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Theory for ion diffusion and conduction in glasses based on site energy distributions derived from network former unit concentrations

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Ion conducting glasses are useful materials for solid-state batteries, electrochromic devices, optical wave guides, supercapacitors, and chemical sensors. A better understanding of the ion transport in glasses allows us to optimise material properties for their various applications. Developing theories for such transport is challenging because of the absence of a regular host structure in glassy materials. Some time ago, we have developed a structure-informed hopping model based on the distributions of site energies at the residence sites of the mobile ions [1]. The respective site energy distributions were derived from information on the chemical units forming the glassy networks. Relative fractions of these network former units can be determined in solid-state NMR and by Raman spectroscopy, and a statistical mechanical approach has been suggested to predict their concentrations. In the first evaluation of the model, we performed kinetic Monte-Carlo simulation to determine diffusion coefficients of the mobile ions, and calculated ion conductivities and their activation energies by applying the Nernst-Einstein relation. Both the hopping model and the statistical mechanical approach have been further developed recently [2, 3]. We have succeeded to derive conductivities by analytical methods without the need to perform extensive computer simulations. The analytical methods require only a numerical calculation of percolation thresholds and of total conductivities for disordered conductance networks, where the distribution of local conductances in a network follows from the structure-informed hopping model. Figure 1 shows that our theoretical modelling yields good agreement with experiments.

In this contribution, we present the theoretical advances and demonstrate their power in applications to alkali oxide glasses. We are considering further refinements, which should allow an application to an even broader class of ion conducting glasses.

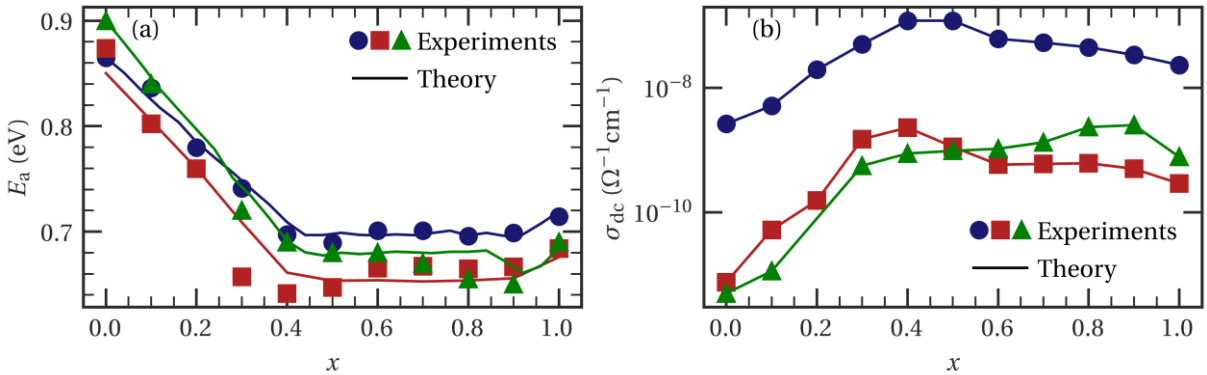

Figure 1: (a) Conductivity activation energies E_a and (b) conductivities σ_{dc} for three series of alkali borophosphate glasses in dependence of the borate-to-phosphate mixing ratio: $0.33Li_2O$-$0.67[xB_2O_3$-$(1-x)P_2O_5]$ (blue circles), $0.35Na_2O$-$0.65[xB_2O_3$-$(1-x)P_2O_5]$ (red squares), and $0.4Na_2O$-$0.6[xB_2O_3$-$(1-x)P_2O_5]$ (green triangles). The symbols refer to experimental data, and the lines are theoretical predictions from the structure-informed hopping model (data and lines were redrawn from Ref. [3]).

References

[1] M. Schuch, C. Trott, P. Maass: *Network Forming Units in alkali borate and borophosphate glasses and the mixed glass former effect*. RSC Adv. **1**, 1370-1382 (2011).

[2] M. Bosi, J. Fischer, P. Maass: *Network-forming units, energy landscapes, and conductivity activation energies in alkali borophosphate glasses: analytical approaches*. J. Phys. Chem. C **125**, 6260-6268 (2021).

[3] M. Bosi, P. Maass: *Predicting conductivities of alkali borophosphate glasses based on site energy distributions derived from network former unit concentrations*. Z. Phys. Chem. (2021), published online, https://doi.org/10.1515/zpch-2021-3137.