Synthesis, structure and ionic conductivities of novel Li-ion conductor $A_3Li_xTa_{6-x}Zr_xSi_4O_{26}$ ($A = Sr$ and Ba)

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Abstract

The solid state oxide Li-ion conductors with high electrochemical stability as well as high ionic conductivity are needed for application to all-solid-state Li-ion battery. In this study, $A_3\text{Li}_x\text{Ta}_{6-x}\text{Zr}_x\text{Si}_4\text{O}_{26}$ ($A = \text{Sr}$ and Ba) as the candidate solid electrolytes stable against Li metal were synthesized by a conventional solid state reaction, and their structure and ionic conductivities were investigated. Both the compounds with $A = \text{Sr}$, Ba crystallize in hexagonal structure with space group $P\bar{6}2m$ the same as $A_3\text{Ta}_6\text{Si}_4\text{O}_{26}$ does. MEM analysis, first principles calculation, and NMR spectroscopy showed that Li ions reside in interstice sites. The sample with $A = \text{Ba}$ exhibits higher ionic conductivity (e.g. $6.9 \times 10^{-8} \text{ S cm}^{-1}$ at 500 K in $x = 1.0$) than that with $A = \text{Sr}$ (e.g. $3.2 \times 10^{-8} \text{ S cm}^{-1}$ at 500 K in $x = 1.0$). Ionic conductivity was enhanced with an increase of the substitution of Li and Zr. Further enhancement of ionic conductivity was derived by making deficiency at A site cation. Consequently, $\text{Ba}_{2.75}\text{Li}_{1.5}\text{Ta}_5\text{ZrSi}_4\text{O}_{26}$ exhibits the highest total ionic conductivity of $4 \times 10^{-7} \text{ S / cm}$ at 500 K and the lowest activation energy of 0.72 eV. The consideration of the size of bottlenecks and nudged elastic band calculations suggest that Li ions diffuse in the A-site deficient layer perpendicular to c -axis.

Keywords

Li-ion conductivity, Li-ion conducting oxide, Structure, Bottleneck, Ion-conducting mechanism

1. Introduction

The demand for battery with high energy density, high reliability and safety continues to increase¹. Li metal anode, which is the most electropositive and has large capacity, is expected to meet the properties of high energy density. However, applying Li metal as anode with liquid electrolyte is difficult because dendritic growth of Li metal during discharge-charge cycles leads to explosion hazards². All-solid-state Li ion battery using ceramic electrolytes is expected to have high energy density, reliability and safety by preventing dendritic growth of Li metal and getting rid of using flammable organic-based electrolytes. Indeed, Ohta et al. reported that an all-solid-state Li ion battery using Li metal and garnet-type $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Nb}_{0.25}\text{O}_{12}$ oxide as an anode and a solid state electrolyte, respectively, retained 98 % of discharge capacity after 100th cycle³.

However, there are some difficulties when oxide solid state electrolytes are applied to all-solid-state-batteries, though they have the advantage of stability under ambient

atmosphere with moisture over sulfide electrolytes⁴. One difficulty is high resistivity of electrolyte as well as the interface between electrolyte and electrodes. The other is the lack in electrochemical stability e.g. the reduction of electrolyte by Li containing anode⁵. Therefore, the oxide solid state electrolyte exhibiting both the high ionic conductivity and electrochemical stability is desired to be applied as all-solid-state battery.

There are some oxide electrolytes possessing high bulk conductivity at room temperature such as perovskite-type $\text{La}_{2/3-x}\text{Li}_{3x}\text{Ti}^{4+}\text{O}_3$ ($x \approx 0.1$) ($1 \times 10^{-3} \text{ S / cm}$)⁶, $\text{La}_{0.29}\text{Li}_{0.04}\text{Nb}^{5+}\text{O}_3$ ($4 \times 10^{-5} \text{ S / cm}$)⁷, LISICON-type $\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}^{5+}_{0.4}\text{O}_4$ ($4 \times 10^{-5} \text{ S / cm}$)⁸, NASICON-type $\text{Li}_{1.3}\text{Ti}^{4+}_{1.7}\text{Al}_{0.3}(\text{PO}_4)_3$ ($7 \times 10^{-4} \text{ S / cm}$)⁹, and garnet-type $\text{Li}_7\text{La}_3\text{Zr}^{4+}_2\text{O}_{12}$ ($5 \times 10^{-4} \text{ S / cm}$)¹⁰. Most of these solid oxide electrolytes includes transition metal ion with electron configuration of d^0 . High ionic conductivity of those oxides is probably attributable to the flexibility of framework originated from hybridization between filled $2p$ orbital of oxygen and empty d orbital of transition metal, so-called second-order Jahn-Teller (SOJT) effect¹¹. The migration of Li ion in solid electrolytes causes local distortion of structural framework. The electrolytes containing SOJT active cation can accept such distortion and therefore exhibit high ionic conductivity.

