Comparing and contrasting proton conduction pathways in yttrium and aluminum doped $BaZrO_3$

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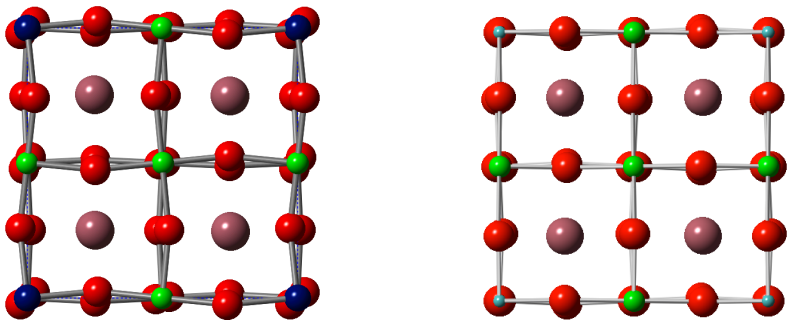
Perovskite oxides with the general formula ABO_3 are often doped with ions of lower valency at the B site to change local structure and proton conducting properties. When $BaZrO_3$, a promising proton conductor for fuel cell applications, is doped at the B site with a larger ion, tilting of the ZrO_6 octahedron is enhanced. In contrast, doping with a smaller ion decreases tilting. This poster compares and contrasts the energetics and proton conduction pathways in Al (smaller) and Y (larger) doped $BaZrO_3$.

Density functional theory was used to find approximate solutions to the many-bodied Schrödinger equation of each doped system. As shown in Figure 1, the lowest energy configuration of Y-doped $BaZrO_3$ showed significant octahedral tilting in contrast with the nearly cubic lowest energy Al-doped $BaZrO_3$. Proton binding sites were found with the conjugate gradient method and transition states between the binding sites were found using the nudged elastic band method. Vineyard prefactors are found from the normal mode frequencies at the transition state and the minima. The prefactors and barriers are used to find transition state theory rate constants for all possible transitions (transfers and rotations). Protons transferred between oxygens in the same octahedron and between adjacent octahedra in the yttrium doped system[1]. However, inter-octahedral transfers had significant energy cost in the more cubic aluminum doped system that had longer inter-octahedral OO distances.

Graph theory is used to find proton conduction pathways. Each binding site represents a vertex in the graph. Edges connect vertices that are connected via a single transition state. Rate constants are used to calculate probabilities of moving from vertex to vertex and the probabilities are used to assign weights to the edges. Vertex coding is used to find all the possible proton conduction pathways in the graph and their probabilities. Local structure around the dopant affects the probability ordering of the proton conduction paths.



(a) (b)

Figure 1. The lowest energy configuration of Y-doped $BaZrO_3$ (a) showed significant octahedral tilting in contrast with the nearly cubic lowest energy Al-doped $BaZrO_3$ (b).

[1]M.A. Gomez, M. Chunduru, L. Chigweshe, L. Foster, S.J. Fensin, K.M. Fletcher, and L.E. Fernandez, J. Chem. Phys. **132**, 214709 (2010).