Supporting information for

Experimental visualization of lithium conduction pathways in Garnet-type Li₇La₃Zr₂O₁₂

Jiantao Han,a Jinlong Zhu,a Yutao Li,b Xiaohui Yu,a Shanmin Wang,a Gang Wu,a Hui Xie,b Sven C. Vogel,a Fujio Izumi,c Koichi Momma,a Yukihiko Kawamura,e Yunhui Huang,f John B. Goodenough,b Yusheng Zhaoa

a LANSCE-Lujan Neutron Scattering Center, Los Alamos National Laboratory, Los Alamos, New Mexico, 87545
b Texas Materials Institute, ETC 9.102, the University of Texas at Austin, TX 78712, USA
c Quantum Beam Center, National Institute for Materials Science, Namiki, Tsukuba, Ibaraki 305-0044, Japan
d National Museum of Nature and Science, Tsukuba, Ibaraki 305-0005, Japan
e Research Center for Neutron Science and Technology, Tokai-mura, Naka-gun, Ibaraki 319-1106, Japan
f School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China

Experimental Section

Neutron diffraction includes some important information on lithium, because the scattering ability of the lithium nucleus is relatively large and independent of scattering vector $Q = 4\pi\sin\theta/\lambda$. This nature is amenable for detailed analysis of the thermal motion of the lithium nucleus, in contrast to the negligible X-ray scattering ability of lithium or lithium ions with only two or three electrons. To enhance this advantage, $^{7}$Li₇La₃Zr₂O₁₂ was prepared using $^{7}$Li enriched Li₂CO₃ as the raw material. Li₇La₃Zr₂O₁₂ was prepared by solid-state reaction of stoichiometric amounts of Li₂CO₃, La₂O₃ (heated at 900°C for 12 h) and ZrO₂. 10 wt% excess Li₂CO₃ was added to compensate for the loss of lithium during annealing. The powders were ground and heated to 900°C to decompose the metal salts. Finally, the powders were ground again, pressed into a pellet, and annealed at 1120°C, 1140°C, and 1230°C while the pellet was covered with the same mother powder. The annealing was done in an alumina crucible.

Powder X-ray diffraction (Philips PW1830, Cu Ka) was employed to monitor the phase formation in the 2θ range from 10 to 70° with a step size of 0.02°. The lattice parameters were calculated from the diffraction peaks in the range 20-60° with Jade software. Neutron diffraction experiments were conducted on the high-pressure preferred orientation neutron diffractometer (HIPPO) at the Lujan Neutron Scattering Center, Los Alamos National Laboratory. Bulk samples were placed in a vanadium can and time-of-flight data were collected under vacuum. Neutrons were detected with 27 detector panels of $^{3}$He detector tubes arranged on three rings with nominal diffraction angles of 40°, 90°, and 144°. The GSAS program was used to perform Rietveld refinement with background functions type 1 and 16 for background coefficients.
Figure S1. (a) The atomic structure of garnet-type c-LLZO, (b) Wyckoff positions that the Li ions could be located. The centers of Li(1), Li(2) and Li(3) sites are noted as 24d, 48g and 96h sites, respectively, and the 96h sites are slightly displaced off the 48g sites but they are still inside the octahedra.
Figure S2. Lattice parameters of the garnet-tape $c$-LLZO as a function of temperature from Rietveld refinements of HTND data.
Figure S3. The anisotropic atomic displacement parameters of $c$-Li$_7$La$_3$Zr$_2$O$_{12}$ as a function of temperature from Rietveld refinements of HTND data.
Figure S4. The occupancy of each Li site of the garnet-type $c$-LLZO as a function of temperature from Rietveld refinements of HTND data.