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Crystal Structure of Fast Lithium-ion-conducting Cubic $Li_7La_3Zr_2O_{12}$

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The detailed crystal structure of cubic $Li_7La_3Zr_2O_{12}$ has been successfully determined by single-crystal X-ray structure analysis. The three-dimensional network of the Li-ion migration pathway with short Li–Li distance and occupational disordering is formed in the garnet-type framework structure. The basic unit of the pathway can be expressed as a loop constructed by the Li1 and Li2 sites. The loop links to another one, where only the Li1 site is shared by two loops as a junction.

Chemical batteries will become increasingly important for future energy storage technologies. Rechargeable Li-ion batteries are the most advanced energy storage devices, but their application has been presently limited to several portable electronic devices including mobile phones and notebook computers. In the case of applications to large electrical power storage systems such as electrical vehicles, all-solid-state Li-ion batteries have attracted attention because of their high energy density and safety issues. Therefore, there has been an extensive effort to develop Li-ion-conducting inorganic materials for the use as solid-state electrolyte which is a crucial component of all-solid-state Li-ion batteries, including NASICON $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$,[1] perovskite-$La_{2/3-x}Li_{3x}TiO_3$,[2] and Li_2S sulfide glasses.[3]

Recently, Li-ion-conducting oxides with garnet-related structure[4,5] have gained attention as solid-state electrolyte. In particular, cubic $Li_7La_3Zr_2O_{12}$ exhibits high bulk Li-ion conductivity of $\sigma = 5 \times 10^{-4}\,S\,cm^{-1}$ at room temperature among the crystalline Li-ion-conducting oxides.[6,7] Additionally, as this material shows excellent thermal performance and chemical stabilities against molten lithium, air, and moisture, cubic $Li_7La_3Zr_2O_{12}$ is an exciting key material for the development of future battery systems.

Although crystal structure is the predominant indicator revealing Li-ion conduction mechanisms, the detailed structure of cubic $Li_7La_3Zr_2O_{12}$ is still unclear, because of the difficulty in sample preparation. In addition, another polymorph having tetragonal symmetry for $Li_7La_3Zr_2O_{12}$ was recently reported.[8] The Li-ion conductivity of tetragonal $Li_7La_3Zr_2O_{12}$ is lower by two orders of magnitude than that of cubic $Li_7La_3Zr_2O_{12}$. Because the preparation temperature (950 °C) of tetragonal phase was lower than that (1230 °C) for the cubic material, the possibility of phase transformation upon heating should be considered. However, in the absence of structural and chemical analyses of the cubic form, the phase relationship has also not been revealed yet. Moreover, it should be emphasized that a comparison of crystal structure of cubic $Li_7La_3Zr_2O_{12}$ with those of known Li-ion-conducting oxide materials may provide clues to help improve the Li-ion-conduction property in garnet-related oxides.

To clarify the true chemical composition, crystal symmetry, and structure of cubic $Li_7La_3Zr_2O_{12}$, well-crystallized single-crystal specimens have highly been desired. Especially, an accurate single-crystal X-ray diffraction study is one of the most indispensable methods for a precise understanding of the positions and populations for the Li sites, as we have previously demonstrated in structural studies of electrode materials such as $LiMn_2O_4$,[9] $LiMnO_2$,[10] and $Li_4Ti_5O_{12}$.[11]

In the present study, we revealed the crystal structure of the cubic form of $Li_7La_3Zr_2O_{12}$ by single-crystal X-ray structure analysis for the first time. We also demonstrated the characteristic Li-site population in the garnet framework structure.

Single crystals of cubic $Li_7La_3Zr_2O_{12}$ were synthesized by high-temperature heating at 1250 °C in air. The starting materials used in this study were Li_2CO_3 (99.9% purity), La_2O_3 (99.9% purity, predried at 900 °C for 12 h), and ZrO_2 (99.9% purity). They were mixed in a molar ratio of $Li_2CO_3:La_2O_3:ZrO_2 = 3.85:1.5:2.0$. The obtained crystals were colorless and transparent, and approximately sphere-shaped with a typical diameter of 0.05 mm. The chemical formula, analyzed by inductively coupled plasma spectroscopy using pulverized crystals, confirmed the stoichiometric chemical composition; the result was consistent with that of the present structure refinement. X-ray oscillation photographs showed a good single crystallinity of the obtained crystal.

