

Exploring aliovalent substitutions in the lithium halide superionic conductor $\text{Li}_{3-x}\text{In}_{1-x}\text{Zr}_x\text{Cl}_6$ ($0 \leq x \leq 0.5$)

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Over the last years, the attention for the search of superionic materials shifted to the ternary rare-earth metal halides Li_3MX_6 ($M = \text{Y, Er, In}$; $X = \text{Cl, Br, I}$) because of their promising high room-temperature conductivities. To date, the influence of iso- or aliovalent substitutions within this material class is rarely understood due to the absence of substitution studies in the ternary halides which are a common tool to link changes in structure with the observed ionic transport. In this work, we investigate the impact of Zr substitution on the structure and ionic conductivity of Li_3InCl_6 ($\text{Li}_{3-x}\text{In}_{1-x}\text{Zr}_x\text{Cl}_6$ with $0 \leq x \leq 0.5$) using a combination of neutron diffraction, nuclear magnetic resonance and impedance spectroscopy. Analysis of high-resolution neutron diffraction data indicates a cation-site disorder as well as an additional tetrahedrally coordinated site, which has not been reported in Li_3InCl_6 yet. The newly introduced Li^+ positions and the already known Li^+ positions form a three-dimensional polyhedral network and therefore 3D diffusion is enabled. The Zr^{4+} substitution within Li_3InCl_6 induces non-uniform volume changes and increases the number of vacancies in the structure, all of which lead to an increasing ionic conductivity in this series of solid solutions.