

The Site Preference of Al and Ga in Mixed Doped $\text{Li}_{7-3(x+y)}\text{Ga}_x\text{Al}_y\text{La}_3\text{Zr}_2\text{O}_{12}$ Garnet Solid Solutions with $x, y \in \{0.1, 0.2, \dots, 0.8 \wedge y + x \leq 0.8\}$ and its Influence on Li-Ion Mobility.

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Since the initial study of Murugan *et al.* in 2009 [1], $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) garnet is receiving much scientific attention as fast lithium-ion conductor. Superior chemical and thermal stability, electrochemical inertness in a wide potential window, particularly its stability against Li metal, make LLZO an excellent candidate to be used as solid electrolyte in both lithium-ion and Li-oxygen batteries. The garnet-based structure occurs in at least two structural modifications [2,3]. Compared to the tetragonal form (*I41/acd*), which is stable at room temperature (RT), ion conductivity of the cubic polymorph (*Ia-3d*), $T > 150$ °C, is two orders of magnitude higher.

As the first group, Weppner and co-workers reported on cubic LLZO stabilized with Al at RT [4]. The stabilizing effect of Al has latter been confirmed by a number of intensive investigations. Thereafter, attention has also been directed at other dopant cations. Gallium is located directly below aluminum in the periodic table, hence, it should show similar crystal-chemical behavior as Al does in LLZO. Indeed, the stabilization of cubic LLZO via the incorporation of Ga has been reported recently [5]. Much experimental as well as theoretical effort has been undertaken to collect information on the local coordination as well as the site preferences in LLZO.

Finally, we could show that Al preferentially occupies the tetrahedrally coordinated *24d* site and a distorted 4-fold coordinated *96h* site in LLZO [6]. On the other hand, it turned out that Ga is solely located on the *96h* site irrespective of the amount of Ga introduced [7]. Since the *24d* site forms a junction between the loops of the Li-ion pathways in LLZO, the occupation of the *24d* sites is suspected to be more hindering for the mobile Li ions; this is in contrast to the situation when only the *96h* sites are occupied. Consequently, the location of Al and Ga is expected to strongly correlate with the Li-ion transport properties of LLZO.

In order to proof this assumption, we systematically varied the site occupation of *24d* and *96h* sites. This was done by synthesizing mixed-doped Al-Ga-LLZO with different portions of Al and Ga. Indeed, preliminary measurements show that reducing the *24d* site occupation leads to an increase of Li-ion dynamics.

References

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