X-ray intensity data were collected by a single-crystal X-ray diffractometer with an imaging plate (Rigaku R-AXIS RAPID-II) using graphite-monochromatized Mo $K\alpha$ radiation at room temperature. A total of 30437 reflections were measured, of which 214 unique reflections ($R_{int} = 1.74\%$) were used in the structure refinement. The intensity data can be well explained by an extinction rule suggesting the cubic symmetry with a space group of $Ia\bar{3}d$ (no. 230). The cubic lattice parameter was determined to be $a = 12.9827(4)\,Å$ using the single-crystal data. The value agreed well with the previous powder data ($a = 12.9682(6)\,Å$).[6]

The structure refinement was initiated with the garnet-framework structure finding that the La, Zr, and O atoms located at 24*c*, 16*a*, and 96*h* sites, respectively. All calculations were carried out using a computer program Jana2006.[12] Subsequently, two Li sites were determined using the difference-Fourier map (summarized in the Supporting Information; SI[20]). A further site population refinement for these Li sites was applied where the total Li content was fixed at 7 in the $Li_7La_3Zr_2O_{12}$ stoichiometry. The population values for the La, Zr, and O atoms were refined to the nominal value within the experimental error. Finally, the refinement was converged to give $R = 1.61\%$ and $wR = 3.56\%$. It should be noted that the very low R values strongly support the present Li-site population model. The final structure parameters are listed in Table 1.

Table 1. Site, occupancy value, fractional coordinates, and atomic displacement parameter of cubic $Li_7La_3Zr_2O_{12}$

Atom	Site	g	x	y	z	U/Å^2
Li1	24*d*	0.94(7)	3/8	0	1/4	0.021(4)^c
Li2	96*h*	0.349^a	0.0959(15)	0.6922(14)	0.5731(15)	0.021^{b,c}
La	24*c*	1	1/8	0	1/4	0.0097(2)^d
Zr	16*a*	1	0	0	0	0.0064(2)^d
O	96*h*	1	−0.03163(18)	0.0538(2)	0.1501(2)	0.0107(7)^d

[a] $g(\text{Li2}) = 56/96 - 24/96 \times g(\text{Li1})$. [b] $U(\text{Li2}) = U(\text{Li1})$. [c] Isotropic atomic displacement parameter. [d] Equivalent isotropic atomic displacement parameter (Anisotropic atomic displacement parameters determined by this work are described in the CIF file[13]).

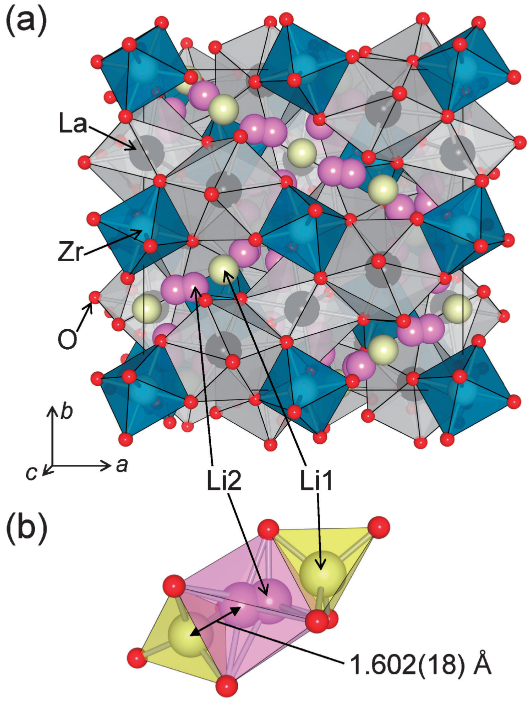

Figure 1. (a) Crystal structure of cubic $Li_7La_3Zr_2O_{12}$. (b) Coordination polyhedra around the Li1 and Li2 sites.

The refined crystal structure is shown in Figure 1a. Crystal structures were illustrated using a computer program VESTA.[14] The garnet framework structure was composed of dodecahedral LaO_8 and octahedral ZrO_6. The Li atoms occupied two types of crystallographic sites in the interstices of the framework structure. As shown in Figure 1b, the Li1 and Li2 atoms were located in the tetrahedral 24*d* site and distorted octahedral 96*h* site, respectively. The Li2 site is vacant in the ideal garnet structure.[15,16] Because the Li2 atom was situated at two equivalent positions in the distorted octahedron as a positional disorder in the lithium distribution, the local coordination environment of the Li2 atom may be considered as to be near fourfold LiO_4 coordination.[5] The disordering and partial occupation of the Li atoms at the Li2 site was reported as a key role of Li-ion conduction in these Li-ion conductors.[17] In fact, the occupation value for the Li2 site in the present $Li_7La_3Zr_2O_{12}$ was in rough agreement with those for the other cubic garnet-related type compounds such as $Li_6SrLa_2Nb_2O_{12}$ and $Li_6CaLa_2Nb_2O_{12}$.[18] On the other hand, the occupancy value ($g = 0.94(7)$) for the present Li1 site is highest among the known Li-ion-conducting garnet-related oxides. These results indicate that the highest Li content of 7 per garnet formula unit affects only the increasing Li occupation at the Li1 site in the structure.

