Dual Substitution Strategy to Enhance Li\textsuperscript{+} Ionic Conductivity in Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12} Solid Electrolyte

Lucienne Buannic,\textsuperscript{*1,10}† Brahim Orayech,\textsuperscript{†} Juan-Miguel López Del Amo,\textsuperscript{†} Javier Carrasco,\textsuperscript{†} Nebil A. Katcho,\textsuperscript{†} Frédéric Aguesse,\textsuperscript{†10} William Manalastas,\textsuperscript{†} Wei Zhang,\textsuperscript{†2} John Kilner,\textsuperscript{†,8} and Anna Llordés\textsuperscript{*1,‡}

\textsuperscript{1}CIC EnergiGUNE, Parque Tecnológico de Álava, 48, 01510 Miñano, Álava, Spain
\textsuperscript{2}IKERBASQUE, The Basque Foundation for Science, 48013 Bilbao, Spain
\textsuperscript{§}Department of Materials, Imperial College, London SW7 2AZ, United Kingdom

Supporting Information

ABSTRACT: Solid state electrolytes could address the current safety concerns of lithium-ion batteries as well as provide higher electrochemical stability and energy density. Among solid electrolyte contenders, garnet-structured Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12} appears as a particularly promising material owing to its wide electrochemical stability window; however, its ionic conductivity remains an order of magnitude below that of ubiquitous liquid electrolytes. Here, we present an innovative dual substitution strategy developed to enhance Li-ion mobility in garnet-structured solid electrolytes. A first dopant cation, Ga\textsuperscript{3+}, is introduced on the Li sites to stabilize the fast-conducting cubic phase. Simultaneously, a second cation, Sc\textsuperscript{3+}, is used to partially populate the Zr sites, which consequently increases the concentration of Li ions by charge compensation. This aliovalent dual substitution strategy allows fine-tuning of the number of charge carriers in the cubic Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12} according to the resulting stoichiometry, Li\textsubscript{7-}\textsubscript{3x}Ga\textsubscript{x}La\textsubscript{3}Zr\textsubscript{2-x}Sc\textsubscript{x}O\textsubscript{12}. The coexistence of Ga and Sc cations in the garnet structure is confirmed by a set of simulation and experimental techniques: DFT calculations, XRD, ICP, SEM, STEM, EDS, solid state NMR, and EIS. This thorough characterization highlights a particular cationic distribution in Li\textsubscript{6.65}Ga\textsubscript{0.15}La\textsubscript{3}Zr\textsubscript{1.95}Sc\textsubscript{0.10}O\textsubscript{12}, with preferential Ga\textsuperscript{3+} occupation of tetrahedral Li\textsubscript{3Ga} sites over the distorted octahedral La\textsubscript{3Ga} sites. \textsuperscript{7}Li NMR reveals a heterogeneous distribution of Li charge carriers with distinct mobilities. This unique Li local structure has a beneficial effect on the transport properties of the garnet, enhancing the ionic conductivity and lowering the activation energy, with values of 1.8 × 10^{-3} S cm^{-1} at 300 K and 0.29 eV in the temperature range of 180 to 340 K, respectively.