Supporting information for

Experimental visualization of lithium conduction pathways in Garnet-type $Li_7La_3Zr_2O_{12}$

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,[d] Yukihiko Kawamura,[e] Yunhui Huang,[f] John B. Goodenough,[b] Yusheng Zhao[a]

[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, $^7Li_7La_3Zr_2O_{12}$ was prepared using ^7Li enriched Li_2CO_3 as the raw material. $Li_7La_3Zr_2O_{12}$ was prepared by solid-state reaction of stoichiometric amounts of Li_2CO_3, La_2O_3 (heated at 900°C for 12 h) and ZrO_2. 10 wt% excess Li_2CO_3 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 Kα) 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 ^3He 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.

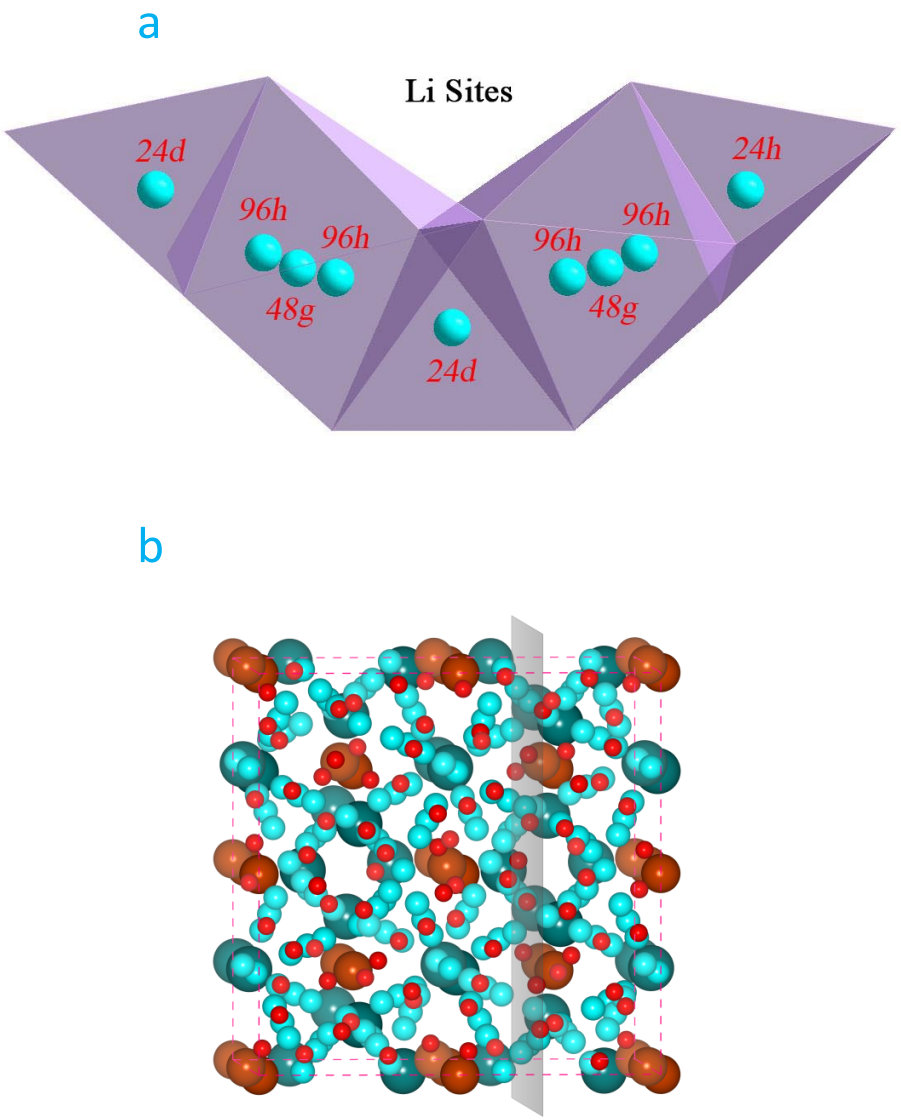

Figure S1. (a) The atomic structure of garnet-type *c*-LLZO, (b) Wyckoff positions that the Li ions could be located. The centers of Li(1), Li(2) and Li(3) sites are noted as 24*d,* 48*g* and 96*h* sites, respectively, and the 96*h* sites are slightly displaced off the 48*g* sites but they are still inside the octahedra.

