

Effect of Rb and Ta doping on the ionic conductivity and stability of the garnet $\text{Li}_{7+2x-y}(\text{La}_{3-x}\text{Rb}_x)(\text{Zr}_{2-y}\text{Ta}_y)\text{O}_{12}$ ($0 \leq x \leq 0.375$, $0 \leq y \leq 1$) superionic conductor – a first principles investigation

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In this work, we investigated the effect of Rb and Ta doping on the ionic conductivity and stability of the garnet $\text{Li}_{7+2x-y}(\text{La}_{3-x}\text{Rb}_x)(\text{Zr}_{2-y}\text{Ta}_y)\text{O}_{12}$ ($0 \leq x \leq 0.375$, $0 \leq y \leq 1$) superionic conductor using first principles calculations. The cubic garnet system shows promise as a solid electrolyte material for future all solid state battery systems¹ (Fig. 1). However, despite numerous experimental examinations, researchers have not been able to satisfactorily correlate composition changes from doping with aliovalent cations to changes in conductivity^{2,3}. This is largely due to the difficulties in obtaining uniform solid solutions, and also in the difficulty of identifying the effects of grain boundary resistance in conductivity measurements⁴.

Using first principles techniques we are able to control the concentration precisely and explore the effect of doping on diffusivity. Using ab initio molecular dynamics (AIMD), we confirm experimental findings that the cubic structure allows more rapid diffusion. Then, starting with the cubic structure, we dope the Zr site with Ta and the La site with Rb, along with charge compensation by changing the lithium concentration.

The separate effects of geometry changes and lithium concentration changes on diffusivity are studied. Broadly, our results indicate that doping does not greatly alter the topology of the migration pathway, but instead acts primarily to change the lithium concentration. Our results find higher conductivity and lower activation energy than is typically reported in the experimental literature, which suggests that there is room for improving the total conductivity in these promising materials.

References

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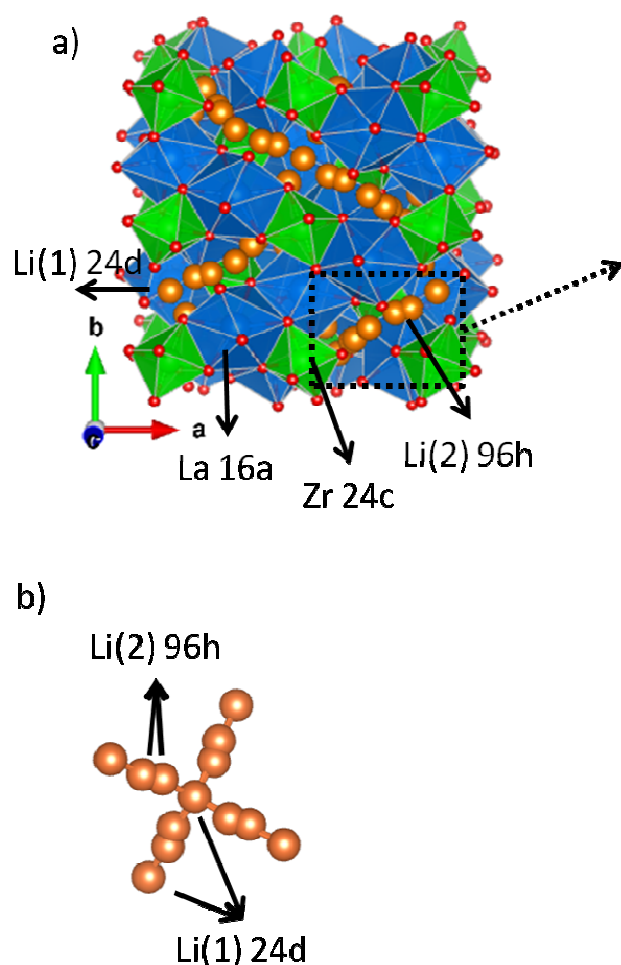


Figure 1: (a) The cubic garnet structure with space group $Ia-3d$ (In. No. 142). The Li(1) are in tetrahedral 24d sites while Li(2) are in octahedral 96h sites. The La (blue) and Zr (red) are coordinated by 8- and 6- oxygen (red) respectively. (b) The 3d network of Li (brown) atoms is shown. The Li(1) site is surrounded by four Li(2) octahedral sites.