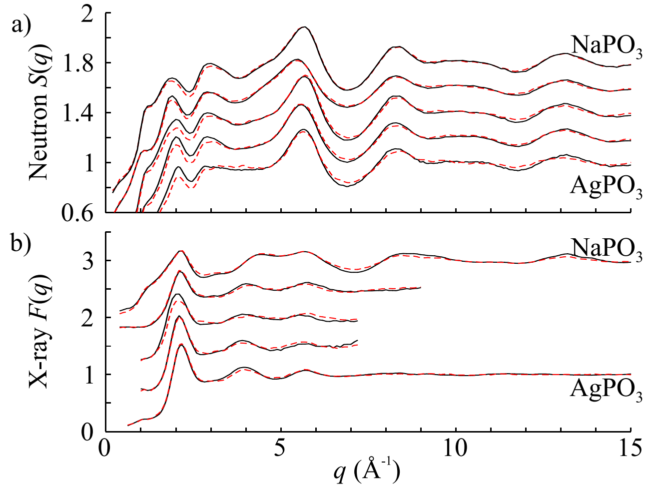

FIG. 1 (color online). Structure factors of all glass compositions from (a) neutron and (b) x-ray diffraction. Solid lines are experimentally measured and dashed lines are the corresponding structure factors computed from the RMC modeled structures. Consecutive data sets are shifted vertically for clarity.

whereas the parameter b reflects the bond softness of the ion pair. BV parameters used in this Letter are taken from Ref. [20]. A monovalent cation should have a total valence close to $V_{\mathrm{ideal}} = 1$ when it is located in an energetically favorable position, and it is then reasonable to assume that ionic transport takes place in regions where the bond-valence mismatch ($\Delta V = |V - V_{\mathrm{ideal}}|$) is as low as possible. Long-range transport, i.e., dc conductivity, then takes place in the percolating volume in which $\Delta V \leq \Delta V_{\max}$: the ionic pathway, P. In glasses the dc conductivity (σ_{dc}) of an ion is related to the fractional volume F of the percolating pathway [21,22] through

$$\log(\sigma_{\mathrm{dc}}(M)T\sqrt{m_M}) = A\sqrt[3]{F(P_M)} + B,$$
$$F(P_M) = \frac{\mathrm{vol}(P_M)}{\mathrm{vol(model)}}, \qquad (2)$$

where A and B are constants. In this study, we have calculated pathways for Ag and Na ions in all glass compositions using $\Delta V_{\max}(M) = \Delta_0\sqrt{m_M}$ (see Ref. [22]), where Δ_0 is a constant, yielding $\Delta V_{\max}(\mathrm{Ag}) = 0.27$ and $\Delta V_{\max}(\mathrm{Na}) = 0.127$ valence units. In the case of the single ion glass MPO$_3$, the pathways of the foreign ion N may be viewed as pathways of trace amounts of N. Further details on pathway calculations are given in Ref. [22].

Figure 2(a) depicts an approximately 4 Å thick slice of the Ag and Na percolation pathways in the $x = 0.5$ composition. From this picture alone it is clear that the Ag and Na pathways are very similar to each other. Not only do they have a strong resemblance in topography but are located along the same regions in the glass and share a significant fraction of their pathway volume. This common region, $P_{\mathrm{common}} = P_{\mathrm{Ag}} \cap P_{\mathrm{Na}}$, depicted in Fig. 2(b), does in itself form a percolating pathway for both types of ions and constitutes roughly half of the volume accessible to Ag ions, and two thirds of that accessible to Na ions. It is important to note that the pathway volume of neither P_{Ag}, P_{Na}, or P_{common} nor their topography show a strong dependence on composition: no fractional pathway volume change more than 11% due to compositional changes (see Table I). This is expected from our earlier study [10] that showed no significant structural differences in the PO network between the compositions. Figure 2(a) is thus a good representation of the pathway volumes and topographies in all compositions.

The situation in the Ag/Na glass system is therefore in stark contrast to that of the Li$_x$Rb$_{1-x}$PO$_3$ glass system we have previously investigated [8]. Figure 2(c) depicts the BV pathways of Li and Rb in the $x = 0.5$ composition calculated at the same Δ_0 as for the Ag and Na pathways. The pathways of the two ions are topologically very different; P_{Li} is of drastically lower local dimensionality than P_{Rb}, and the two pathways are also located in separate regions of the structure. There is in fact no overlap at all of the two ionic BV pathways in this system (for the present value of Δ_0) for any composition. The difference in alkali