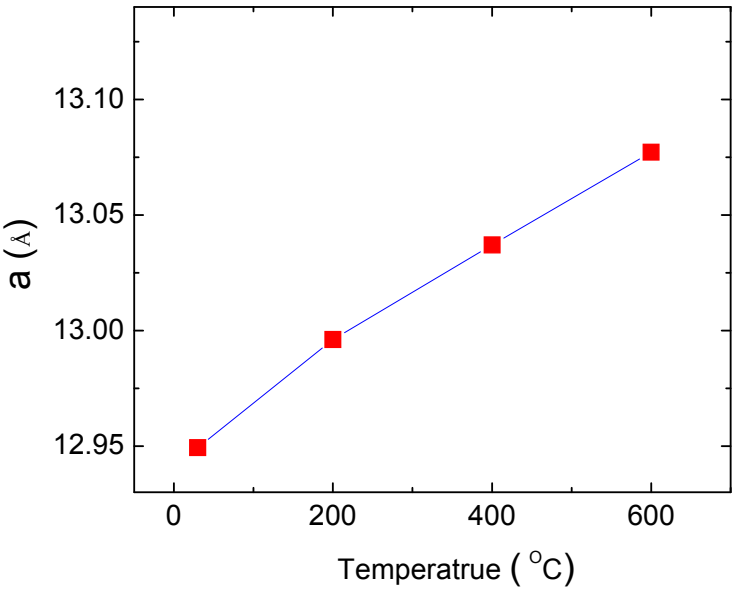

Figure S2. Lattice parameters of the garnet-tape *c*-LLZO as a function of temperature from Rietveld refinements of HTND data.

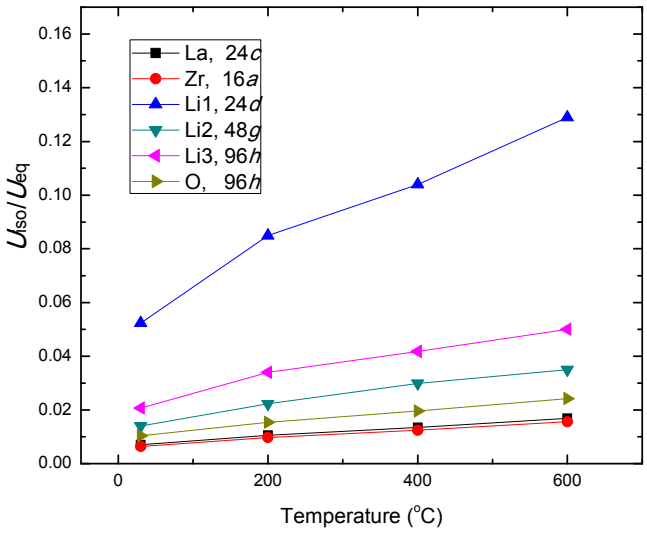

Figure S3. The anisotropic atomic displacement parameters of *c*-$Li_7La_3Zr_2O_{12}$ as a function of temperature from Rietveld refinements of HTND data

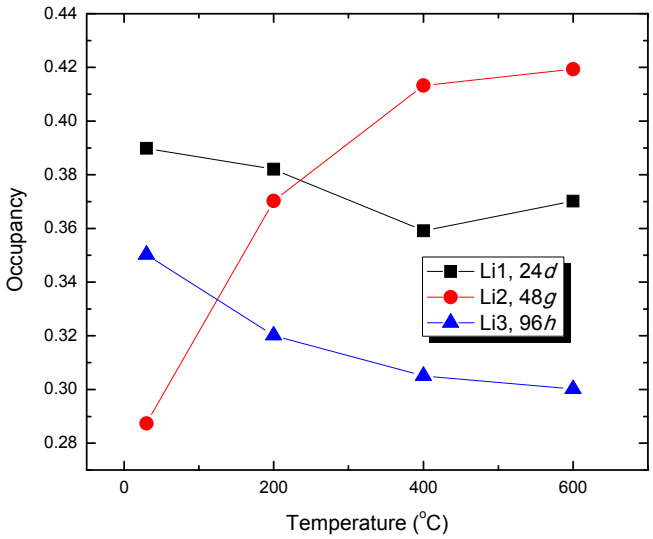

Figure S4. The occupancy of each Li site of the garnet-type *c*-LLZO as a function of temperature from Rietveld refinements of HTND data