Glass former units and transport in ion-conducting network glasses

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A new theoretical approach is presented for relating structural information to transport properties in ion conducting network glasses. It relies on the consideration of the different types of glass forming units and the charges associated with them. Changes in the compositions of these units lead to a re-distribution of Coulomb traps for the mobile ions and to a subsequent change in long-range ionic mobilities. It is furthermore shown how measured changes of the unit compositions can be explained by thermodynamic modeling. The theories are tested against experiments on borophosphate glasses and yield good agreement with the measured data both for the compositional changes of the units and the variation of the activation energy.

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The chemical composition of ion conducting glasses can be varied to a large extent and this offers many possibilities to optimize these materials with respect to different demands, in particular to high ionic conductivities [1]. It is therefore important to get an understanding of the connection between the network forming structure and the long-range ionic transport properties. Considerable progress has been made in the past to gain insight into near and medium range order properties of ion conducting glasses by various experimental probes such as X-ray and neutron scattering, infrared and Raman spectroscopy, and solid-state NMR techniques (for a review, see [2]). A challenge is to utilize this information for theoretical models of the ionic transport. One promising route was suggested some time ago by building Reverse Monte Carlo models of the glass structure based on diffraction data [3] and by further analyzing these structural models with the bond valence method [4] to explore the preferred diffusion pathways of the mobile ions.

In this Letter we will present a new theoretical approach, which is applicable to network forming glass structures and relies on the different network forming units (NFUs) that build up the host structure for the ionic motion (cf. Fig. 1). We argue that the charges associated with the NFUs and the way how they are localized are of crucial relevance for characterizing the statistical properties of the energy landscape that govern the long-range ionic transport properties. To demonstrate the new approach we apply it to the mixed glass former effect in sodium borophosphate glasses, where detailed information on the NFU concentrations has been gained recently by MAS-NMR [5, 6], see Fig. 2. We first show how the observed changes of NFU concentrations with the borate-to-phosphate mixing ratio can be understood from a thermodynamic model. Then we will use this structural information on the NFUs to calculate changes of the conductivity activation energy upon the mixing ratio.

In borophosphate glasses of composition \( y \text{Na}_2\text{O} \cdot (1 - y) \text{xB}_2\text{O}_3 \cdot (1 - x) \text{P}_2\text{O}_5 \) we distinguish seven NFUs as in [3]: the neutral trigonal \( \text{B}^{(3)} \) units with three bridging oxygens (bOs) and zero non-bridging (nBOs), the negatively charged tetrahedral \( \text{B}^{(4)} \) units with four bOs and zero nBOs, the trigonal \( \text{B}^{(2)} \) units with two bOs and one negatively charged nBO, and the tetrahedral phosphate units \( \text{P}^{(n)} \), \( n = 0, \ldots, 3 \) with \( n \) bOs and \( (3 - n) \) nBOs, see the Fig. 1. MAS-NMR measurements redrawn in Fig. 2 (symbols) show that, when starting the mixing from the phosphate rich side (\( x = 0 \)), first the \( \text{B}^{(4)} \) units replace \( \text{P}^{(2)} \) units. This replacement continues until the \( \text{B}^{(4)} \) concentration saturates at about \( x \approx 0.4 \). Above this mixing concentration the neutral \( \text{B}^{(3)} \) units start to appear, replacing now the neutral \( \text{P}^{(3)} \) units to keep the total amount of negative charge constant. This is needed to compensate the positive charge of the mobile sodium ions. With further increasing \( x \), the behavior becomes more complex until at the boron rich side all NFUs are somehow involved in forming the network structure.

To understand this behavior we developed a thermodynamic model, which is based on a hierarchy of formation enthalpies \( G(X) \) for the NFUs. The \( \text{B}^{(4)} \) are the most preferable NFUs for the charge compensation of the alkali ions, since they are most highly connected in the network with their four bOs. However, their concentration is lim-

FIG. 1: Sketch of the NFUs in borophosphate glasses.


\[ \mu = \mu_A - \mu_B = \frac{1}{2} \ln \left( \frac{y}{1-y} \right) \]

where all energies are given in units of the thermal energy \( k_B T \) and the chemical potentials have to be determined from Eqs. (2a)-(2c).

Equations (1) with the single parameter \( \Delta \) describe the hierarchy between the formation enthalpies. Specific values for these enthalpies should be irrelevant as long as the system is in the low-temperature regime. To evaluate the behavior in this regime we solve the set of Eqs. (2) for \( \Delta \to \infty \). The results shown as solid lines in Fig. 2 are in good agreement with the MAS-NMR data from ref. [3] (diamonds), except for \( x = 1 \), where the measured \( [B^{(4)}] \) is much smaller than the presumed saturation value \( [B^{(4)}]_{\text{sat}} = 0.43 \), and correspondingly the \( [B^{(2)}] \) value larger than the theoretical prediction. With respect to the deviation at \( x = 1 \), we note that MAS-NMR measurements reported by another group [4] yield the data marked by the open symbols in Fig. 2 which are in better agreement with the theoretical predictions. On the basis of the thermodynamic model, one can, of course, reproduce the behavior found in ref. [3] by assuming a lower saturation value \( [B^{(4)}]_{\text{sat}} \) for \( x = 1 \). Indeed, for the sodium borate glass, the maximal \( [B^{(4)}] \) was found to be slightly smaller than 0.43 [7], which can be explained by requiring that a bO cannot link two \( B^{(4)} \) units [11]. However, to describe all details, including different behaviors for different types of alkali ions, one needs to weaken this rule and allow for the formation of diborate groups [12]. Let us note that by including such refinements it is also possible to model the \( [B^{(4)}]_{\text{max}} \) in the borophosphate system. To keep things simple we have focused on the essential idea and used the limit \( [B^{(4)}]_{\text{max}} \simeq 0.43 \) here.