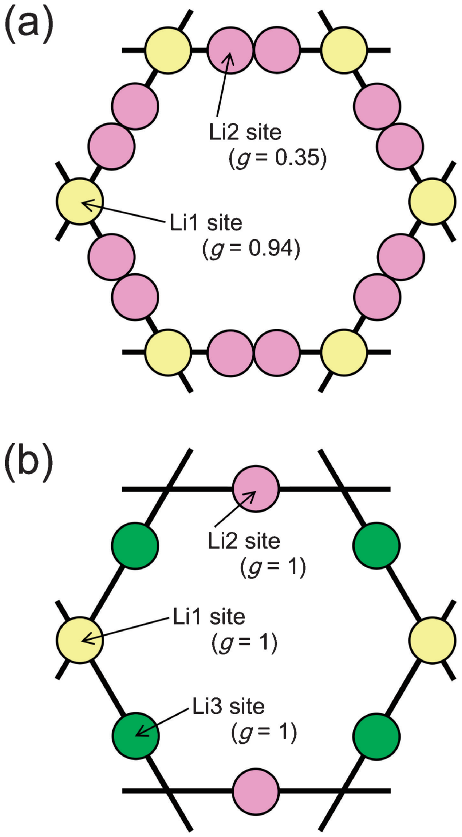

Figure 2. The loop structures constructed by Li atomic arrangement in (a) cubic and (b) tetragonal $Li_7La_3Zr_2O_{12}$. The occupancy value g for each site is noted in the parenthesis.

From a structural view point, the Li-ion migration pathway should correspond to the Li atomic arrangement in the structure. As shown in Figure 1a, cubic $Li_7La_3Zr_2O_{12}$ shows the complicated Li atomic arrangement in the interstices of the garnet-type framework structure. However, by focusing attention only to the Li atoms in the structure, the basic unit of the arrangement can be simply drawn as a loop constructed by the Li1 and Li2 sites (Figure 2a). This loop links to another one, where only the Li1 site was shared by two loops as a junction, and a three-dimensional network of the Li-ion migration pathway is formed in the structure, as shown in Figure 3.

In the loop structure, the tetrahedral $Li1O_4$ and distorted octahedral $Li2O_6$ shared with the face, which results in the very

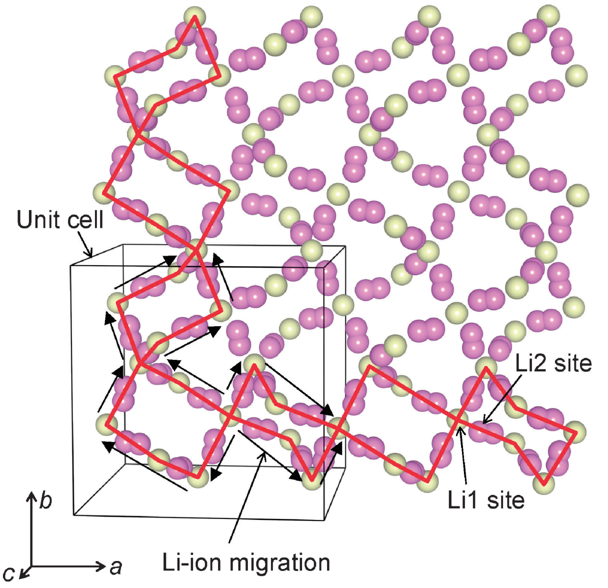

Figure 3. Three-dimensional network structure of the Li atomic arrangement in cubic $Li_7La_3Zr_2O_{12}$.

short Li–Li distance in this migration pathway (Figure 1b). This is a significant feature of the cubic garnet-related Li-ion conductors[19] and may be related to the good Li-ion-conduction properties compared to the other compounds.

On the other hand, tetragonal $Li_7La_3Zr_2O_{12}$[8] shows a complete ordering of the Li atoms. Namely, tetragonal $Li_7La_3Zr_2O_{12}$ has two tetrahedral sites (Li1 site and vacancy), and two distorted octahedral sites (Li2 and Li3 sites) in the loop structure (Figure 2b). The Li1, Li2, and Li3 sites are fully occupied by the Li atoms. Accordingly, the Li–Li distances were normally long with the Li–Li distance of >2.5 Å.

In summary, a valid crystal structure of cubic $Li_7La_3Zr_2O_{12}$ was determined by single-crystal X-ray structure analysis for the first time. The three-dimensional Li-ion network composed of the loop structure with the short Li–Li distance and the occupational disordering was revealed. One of the notable structural features of cubic $Li_7La_3Zr_2O_{12}$ was the full occupation of the Li1 site in comparison with the other garnet-related Li-ion conductors. The Li1 site was the junction of the network structure.

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13 Details of the crystallographic data in CIF format for cubic $Li_7La_3Zr_2O_{12}$ determined by this work have been electronically deposited with Fachinformationszentrum (FIZ) Karlsruhe ICSD-Database (CSD-number: 422259).

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