Experimental visualization of lithium conduction pathways in garnet-type Li$_7$La$_3$Zr$_2$O$_{12}$†

Jiantao Han, Jinlong Zhu, Yutao Li, Xiaohui Yu, Shanmin Wang, Gang Wu, Hui Xie, Sven C. Vogel, Fujio Izumi, Koichi Momma, Yukihiko Kawamura, Yunhui Huang, John B. Goodenough and Yusheng Zhao*

Received 16th July 2012, Accepted 7th August 2012
DOI: 10.1039/c2cc35089k

The evolution of the Li-ion displacements in the 3D interstitial pathways of the cubic garnet-type Li$_7$La$_3$Zr$_2$O$_{12}$, was investigated with high-temperature neutron diffraction (HTND) from RT to 600 °C; the maximum-entropy method (MEM) was applied to estimate the Li nuclear-density distribution. Temperature-driven Li displacements were observed; the displacements indicate that the conduction pathways in the garnet framework are restricted to diffusion through the tetrahedral sites of the interstitial space.

Recently the Li-ion conductors with a garnet-type framework have attracted attention because of their high conductivity as solid-state electrolytes for lithium batteries. Thangadurai et al.1 initially reported Li-ion conduction in Li$_5$La$_3$M$_2$O$_{12}$ ($M$ = Nb, Ta) as a new class of Li-ion conductors, which are different from the well known Li-ion conductors, viz. layered Li$_3$N and Li-β-alumina, Li$_1$Ti$_2$AlO$_4$ (PO$_4$)$_3$ with a NASICON-type framework (open channel),3 interstitial (Li$_2$ZnGe$_2$O$_6$), and defective perovskite (Li$_{1.3}$Ti$_{1.7}$Al$_{0.3}$(PO$_4$)$_3$) structures.4 The garnets contain a cubic La$_3$M$_2$O$_{12}$ framework with a 3D interstitial pathway of 9 interconnected interstitial sites per formula unit (f.u.), and hence isotropic Li-ion conductivity occurs in three dimension similar to the case of Li-ion conductors with the NASICON framework.5 The highest Li-ion conductivity has been reported in a nominal cubic Li$_6.5$La$_3$Zr$_{1.5}$Ta$_{0.5}$O$_{12}$ (c-LLZO) that is stable at 1230 °C, which is needed for sintering a dense ceramic.6 Significant advances in this field have established (1) the existence of a second tetragonal phase (t-LLZO) with a much lower energy pathway is via the 24d tetrahedral sites that are occupied by Li in a Li$_6.5$La$_3$Zr$_{1.5}$Ta$_{0.5}$O$_{12}$ garnet as well as octahedral sites that bridge the tetrahedral sites with shared faces on opposite sides of the octahedral (see Fig. S1a, ESI†). A similar 3D interstitial pathway is found in the $[M_2]$O$_4$ spinels. Adams and Rao7 have argued that the lower energy pathway is via the 24d sites. Using high-temperature neutron diffraction (HTND), we have studied the evolution with temperature of the Li distribution and displacements in the 3D interstitial pathways of the c-LLZO polycrystalline samples prepared by solid-state reaction as reported elsewhere,6 but with $^7$LiCO$_3$ in the starting mixture. The ND data were collected at different temperatures (RT, 200, 400, 600 °C) with a high-pressure, preferred-orientation (HIPPO) neutron time-of-flight powder diffractometer at the Lujan Neutron Scattering Center, Los Alamos National Laboratory. Bulk samples were placed in a vanadium can and neutron time-of-flight data were collected under vacuum at room temperature. Neutrons were detected with 42 panels of $^3$He detector tubes arranged in three rings with nominal diffraction angles of 40°, 90°, and 144°. For each of four different temperatures from RT to 600 °C, structures were refined with the General Structural Analysis System GSAS developed by Larson and Von Dreele.8 The refinement results have been obtained with the crystal model reported by Cussen.9 The unit-cell parameters, atomic positions, isotropic displacement parameters, and peak widths in the profile function were all refined.

Fig. 1 shows the Rietveld refinement patterns for c-LLZO obtained by time-of-flight ND data at room temperature and 600 °C, respectively. The patterns were indexed on the cubic
space group $Ia3d$ (no. 230); there was no evidence of a tetragonal modification. The fitting was satisfactory ($R_{wp} = 2.99\%$, $R_p = 0.46\%$, and $\chi^2 = 2.34$ for RT) with precisely refined atomic positions as well as anisotropic atomic displacement parameters for all atoms under the classical harmonic-oscillation model.

The crystal structure and possible Wyckoff positions of Li are shown in Fig. S1 (ESI†). The Li-ion conduction pathways in the Cussen model consist of three distinguishable positions: the 24$d$ tetrahedral sites of the garnet structure, the 48$g$ center of the octahedral sites bridging the 24$d$ sites; and where only one of the two bridged 24$d$ sites is occupied by Li$^+$, a 96$h$ position in the bridging site near the face shared by the empty 24$d$ neighbor. It was postulated that Li is not stable in an octahedral site that bridges two occupied 24$d$ sites, but it is stable in a 48$g$ position if the octahedral site bridges two empty 24$d$ sites.

