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Ion Diffusion in Mixed Alkali Glasses

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1. Introduction

When different types of mobile ions A and B in glasses are mixed, one observes dramatic changes in their tracer diffusion coefficients D_A and D_B. With increasing number fraction x of B ions, i.e. with successive replacement of A by B ions, D_A decreases, while D_B increases. Since corresponding changes are seen in the activation energies $E_\mathrm{A,B}(x)$, $D_\mathrm{A,B}(x)$ vary by many orders of magnitude at low temperatures. This phenomenon is known as the mixed alkali effect [1] and is reflected in all transport properties that are dominated by ionic diffusion.

Particularly puzzling is the steep fall ("vulnerability") of the diffusion coefficient of the majority ion, e.g. A, with beginning replacement by the minority ion B. In most systems, $E_\mathrm{A}(x)$ is a concave function, which means that the increase of $E_\mathrm{A}(x)$ is largest for small x. How can a small number of foreign ions have such a strong influence on the mobility of the majority ions?

A further quantity poorly understood so far is the internal friction, which shows mechanical loss peaks associated with ion diffusion processes well below the calorimetric glass transition temperature. In single ionic glasses there occurs only one loss peak with a peak frequency τ_s^{-1}. When A ions are replaced by B ions, the single alkali peak becomes smaller and an additional loss peak occurs with peak frequency $\tau_\mathrm{m}^{-1} < \tau_\mathrm{s}^{-1}$. This mixed alkali internal friction peak rapidly grows with ongoing replacement and can become comparable in height with the single alkali peak already at small x. While the activation energy E_s of τ_s^{-1} follows closely the activation energy of the diffusion coefficient of the more mobile ion, no simple relation exists between the activation energy E_m of τ_m^{-1} and the mobility of the less mobile ion.

2. Hopping model

Both the vulnerability and the internal friction scenario can be understood based on a hopping model, where only a small fraction c_V of the available sites for the mobile ions is vacant [2]. In the model, a short-range correlated variable μ_i^α, $0 \le \mu_i^\alpha \le 1$ (α=A,B), is assigned to each site i that characterizes its α character: A site with large μ_i^α has a local environment favourably accommodated to an α ion and hence a low site energy $\varepsilon_i^\alpha = -\varepsilon_\mathrm{mis}^\alpha \mu_i^\alpha$, $\varepsilon_\mathrm{mis}^\alpha > 0$. In addition to the ε_i^α the energy barriers $u_{ij}^\alpha = u_0^\alpha + u_\mathrm{mis}^\alpha \left(\mu_i^\beta + \mu_j^\beta\right)/2$, $u_0^\alpha, u_\mathrm{mis}^\alpha > 0$, determine the jump rates of ions to neighbouring sites.

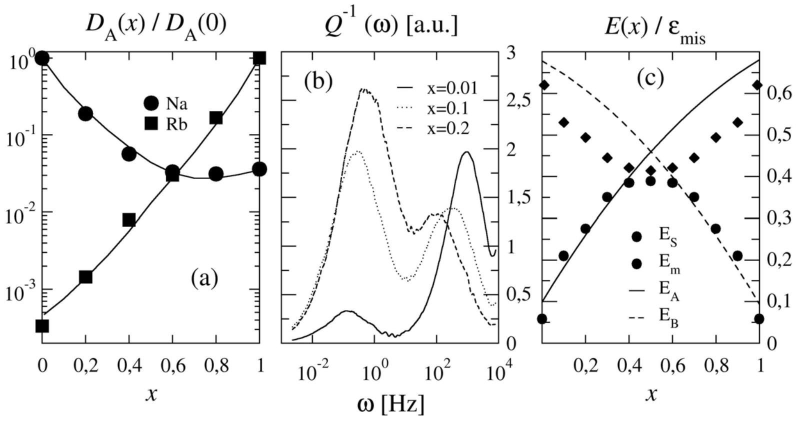

Fig.1: (a) Na and Rb tracer diffusion coefficients in *(1-x)*Na_2O-*x*Rb_2O-4B_2O_3 glasses at 652K (symbols, redrawn from [3]) in comparison with the theory (lines); (b) representative theoretical result for the internal friction as a function of shear frequency ω at beginning replacement of A by B ions; (c) theoretical activation energies for tracer diffusion and internal friction peaks.

3. Tracer Diffusion

The model was analyzed by Monte Carlo simulations and analytical calculations for jump motion in a simple cubic lattice with a small vacancy concentration c_V=5%. Results for the tracer diffusion coefficients are shown in Fig.1a in comparison with experimental data for mixed sodium/rubidium borate glasses. The curves display the peculiar vulnerability discussed above. This is caused by a correlation-induced trapping effect [2].

4. Internal friction

The internal friction Q^{-1} obtained for a typical set of model parameters in Fig.1b mirrors the behaviour found in experiment. The peak at high shear frequencies ω is the single alkali peak, whose peak frequency τ_s^{-1} and height decrease with increasing x. The peak at low ω is the mixed alkali peak, whose peak frequency τ_m^{-1} and height increase with x. Because c_V is small, the mixed alkali peak can be identified already when only 1% of the A ions are replaced by B ions.

As in experiment, the activation energy E_s of τ_s^{-1} follows closely the diffusion activation energy of the more mobile ion E_A or E_B, see Fig.1c. By contrast, the activation energy E_m of τ_m^{-1} differs significantly from the diffusion activation energy of the less mobile ion. The behaviour found in Fig.1c is reminiscent to the experimental one.

References

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