

Crystal structure and Li-ion conductivity in $\text{Li}_7\text{La}_3\text{Zr}_{12}\text{O}_{24}$ garnets: a review

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Recent research has shown that certain Li-oxide garnets with more than 3 Li atoms per formula unit, such as $\text{Li}_7\text{La}_3\text{Zr}_{12}\text{O}_{24}$, have high ionic conductivities, as well as good chemical and physical properties for use in solid-state batteries (Murugan et al. 2007).

“Garnet” is the common name for a large number of natural and synthetic metal-oxide phases. Conventional oxide garnets have the general formula $\text{A}_3\text{B}_2\text{C}_3\text{O}_{12}$ and crystallize in the cubic space group $Ia\bar{3}d$. The O^{2-} ions, in the general crystallographic positions $96h$, form a framework with interstices occupied by the A cations, such as Ca^{2+} , Fe^{2+} , Y^{3+} , La^{3+} in the 8-fold coordinated position $24c$ (point symmetry 222), the B cations, such as Al^{3+} , Fe^{3+} , Zr^{4+} , Sn^{4+} , Sb^{5+} , etc. in the 6-fold coordinated position $16a$ (point symmetry $\bar{3}$), and the C cations, such as Li^+ , Al^{3+} , Fe^{3+} , Ga^{3+} , Ti^{4+} , Si^{4+} , etc. in the 4-fold coordinated $24d$ position (point symmetry 4). In addition to these cation sites, there are other interstices within the oxygen framework, which are empty in the conventional garnet structure, e.g. (i) the 6-fold coordinated $16b$ positions with point symmetry 32 , (ii) the 6-fold coordinated $48g$ positions with point symmetry 2 , and (iii) an additional 4-fold coordinated $96h$ position with point symmetry 1 . In “ $\text{Li}_7\text{La}_3\text{Zr}_{12}\text{O}_{24}$ ” garnet (LLZO), these interstices are filled by “excess” Li^+ ions giving rise to the excellent ionic conductivity.

There is a low temperature tetragonal modification of pure LLZO (SG: $I4_1/acd$) and a high temperature non quenchable cubic phase of LLZO (SG: $Ia\bar{3}d$). The tetragonal phase has distinctly lower ion conductivity than the cubic phase. Fortunately, the cubic phase can be stabilized at low temperatures by doping with low amounts of Al, Ga, and Fe (Buschmann et al. 2011; Rettenwander et al. 2016). In our contribution the results of single crystal X-ray diffraction studies will be presented. While Al-doped LLZO garnets always crystallize within the space group $Ia\bar{3}d$, Ga and Fe-doped LLZO garnets crystallize within the space group $I43d$ (Wagner et al. 2016). This symmetry change is combined with an increase in ionic conductivity up to $10^{-3} \text{ S cm}^{-1}$ which is very high for those kind of solid state electrolytes used in Li-ion batteries. These results will be discussed on the basis of the slightly different topologies of both space groups, respectively. Similar structural changes are observed by the incorporation of Co (Mir et al. 2023).

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