Understanding Fast Ion Conduction in Inhomogeneous Materials

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Functional materials including glasses, solid solutions, and their interfaces contain many types of inhomogeneities at the nanoscale that contribute to their performance in various applications. However, quantifying such inhomogeneities from experiments is often challenging because of the lack of nanoscale probes that can characterize local atomistic environments. First-principles quantification of such systems is also often intractable due to limitations in simulation time or the number of configurations that can be calculated within a reasonable amount of time. To overcome this limitation, we have been employing machine learning surrogate models to speed up first-principles calculations. Here, we report examination of (a) intermediate-range order/disorder in the prototypical network glass system GeO_2, and (b) dopant order/disorder in heavily doped perovskite oxides and its impact on proton conduction.

(a) Intermediate range order in GeO_2 glass [1]-- The atomistic structure of glasses have been of fundamental interest for over a century; although short-range order has often been clarified as being similar to crystalline motifs, intermediate-range order whose existence is implied by small-wavevector diffraction peaks is yet to be unambiguously characterized in real space. Although reverse Monte Carlo (RMC) fitting of diffraction data is often used to construct three-dimensional models, its reliability is sometimes questionable because diffraction data only contains two-body correlations which are not enough to fix the three-dimensional structure. Here, we performed melt-quench simulations in a 3240-atom cell using a neural network potential trained on first-principles data to construct a model of vitreous GeO_2. The structure factor calculated from the obtained model is in good agreement with experiment. Intermediate-range features were characterized using ring distributions and persistent homology, and it was found that the simulated model shows a stronger ordering compared to that obtained by RMC modeling. That is, the underlying density functional approximation in first-principles calculations determines the preferred network assembly more strictly than conventional RMC modeling, even when multiple diffraction data is used in the fitting. This shows the promise and necessity of simulations using machine learning potential based on first-principles data

for accurate determination of the glass structure and its physical properties.

(b) Proton conduction in heavily Sc-doped $BaZrO_3$ [2]--Acceptor-doped perovskite oxides are of interest for application in proton ceramic fuel cells. Acceptor doping is necessary for the introduction of protons into the material, but it has been observed that increased doping leads to a decline in the proton conductivity. This is often explained by trapping of protons by the dopant. However, it was recently discovered that Sc doping leads to continuous conductivity increase up to the solubility limit of ~60 atomic percent. Here we performed Monte Carlo simulation using our abICS code to determine the Sc configuration in the material, followed by molecular dynamics simulation to explain how the detrimental effect of proton trapping is avoided. As seen in Fig. 1, our simulations revealed that a conduction path along the network of Sc dopants is formed, enabling long-range diffusion without detrapping from the dopant.

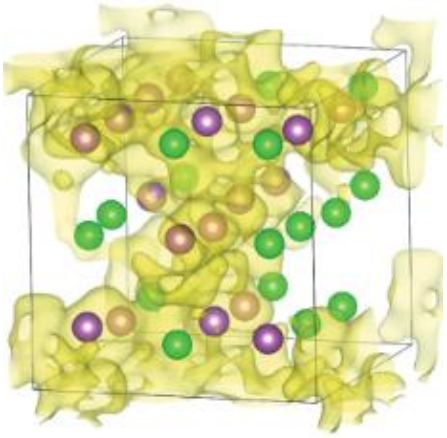

Fig. 1: Proton concentration isosurface in Sc-doped $BaZrO_3$. The Sc and Zr atoms are shown as purple and green spheres, and Ba and O atoms are omitted for clarity. From Ref. [1], reproduced under CC-BY 4.0 license.

References

[1] K. Matsutani et al., J. Chem. Phys. 161, 204103 (2024).

[2] S. Fujii et al., Sci. Technol. Adv. Mater. 25, 2416383 (2024).