Fig. S2 (ESI†) shows the temperature dependence of the cubic $a$ lattice parameter; it reveals a small deviation from linear thermal expansion, but with no evidence of a phase transition. Our data indicate only a minor 1.1% enlargement of the $a$ parameter with temperature from RT to 600 °C. On the other hand, the rise in temperature caused a pronounced increase in the displacement parameters of all the atoms, particularly the Li atoms, as is shown in Fig. S3 (ESI†). The average preferred directions of the Li$_1$ (24$d$) displacements are towards the two opposing tetrahedral-site edges common to two interfaces with bridging octahedra, see Fig. 1(b) and the green ellipsoids of Fig. 2(a). These average preferred displacement directions are indicative of individual displacements toward the center of one of the four shared faces with a bridging octahedron. The smaller Li$_2$ (48$g$) and Li$_3$ (96$h$) displacements are along the axis of a bridge between 24$d$ sites; there is no indication of a bypass of the 24$d$ sites. The strong increase with temperature of the Li$^+$ displacements relative to those of the framework ions signals an enhancement of Li$^+$ transport and disorder within the interstitial pathways in a relatively stable background of framework ions.

From Fig. S3 (ESI†), the amplitude of the Li$_1$ (24$d$) displacements appears to increase above 600 °C at the expense of those of the Li$_1$ (96$h$), but not of the Li$_2$ (48$g$); the Li$^+$ ions are transported between the Li$_1$ (24$d$) and Li$_3$ (96$h$) sites across a common face, and the data appear to be consistent with a more rapid cooperative intersite transfer across two shared faces that involves shifting of Li$_3$ (96$h$) sites within octahedra via a 48$g$ position as the Li$_1$ (24$d$) occupancy shifts from one side to the other of the bridging octahedron.

To obtain experimental evidence for the Li$^+$ pathways and the evolution with temperature of Li$^+$ motions, the maximum-entropy (MEM) was applied with the Dysnomia program to estimate the density distribution of the neutron-scattering
Li(96) ions in the interstitial, interlocking network of stripes become connected to form a continuous 3D network of sites. As temperature increases above about 400°C, 24d–96h site-interchange of the occupied 24d site of a pair of tetrahedral sites. Since 7Li is the only negative neutron-scattering element in the sample, all the stripes observed in the Fourier maps of Fig. 2 are the Li-diffusion pathways. Fig. 2(c)–(f) demonstrate evidence for Li + bypassing the 24d sites. The authors would like to acknowledge: Office of Vehicle Technologies of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231 and the BATT Program subcontract no. 6805919.TA.

The negative nuclear densities obtained with MEM analysis of the HTND data are shown in Fig. 2. Since 7Li is the only negative neutron-scattering element in the sample, all the stripes observed in the Fourier maps of Fig. 2 are the Li-diffusion pathways. Fig. 2(c)–(f) demonstrate a clear enhancement of the Li displacements, hence diffusivity, with increasing temperature from ambient to 600 °C. The broken stripes correspond to Li displacements located at 24d, 48g, and 96h sites, and displacements between 96h sites signal interchange of the occupied 24d site of a pair of tetrahedral sites. As temperature increases above about 400 °C, the broken stripes become connected to form a continuous 3D network of moving Li + ions in the interstitial, interlocking network of 24d–96h–48g–96h–24d segments penetrating in 3D the garnet framework. Thus, our results indicate that the Li + ions in c-LLZO move only within the predicted low-energy pathway and that as the temperature increases from room temperature to 600 °C, the displacements of all the Li + ions remain confined to the interstitial pathways, including the 24d sites. Fig. 3 shows the two-dimensional contour maps sliced on (001) planes with z = 0.4 at T = room temperature, 200, 400, and 600 °C, respectively; they show a clear delocalization process of lithium located at (24d) and (96h) sites. Although the thermal vibrations of the other atoms, La, Zr and O, are also enhanced based on the MEM analysis, they remain in their initial positions and do not have diffusion pathways such as Li.

In summary, polycrystalline c-LLZO was prepared by conventional solid-state synthesis and investigated by high-temperature neutron diffraction techniques coupled with the MEM analysis. Temperature-driven dynamic Li + ion displacements show a Li 3D diffusion pathway consisting of interlocking Li(24d)–Li(96h)–Li(48g)–Li(96h)–Li(24d) chain segments. The results indicate that c-LLZO possesses a stable cubic phase at high temperature and that the Li + diffusion pathway in the compound contains the tetrahedral 24d sites; there is no evidence for Li + bypassing the 24d sites.

Notes and references


