The role of Al^{3+}, Dy^{3+} co-doping on the structure-property correlations in NASICON-type $LiTi_2(PO_4)_3$ solid-state electrolytes

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NASICON-type $LiTi_2(PO_4)_3$ (LTP, space group *R-3c*) has been studied as a potential solid-state electrolyte material in Li ion batteries (LIBs), owing to its thermal stability and high ionic conductivity. [1] The structure of LTP consists of TiO_6 octahedra corner-linked to PO_4 tetrahedra, forming a helix about the c-axis. Li^+ can occupy two sites in the structure: the more stable six-fold O coordinated M1 (*6b*) and the eight-fold O coordinated M2 (*18e*), which is less stable. The net ionic movement is described as M1 (*6b*) - M2 (*18e*) - M1 (*6b*).

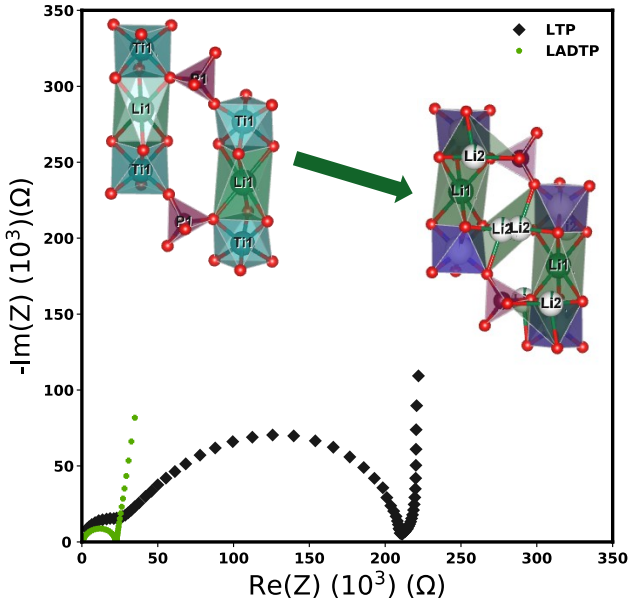

Figure 1. The effect of Al^{3+}/Dy^{3+} on the structure-property correlations of LTP.

The 3D network allows for the migration of alkali ions through the structure, making the material a candidate as an electrolyte in LIB. However, its room temperature conductivity in the order of 10^{-7} S/cm is too low for practical applications in LIBs. [1-2] Lattice site substitutions of $Ti^{4+}$with isovalent and aliovalent cations have been proposed to improve ionic conductivity. This is achieved by tuning the tunnel size of Li^+ in the structure and by altering the energy barriers around the dopant sites for faster Li^+ migration. Aliovalent cationic substitution significantly improves ionic conductivity by densifying the pelletized material, and because of the high Li content that is introduced for charge balance. [3-4]

In this work, we investigate the effect of Al^{3+}/Dy^{3+} substitution at the Ti^{4+} site on the room temperature conductivity of LTP. Synchrotron XRD provided insight into the structure, showing that the material under study has a NASICON structure. Raman spectroscopy and Pair Distribution Function provided information on the changes in local order around the substitution sites as well as confirming the phase composition of the material in question. LADTP showed improved ionic conductivity of 1.28×10^{-5} S/cm.

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