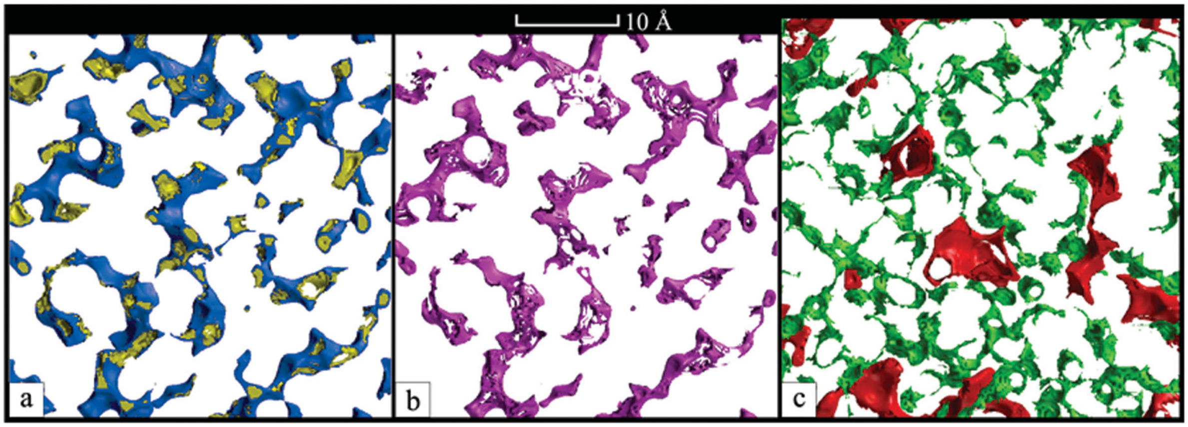

FIG. 2 (color). 4 Å thick slices through the model structures showing (a) P_{Ag} (yellow), P_{Na} (blue), and (b) P_{common} (magenta) in Ag$_{0.5}$Na$_{0.5}$PO$_3$, compared to (c) P_{Li} (green) and P_{Rb} (red) in Li$_{0.5}$Rb$_{0.5}$PO$_3$.

TABLE I. Fraction of glass volume that is a part of diffusion pathways of Ag ions, Na ions and both, given in percent.

$x =$	1	0.75	0.5	0.25	0
$F(P_{\mathrm{Ag}})$	7.38	7.18	6.69	6.67	6.64
$F(P_{\mathrm{Na}})$	5.47	5.42	5.29	5.14	5.22
$F(P_{\mathrm{common}})$	3.88	3.81	3.72	3.57	3.72

ion size and preferred coordination lead to changes in the intermediate range structure of the PO network such that the volume of P_{Li} drops by a factor 2 between the end compositions, whereas P_{Rb} does not exhibit a percolating pathway cluster unless Rb comprises ≥ 50% of the metal ions.

The definition of the BV pathway P_M presented above yields the subspace of the structure in which an M ion has a suitable coordination to surrounding anions and is not unphysically close to any phosphorous atom. It does not, however, take into account possible interactions with other mobile cations in the structure, which would take the form of further restrictions in the pathway volume. If an ion N lies within, or close to, P_M it will block any M ion from moving within the nearest neighbor distance R_{MN} of this ion pair unless M and N take part in a cooperative hopping process. Within the BV approach we model this blockage by defining the effective pathway P_M^{eff} as the part of the pathway that is at least R_{MN} away from any mobile ion that is considered to block the pathway. In single mobile ion systems we have reached good results by assuming the hopping process to be highly correlated and thus the M ion in $M\mathrm{PO}_3$ will not block the pathway for any other M ion. In these systems good predictability of conductivity is reached by using $P_M^{\mathrm{eff}} = P_M$. In mixed systems, however, the hopping of the two different ions might not be correlated.

In the $\mathrm{Li}_x\mathrm{Rb}_{1-x}\mathrm{PO}_3$ system with its distinctly different pathways a cooperative Li-Rb hopping process is excluded and the pathway is thus expected to be blocked by all dissimilar ions. Cooperative hopping may, however, still be present between ions of the same specie. By defining the effective conduction pathways to agree with these assumptions, σ_{dc} can be estimated within experimental errors [8]. The pronounced MMIE in the Li/Rb system can thus be understood as a strong steric blocking by dissimilar ions.

Using the same approach in the $\mathrm{Ag}_x\mathrm{Na}_{1-x}\mathrm{PO}_3$ system and defining P_M^0 as the part of P_M not within R_{MN} of any N ion leads to a drastic underestimation of σ_{dc}, with a minimum some 20 decades below experimentally measured conductivity (see Fig. 3). This is not surprising given the similarities between Ag and Na pathways and the tendencies of the ions to be located in similar local environments, thus being more or less randomly mixed in each other's pathways. The large overlap of pathways instead suggests that cooperativity between Ag and Na diffusion may occur, and far from all N ions are expected to block M pathways. This may be understood, e.g., by considering a mixed

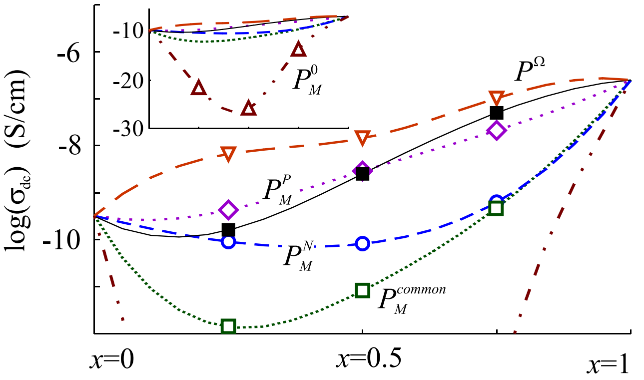

FIG. 3 (color online). Comparison of the experimentally measured σ_{dc} (solid squares) versus x in the $\mathrm{Ag}_x\mathrm{Na}_{1-x}\mathrm{PO}_3$ glass system and conductivity estimations from the five different effective pathways. The inset is the same data rescaled to show P_M^0 fully. The lines are guides for the eye.

