





Atomistic Insight into Ion Transport and Conductivity in Ga/Al-Substituted $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ Solid Electrolytes

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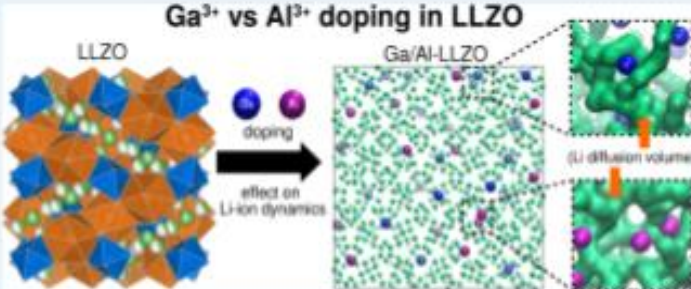
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DOI: 10.1021/acsami.8b17217

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ABSTRACT: Garnet-structured $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ is a promising solid electrolyte for next-generation solid-state Li batteries. However, sufficiently fast Li-ion mobility required for battery applications only emerges at high temperatures, upon a phase transition to cubic structure. A well-known strategy to stabilize the cubic phase at room temperature relies on aliovalent substitution; in particular, the substitution of Li^+ by Al^{3+} and Ga^{3+} ions. Yet, despite having the same formal charge, Ga^{3+} substitution yields higher conductivities (10^{-3} S/cm) than Al^{3+} (10^{-4} S/cm). The reason of such difference in ionic conductivity remains a mystery. Here, we use molecular dynamic simulations and advanced sampling techniques to precisely unveil the atomistic origin of this phenomenon. Our results show that Li^+ vacancies generated by Al^{3+} and Ga^{3+} substitution remain adjacent to Ga^{3+} and Al^{3+} ions, without contributing to the promotion of Li^+ mobility. However, while Ga^{3+} ions tend to allow limited Li^+ diffusion within their immediate surroundings, the less repulsive interactions associated with Al^{3+} ions lead to a complete blockage of neighboring Li^+ diffusion paths. This effect is magnified at lower temperatures and explains the higher conductivities observed for Ga-substituted systems. Overall, this study provides a valuable insight into the fundamental ion transport mechanism in the bulk of Ga/Al-substituted $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ and paves the way for rationalizing aliovalent substitution design strategies for enhancing ionic transport in these materials.

LLZO Ga^{3+} vs Al^{3+} doping in LLZO



effect on Li-ion dynamics

(Li) diffusion volume

KEYWORDS: solid electrolytes, Ga/Al-substituted LLZO, molecular dynamics, enhanced sampling hybrid Monte Carlo, GSHMC, Li-ion conductivity/diffusion