Atmosphere Controlled Processing of Ga-Substituted Garnets for High Li-ion Conductivity Ceramics

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Supporting Information

ABSTRACT: Ga-substituted La$_{3}$Zr$_{2}$Li$_{7}$O$_{12}$ garnet is shown to be a promising Li-ion conducting electrolyte material. The strategy adopted in this study is the substitution of Li by Ga, thereby creating Li vacancies and enhancing the Li conductivity. Solid State Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) measurements have been used to identify the location of the substituted Ga in the structure and its effect on the Li distribution and mobility. In addition MAS NMR was used to follow the effect of protonation due to atmospheric moisture on the sintering behavior of these materials. In particular, it is shown that the Ga atoms are located in tetrahedral positions promoting the random distribution of lithium over the available sites, hence promoting an increase in the conductivity. Control of the sintering conditions by using a dry O$_{2}$ atmosphere leads to the formation of dense ceramic materials and avoids the degradation process due to the exchange of Li$^{+}$ by H$^{+}$ from atmospheric moisture. Electrochemical Impedance Spectroscopy data show total conductivities as high as 1.3 and 2.2 mS cm$^{-1}$ at 24 and 42 °C, respectively, which are among the highest Li ion conductivities reported for garnet-structured materials to date.