Next we show how one can, based on the information on the NFU concentrations, successfully model long-range ionic transport properties. To this end we developed a model, which we call the Network Unit Trapping (NUT) model. It relies on the following idea: the nbOs create localized Coulomb traps for the mobile ions, while delocalized charges, as those of the \( B^{(4)} \) units, give a partial Coulomb contribution to several neighboring ion sites. In this way the structural energy landscape for the ionic pathways is modified with the mixing concentration \( x \) and this effect can be conjectured to govern the change of the activation energy \( E_a(x) \) for the long-range ionic transport.

To test this model we randomly distribute the NFUs with their concentrations from Eqs. (3) on the sites of the generalized Fermi distributions

\[ [X^{(n)}] = \frac{1}{\exp[-\mu_n] + 1}, \quad X = B^{(3)}, P^{(3)} \]

\[ [B^{(2)}] = \frac{1}{\exp[3\Delta - \mu_q - \mu_p] + 1} \]

\[ [P^{(n)}] = \frac{1}{\exp[(2-n)(\Delta - \mu_q - \mu_p)] + 1}, \quad n = 0, 1, 2 \]

In a grand-canonical treatment we can assign the chemical potentials \( \mu_A, \mu_B \) and \( \mu_F \) to these constraints (2a)-(2c), respectively. Considering a set of sites to be occupied by the NFUs with mutual site exclusion, we obtain

\[ [B^{(4)}] + [B^{(2)}] + [P^{(2)}] + 2[P^{(1)}] + 3[P^{(0)}] = \frac{y}{1-y} \]

\[ [B^{(4)}] + [B^{(3)}] + [B^{(2)}] = x \]

\[ [P^{(3)}] + [P^{(2)}] + [P^{(1)}] + [P^{(0)}] = (1-x) \]
a simple cubic lattice. These sites are called NFU sites. The mobile ions are considered to perform a hopping motion between the centers of the lattice cells, which represent the ion sites. An NFU \( \alpha \) with \( k_\alpha > 0 \) nbOs and charge \( -z_\alpha e \) adds a Coulomb contribution \( -z_\alpha e/k_\alpha \) to \( k_\alpha \) randomly selected neighboring ion sites, as illustrated in Fig. 3. Note that this implies that the delocalization of electrons belonging to the double bond in the charged P\( ^{3-} \) unit on an NFU site \( \alpha \) adds a Coulomb contribution \( -e/k_\alpha \). Hence \( k_\alpha \) is the only tunable parameter in the modeling. To determine the activation energy \( E_\alpha \) we have chosen a lattice with 50\(^3\) sites, occupied all NFU sites according to the occupation probabilities given by Eqs. \( \text{(3)} \), and the ion sites randomly with concentration \( y/(1-y) \). Then Kinetic Monte-Carlo simulations with periodic boundary conditions and Metropolis transition rates \( \text{(14)} \) were performed. After thermalization the time-dependent mean-square displacement \( R^2(t) \) of the mobile ions and the diffusion coefficient \( D = \lim_{t \to \infty} R^2(t)/6t \) are determined. The diffusion coefficient is shown for \( \sigma = 0.25 \) and various mixing concentrations in an Arrhenius plot in Fig. 4a. From the slopes of the straight lines we calculated the activation energy \( E_\alpha(x) \), and the behavior of the normalized activation energy \( E_\alpha(x)/E_\alpha(0) \) is compared with the experimental results from \( \text{[6]} \) in Fig. 4b. The overall agreement between the theoretical (open symbols, solid line) and the experimental data (full symbols) is surprisingly good. Note that we needed to fit only one parameter \( \sigma \) to achieve this agreement. A significant difference between the theoretical and experimental curve can be seen for \( x \to 1 \): while the theoretical \( E_\alpha(x) \) decreases monotonously with \( x \), the experimental \( E_\alpha(x) \) fi-

FIG. 3: Two-dimensional sketch of the NUT model. The arrows indicate charge transfer to ion sites as described in the text.
nally rises for the sodium-borophosphate glass \((x = 1)\). Interestingly, this rise is reproduced by the NUT model (dashed line), if instead of the NFU concentrations predicted by Eqs. \(3\), the NFU concentrations measured in \(5\) are used. In view of the discrepancies at \(x = 1\) between experiments discussed in connection with Fig. 2, this calls for a reevaluation of the activation energy in the sodium borate system.

In summary we have presented a new approach to relate structural information to transport properties in ion-conducting network glasses. This approach is based on a consideration of the properties of the different NFUs building the network structure with respect to total charge and charge delocalization. In addition we showed how MAS-NMR results for NFU concentrations can be understood from thermodynamic modeling. The potential of our new approach is manifold, since one can apply it quite generally to other network glasses with different compositions. One immediate application, for example, could be the investigation of glass series with varying modifier content. It is known that the activation energy often shows a logarithmic decrease with the concentration of mobile ions \(15\) and it would be important to see whether this behavior can be captured by the NUT model.

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