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Abstract title: The Better Garnet — Faster Li-Ion Conduction of $Li_7La_3Zr_2O_{12}$ with Uncommon *I*-43*d* Structure

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Abstract body:

The need for new battery concepts shifts solid Li-ion conductors into the focus of research. Li-stuffed oxide garnets such as $Li_7La_3Zr_2O_{12}$ (LLZO) are among the most promising candidates. LLZO does not only show a very high Li-ion conductivity; also its electrochemical inertness over a wide potential window and its stability against Li metal makes LLZO exceptionally well suited to be used as an electrolyte for Li-metal based batteries.[1, 2]

Pure LLZO has a tetragonal low-temperature phase with space group (SG) $I4_1/acd$ (no. 142) that shows a comparatively poor Li-ion conductivity of ~10^{-6} S cm^{-1}. For use as solid-state electrolyte, the cubic "high-temperature" modification with SG *Ia*-3*d* (no. 230) is much more desirable, as it shows a Li-ion conductivity in the order of $10^{-4} - 10^{-3}$ S cm^{-1}. Fortunately, the cubic high-temperature modification can be stabilized at room temperature by the introduction of small amounts of supervalent cations such as Al^{3+}, Ta^{5+} and Nb^{5+}.[2]

Recent studies show that the introduction of certain cations such as Ga^{3+} and Fe^{3+} causes the formation of a different cubic structural modification showing the acentric cubic SG *I*-43*d* (no. 220).[3, 4] The reduced symmetry compared to the *Ia*-3*d* modification results from the site preference of Ga^{3+} and Fe^{3+}.

These new garnet-similar materials show exciting electrochemical properties. ^{7}Li NMR relaxometry experiments revealed an additional dynamic process for Ga-stabilized LLZO with SG *I*-43*d* compared to Al-stabilized LLZO with SG *Ia*-3*d*.[3] The Li-ion conductivity of both LLZO modifications with SG *I*-43*d* is higher than 1.0×10^{-3} S cm^{-1} and therefore among the highest values for garnet-type materials, exceeding Al-stabilized LLZO.[4, 5] These results highlight the impact of structure-property relationships for these kind of materials.

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