Structural disorder and lithium diffusion pathways in lithium halide solid electrolytes

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All-solid-state lithium batteries require solid electrolytes combining high ionic conductivity with chemical and mechanical stability.[1] Lithium halides have recently emerged as promising candidates due to their wide electrochemical stability window and compatibility with high-voltage cathodes.[2] However, the structural factors governing lithium transport in these materials remain poorly understood, particularly in mechanochemically synthesized compounds where significant disorder may be present.[3, 4]

Here we investigate a series of lithium halides including Li_2ZnCl_4, Li_2MgCl_4, Li_2ZrCl_6 and related mixed cation and mixed-halide compositions obtained *via* partial Br substitution. The materials are synthesized using mechanochemical routes that enable rapid formation of crystalline phases at low temperatures. Their structural properties are examined using high-resolution synchrotron and neutron powder diffraction combined with Rietveld refinement to determine the average crystal structure, cation distribution, and lithium site occupancies.

Additional insight into the local structure is obtained from total scattering measurements and pair distribution function (PDF) analysis. For Li_2ZnCl_4, Rietveld refinement indicates a normal spinel-type framework, however, PDF analysis reveals deviations from the ideal average structure at short length scales, suggesting local distortions and disorder within the halide framework.

Furthermore, partial substitution of Cl by Br systematically modifies the lattice parameters and local coordination environment, providing a means to tune the structural landscape for lithium migration. Bond-valence energy landscape calculations based on the refined structures identify low-energy Li^+ diffusion pathways connecting octahedral sites *via* tetrahedral intermediates.

These results demonstrate how combined powder diffraction and total scattering approaches can elucidate both average and local structural features governing lithium-ion transport in halide solid electrolytes.

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