Dopant Size Matters: The distorting effect of yttrium and aluminum dopant on proton conducting perovskite $BaZrO_3$

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Barium zirconate is among one of the most promising proton conducting ceramic electrolyte due to its robust mechanical and chemical stability and its ability to operate at intermediate temperature.[1] Replacing zirconium ions with different concentrations of lower valency ions such as yttrium or aluminum results in varying degree of oxygen vacancies to compensate for charge imbalance, thus affecting proton conductivity. By approximating the many-bodied Schrödinger equation with density functional theory and using conjugate gradient method to optimize the bulk geometry, the optimal geometry and lattice constant for each of our bulk systems were determined. Then, normal mode calculations further minimized the structural energies by attempting to eliminate each imaginary mode corresponding to a saddle point. In the 12.5% doped Y-$BaZrO_3$ system, the optimal lattice constant was 4.29Å whereas in the 6.25% Y-doped system the optimal lattice constant was 4.28Å. On the other hand, both 12.5% and 6.25% doped Al-$BaZrO_3$ had the optimal lattice constant of 4.24Å. In the undoped $BaZrO_3$, the lattice constant was 4.26Å. The lattice constants were directly correlated with the different radii of Zr, Y, and Al. While $BaZrO_3$ was perfectly cubic, doping at the zirconium site with yttrium caused significant octahedral tilting and enhanced proton conductivity due to reduced OO distances. On the other hand, doping with aluminum maintained a near-cubic bulk, eliminating inter-octahedral proton transfer due to greater OO distance.[2] Lowering the concentration of dopant in both Al and Y doped systems reduced the extent of distortion.

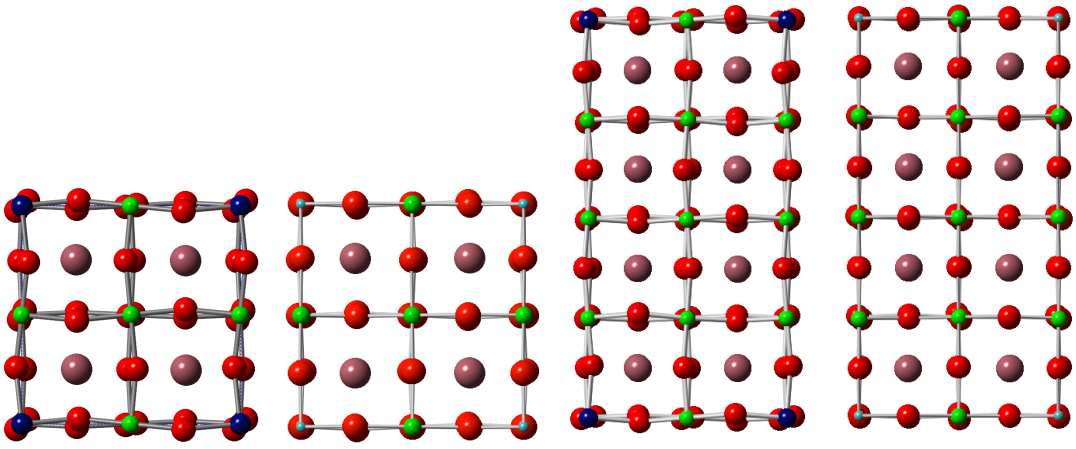

Figure 1. The lowest energy configuration of 12.5% doped Y-$BaZrO_3$ (a) showed significant octahedral tilting in contrast with the nearly cubic lowest energy 12.5% doped Al-$BaZrO_3$ (b). The optimized 6.25% doped Y-$BaZrO_3$ (c) is slightly less distorted than its 12.5% doped counterpart. The 6.25% doped Al-$BaZrO_3$ (d) is also near-cubic.

[1] K.D. Kreuer, Annu. Rev. Mater. Res. (2003), 33:333–59.
[2] M.A. Gomez, F.-J. Liu, Solid State Ionics (2013), http://dx.doi.org/10.1016/j.ssi.2013.05.014.