$^{107}\mathrm{Ag}/^{109}\mathrm{Ag}$ isotope system. Since BV parameters reflect chemical properties, the two isotopes have the same BV pathways, except for the small difference in ΔV_{max} due to its mass scaling. Asserting noncooperativity in this case would yield a drastic MMIE, while such an Ag isotope effect does not exist. An interspecie cooperative hopping process (ISCH) must therefore be considered in systems with a significant overlap of pathways.

If we, on the other extreme, instead assert that Ag and Na ions are chemically similar enough to form cooperative Ag-Na pairs just as easily as Ag-Ag or Na-Na pairs and thus no blocking occurs, the effective pathways would simply be defined as $P_M^{\Omega} = P_M$. Here we find that we instead overestimate the conductivity of the intermediate compositions. The error is, however, much smaller than in the previous case; at the 75% Na composition it is 1.5 decades above experimental conductivity, and at the 75% Ag composition fall within our experimental errors (±0.3 decades).

It is important to note that the BV method does not account for the possibility of interaction between mobile ions that arise from different dynamics. It has been experimentally found that there might be a mixed isotope effect in a mixed $^6\mathrm{Li}/^7\mathrm{Li}$ system [23]. Here, we are dealing with two ions that are chemically similar in terms of preferred coordination and bond lengths to oxygen, although they differ in mass by a factor of 4. This implies the possibility of an isotopelike "dynamic blocking" effect where predominately the lighter Na ion will scatter against the heavier Ag. Inclusion of this behavior to the full cooperativity model above would lower the estimated conductivity, and do so mostly in the Na rich compositions, where the model overestimates the conductivity.

Nevertheless, if the origin of the small MMIE in the Ag/Na system lies in a blocking effect similar to that found in the Li/Rb system, it can only involve a small subset of all mobile ions, while a majority of the Ag and Na ions are capable of comigration (and probably ISCH) within common conduction pathways. In order to shed some light on the possible conduction process we will here present three hypothetical intermediate conduction models where we allow some of the ions to take part in ISCH, while others block the pathway of the foreign ion, depending on the location of ions with regards to the pathways. A comparison of their estimated conductivities to the experimental data may provide some understanding of the conduction process.

First, we allow ISCH between ions located within P_{common} and treat all other ions as blocking foreign ion movements. This case is modeled in the effective pathway, P_M^{common}, the part of P_M located at least a distance R_{MN} away from any N ion outside the common pathway. As seen in Fig. 3, this conduction model does yield an improved estimation of conductivity over the P_M^0 pathway model, the minimum of σ_{dc} at roughly 75% Na content is reproduced, but the model results in an underestimation of σ_{dc} by approximately 2 decades in the other two mixed compositions.

We could also expect some cooperativity between an M ion within (or close to) the common P_{common} and an N ion in P_N if it may reach the common region with a single hop. Considering that the bulk of single ion pathways are located along P_{common}, we may approximate this through P_M^N, where no ion within its own pathway will block foreign ions. The estimated conductivity now falls within the experimental error (± 0.3 decades) for the 75% Na composition, but does not improve much for the high-Ag containing compositions. Thus, while treating Ag ions located within P_{Ag} as cooperative is sufficient to reach a good estimation of σ_{dc} in Na rich compositions, the conductivity in Ag rich compositions is not estimated correctly unless all ions in any pathway, $P_M \cup P_N$, are considered cooperative (modeled in P_M^P in Fig. 3). If a blocking effect akin to that found in the Li/Rb system is present in the $\mathrm{Ag}_x\mathrm{Na}_{1-x}\mathrm{PO}_3$ glasses, it may thus only involve a small number of the mobile ions, while a majority participates in ISCH. Moreover, if the isotopelike "dynamic blocking" discussed above is of substantial importance for the MMIE in the Ag/Na system, the conduction process in these mixed mobile ion glasses has to be even more fundamentally different from that in the analogous Li/Rb glass system.

In conclusion, the present study of the weak MMIE in the $\mathrm{Ag}_x\mathrm{Na}_{1-x}\mathrm{PO}_3$ glass system shows that the two types of mobile ions share, to a large extent, common conduction pathways. Within the BV approach, a major fraction of the mobile ions must participate in ISCH in order to reproduce experimental conductivity data, a finding which is in strong contrast to our previously studied $\mathrm{Li}_x\mathrm{Rb}_{1-x}\mathrm{PO}_3$ glass system, where the ions located in distinctly different pathways tend to block each other's movements, rather than cooperate. Furthermore, we also propose that a significant part of the MMIE in the Ag/Na system may have its origin in a dynamic scattering process akin to the mobile ion isotope effect.

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