

Structural disorder along the Li diffusion pathway in cubic LiMn_2O_4

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Electron density distribution analysis of synchrotron powder X-ray diffraction from stoichiometric $\text{Li}(\text{Mg}_{1/6}\text{Mn}_{11/6})\text{O}_4$ has revealed a disordered distribution of Li and O atoms. The Li atoms showed an aspherical distribution centred on 8a, in addition to a diffuse population peaked at 0.38 - 0.78 Å from the 16c site along the 8a-16c tie-line. The O atoms also show statistical distributions near their ideal positions, depending on the geometrical configuration of the surrounding metal atoms. The results of molecular dynamics simulation on cubic LiMn_2O_4 not only confirmed the X-ray observations but also revealed the dynamic nature of the lattice structure. Many Li atoms occupy one of the four positions approximately 0.14Å away from the ideal 8a site, and vibrate harmonically around their equilibrium positions. The diffusion of Li atoms are presumably associated with the 3d electron hopping over hetrovalent Mn(III) and Mn(IV) cations.