

# Theory for the activation energy in mixed glass former glasses

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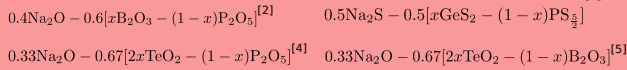
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## Motivation & Objective

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 :

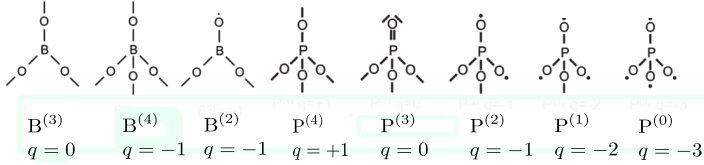


## Network former unit concentrations from thermodynamic modeling

- NFUs 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

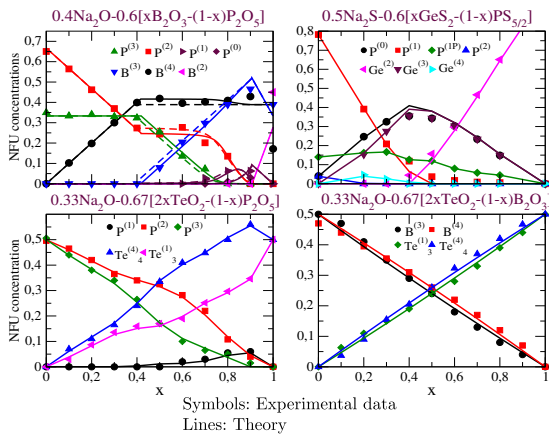
- Example for borophosphate glasses:

– NFUs:



- 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  $K$ .

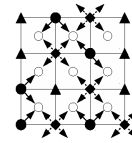
## Results of the thermodynamic modeling



$\rightarrow$  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
  - $\eta_i$ : Gaussian random numbers with zero mean and standard deviation  $\sigma$
  - $n_{ij}^k$ : 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:

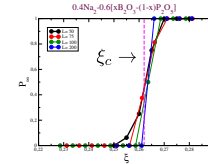


Coulomb contributions of NFUs

$$\begin{array}{ll} \frac{q_k}{z_k} = \frac{1}{4} & \text{for the B(4)} \\ \frac{q_k}{z_k} = \frac{1}{2} & \text{for the P(2)} \\ \frac{q_k}{z_k} = \frac{2}{3} & \text{for the P(1)} \\ \frac{q_k}{z_k} = \frac{3}{4} & \text{for the P(0)} \\ \frac{q_k}{z_k} = 1 & \text{for the B(2)} \end{array}$$

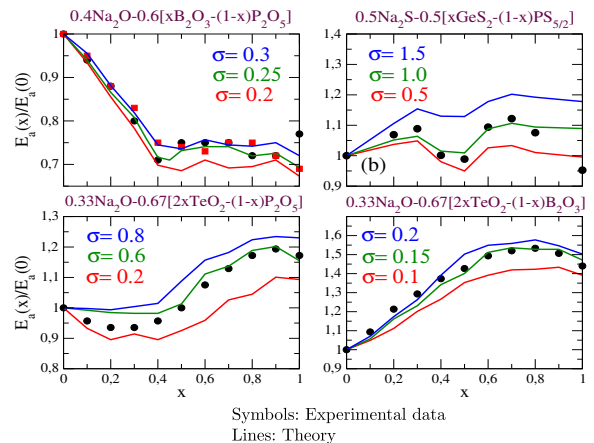
- $E_a$ -determination from percolation theory:
  - Application of linear response theory yields bond percolation problem in the low-temperature limit with bond energy barriers [6]:

$$E_a = \xi_c: \text{critical bond barrier height}$$



Increasing accuracy of  $\xi_c$  with system sizes

## 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

- [1] M. Schick, C. Trotti, P. Maass, RSC Adv. 1, 1370 (2011).
- [2] D. Zelinski, C. Cranner, H. Eckert, Chem. Mater. 19, 3162 (2007).
- [3] C. Bischoff, K. Schuler, S. W. Martin, J. Phys. Chem. B 118, 3710 (2014).
- [4] D. B. Baskar, M. T. Rinke, H. Eckert, J. Phys. Chem. C 112, 12530 (2008).
- [5] D. Larink, M. T. Rinke, H. Eckert, J. Phys. Chem. B 119, 1753 (2015).
- [6] V. Ambegodkar, B. I. Halperin, J. S. Langer Phys. Rev. B 4, 2612 (1971).