Neutron Powder Diffraction Studies of Lithium Ion Conductors

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The garnet-related type lithium oxides are attractive as the fast Li-ion conductors [1,2]. We succeeded in synthesizing Li7La3Zr2O12 with a tetragonal symmetry for the first time by heating at a relatively low temperature of 1253 K [2]. We determined crystal structure of tetragonal Li7La3Zr2O12 by the Rietveld method using neutron powder diffraction data.

Polycrystalline tetragonal Li7La3Zr2O12 was prepared by the solid-state reaction. The starting materials of Li2CO3, La2O3, and ZrO2 were mixed in the calculated ratio, where 10 wt% excess Li2CO3 was added to prevent the loss of the lithium component by volatilization at high temperature. Mixed powder materials were put in an alumina crucible and heated at 1173K for 5 h in ambient atmosphere. The calcined specimen was reground and heated at 1253 K for 5 h.

Neutron powder diffraction data were collected at room temperature on the HERMES powder diffractometer installed at the JRR-3M research reactor of the Japan Atomic Energy Agency. The specimens were contained in a cylindrical vanadium cell with an inner diameter of 10 mm. Incident neutrons with a fixed wavelength of 1.8204(5) angstroms were obtained by a vertically focusing (331) Ge monochromator. The powder diffraction data were measured over a 2 theta range of 7-157 degrees with a step interval of 0.1.

The diffraction data were analyzed by the Rietveld method with RIETAN-2000, and the nuclear scattering density distribution of specimens were visualized by the Maximum-entropy-method (MEM).

Figure 1 depicts the three-dimensional distribution of nuclear scattering length density for tetragonal Li7La3Zr2O12 provided by the MEM analysis. The distribution of all atoms was clearly visible at the appropriate positions in the MEM image. No large unidentified distribution was obtained. Among Li, La, Zr, and O atoms, only the Li atom had a negative nuclear scattering length. The distribution having a negative value obviously indicated Li(1), Li(2), and Li(3) sites, and the distribution having a positive value was consistent with the La, Zr, and O sites.

References

[1] J. Awaka et al., Solid State Ionics 180 (2009) 602.
[2] J. Awaka et al., J. Solid State Chem. 182 (2009) 2046.

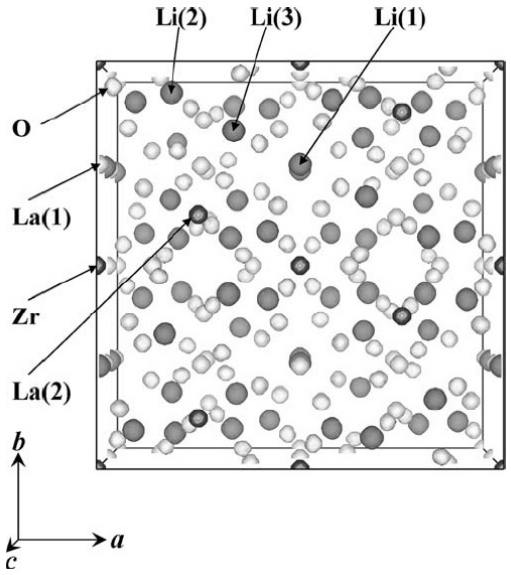

Fig. 1. Three-dimensional distribution of nuclear scattering length density for tetragonal Li7La3Zr2O12. The distribution is colored gray or white to show a negative or positive nuclear scattering length, respectively. The solid box indicates the unit cell.