

Theory for the activation energy in mixed glass former glasses

Mohamad Alhamad and Philipp Maass

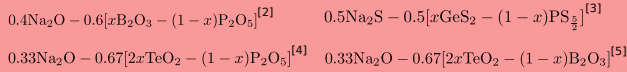
Fachbereich Physik, Universität Osnabrück, Barbarastraße 7, 49076 Osnabrück, Germany



Motivation & Objective

Improved physical and electrochemical properties of glassy electrolytes can be achieved by mixing two glass former cat- or anions at constant mole fraction of the mobile ions. This effect is known as the mixed glass former effect (MGFE). Optimized mixed glass former electrolytes are promising materials for developing next generation solid state batteries. Most important is the optimization of the ionic conductivity and its activation energy.

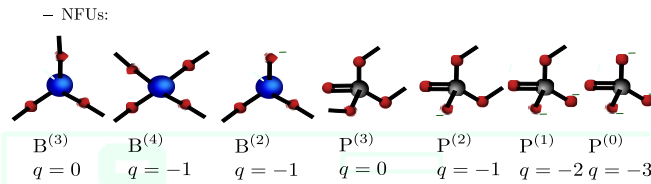
By resorting to percolation theory we extend and refine the modeling in Ref. [1] to predict the dependence of the activation energy on the glass former mixing ratio based on the charge redistribution in the glassy network upon mixing. Application of the theory to different mixed glass former systems leads to excellent quantitative agreement with measurements for the following systems :



Network former unit concentrations from thermodynamic modeling

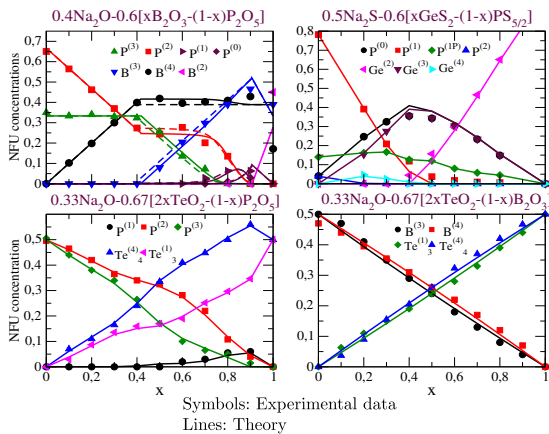
- NFU have different formation enthalpies G_k .
- Concentrations of U_k are given by Boltzmann probabilities $p_k \propto \exp(-\Delta G_k/k_B T_g)$ at glass transition temperature T_g and constraints given by the stoichiometry and charge neutrality.
- Specification of G_k :
 - For NFUs U_j , U_k with $G_j - G_k \gg k_B T_g$, specific values of G_j , G_k do not matter \rightarrow hierarchy of NFU formation.
 - For $G_j - G_k \approx k_B T_g$: enthalpy differences $\Delta G = G_j - G_k$ need to be introduced as parameters (alternative approach: concentration of corresponding NFUs are related via chemical reactions) \rightarrow competing NFUs

- Example for borophosphate glasses:



- Hierarchy: $G_{B^{(4)}} < G_{P^{(2)}} < G_{P^{(1)}} < G_{P^{(0)}} < G_{B^{(2)}}$.
- Competing NFUs: $2P^{(2)} \rightleftharpoons P^{(1)} + P^{(3)}$, with reaction constant K .

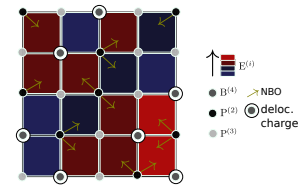
Results of the thermodynamic modeling



\rightarrow Very good description of experimental data

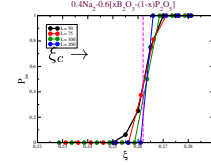
Activation energy from Network Unit Trapping (NUT) model

- Change of the activation energy E_a for mobile ion transport with the glass former mixing ratio relates to modification of the potential energy landscape induced by changes of NFU concentrations.
- Long-range transport (dc-conductivity): critical energy determined from percolation theory yields E_a .
- Specific implementation:
 - simple cubic lattice with site energies: $E_i = -E_0 \sum_{i,j,k} \frac{q_k}{z_k} n_{ij}^k + \eta_i$
 q_k : charge number.
 z_k : number of bridging links.
 η_i : Gaussian random numbers with zero mean and standard deviation σ .
 n_{ij}^k : the occupation number, which is equal to one, if an NFU U_k on site j contributes a Coulomb contribution $\propto \frac{q_k}{z_k}$ to ion site i ; otherwise it is equal to zero.
 - Example for borophosphate glasses:



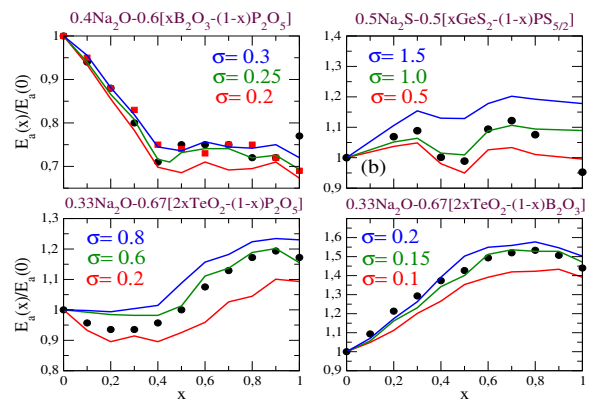
- E_a -determination from percolation theory:
 - Application of linear response theory yields bond percolation problem in the low-temperature limit with bond energy barriers [6]:
 $\xi_{ij} = \frac{1}{2} [|E_i - E_j| + |E_i - E_f| + |E_j - E_f|]$
 E_f : Fermi energy (dependent on mobile ion concentration)

$E_a = \xi_c$: critical bond barrier height



Increasing accuracy of ξ_c with system sides

Conductivity activation energy from NUT model



\rightarrow Very good description of experimental data

Conclusions & Outlook

- Theory successful for all experimentally investigated MGFE systems.
- Critical tests of the theory against further systematic measurements, e.g., change of the mobile concentration and type of mobile ion.
- Application of modeling to other quantities, glass transition temperature, elastic moduli, etc.

References

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