The reduction of the electrolytes are commonly seen in Ti^{4+} containing oxides such as perovskite-type $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ ⁶ and NASICON-type $\text{Li}_{1.3}\text{Ti}_{1.7}\text{Al}_{0.3}(\text{PO}_4)_3$ ⁹. Nakayama et

al. found that the electrochemical stability of electrolytes against Li metal depends on their composition and structure¹². They showed that the electrolytes containing the cations with high effective nuclear charge such as Ti^{4+} , Nb^{5+} and Sb^{5+} were unstable against Li metal. In terms of structure, electrochemical stability of electrolytes is improved by increasing ionicity between ligands and cation. Their compositional criteria are in agreement with those in terms of electronegativity. The electronegativities¹³ of Ti^{4+} and Sb^{5+} are greater than those of Ta^{5+} and Zr^{4+} , resulting in the lower energy level of empty d and s orbital (LUMO) of Ti^{4+} and Sb^{5+} , respectively, compared to the level of LUMO of Ta^{5+} and Zr^{4+} .

In this study, based on the concept above mentioned, we attempted to prepare novel solid state oxide electrolytes for all-solid-state battery. To improve electrochemical stability and ionic conductivity, Ta^{5+} and Zr^{4+} were selected as constituent ions forming framework because they have electron configuration of d^0 and relatively low effective nuclear charge, *i.e.* low electronegativity. Additionally, Si^{4+} was selected to further improve electrochemical stability. We then focused on $\text{A}_3\text{Ta}_6\text{Si}_4\text{O}_{26}$ ($\text{A} = \text{Sr}$ and Ba) as host structure of oxide Li-ion conductor. The crystal structure of $\text{A}_3\text{Ta}_6\text{Si}_4\text{O}_{26}$ is shown in Fig. 1.

single-column Fig. 1 Crystal structure of $A_3Ta_6Si_4O_{26}$ ($A = Sr, Ba$). $1a$, $1b$ and $3g$ represent interstice sites.

This structure is based on a framework of corner-sharing of TaO_6 octahedra and SiO_4 tetrahedra. A ion occupies a half of the interstice sites alternately between octahedra and tetrahedra parallel to c -axis, forming layered structure. A ion vacant layer is expected to be Li-ion conducting path because there are much interstices. We tried to substitute Li^+ and Zr^{4+} for vacancy and Ta^{5+} to compensate charge, respectively, in $A_3Ta_6Si_4O_{26}$. Consequently, we successfully synthesized $A_3Li_xTa_{6-x}Zr_xSi_4O_{26}$ ($A = Sr$ and Ba) and found that these compounds show Li ion conductivity. Their structures, ionic conductivities, and conduction mechanism were investigated.

2. Experimental

Polycrystalline samples of $A_{3-x-y/2}Li_{x+y}Ta_{6-x}Zr_xSi_4O_{26}$ ($A = Sr$ and Ba ; $x = 0.5 - 3.0$; $y =$

0 - 2.0) were synthesized by a conventional solid state reaction. The stoichiometric amount of Li_2CO_3 (Kojundo Chemical Laboratory, 99.99 %), SrCO_3 (Soekawa Chemical Industries, 99.99 %) or BaCO_3 (Soekawa Chemical Industries, 99.99 %), Ta_2O_5 (Rare Metallic, 99.9 %), ZrO_2 (Rare Metallic, 99.99 %), and SiO_2 (Kojundo Chemical Laboratory, 99.9 %) were mixed in an agate mortar with ethanol. The synthesis condition for $\text{A}_3\text{Li}_x\text{Ta}_{6-x}\text{Zr}_x\text{Si}_4\text{O}_{26}$ is as follows. The mixture of starting materials was pressed into a pellet and calcined at 800 °C for 8 h in air, and 1000°C and 1100-1200°C for $\text{A} = \text{Ba}$ and Sr , respectively, for 12 h in air with an intermediate grinding. But only the sample with $\text{A} = \text{Sr}$ and $x = 0.5$ was calcined at 1150 °C for 12 h and then 1200 °C for 12 h before final sintering. After the calcined sample was ground, the obtained powder was pressed into a pellet and sintered at 1000-1350 °C for 8 h in air. The specific synthesis conditions for $\text{A}_3\text{Li}_x\text{Ta}_{6-x}\text{Zr}_x\text{Si}_4\text{O}_{26}$ ($\text{A} = \text{Sr}$ and Ba) are summarized in Table S1 and S2, respectively, in the supporting information. The synthesis condition for A site deficient series $\text{A}_{3-y/2}\text{Li}_{1+y}\text{Ta}_5\text{ZrSi}_4\text{O}_{26}$ is as follows. The mixture of starting materials was calcined at 800 °C for 8 h in air, and then sintered at 1300 °C for 8 h in air. Phase identification was performed by the X-ray powder diffraction (XRD) method using a Rigaku RINT2100 diffractometer ($\text{Cu K}\alpha$ radiation). Synchrotron XRD data for structural analyses were collected on a Debye-Scherrer type powder diffractometer with

an imaging-plate type detector installed in beamline BL02B2 at SPring-8, Hyogo in Japan. The wavelength of the incident synchrotron radiation was fixed at 0.42060 Å. The samples were packed into a glass capillary having an outer diameter of 0.2 mm. The structural parameters were refined by Rietveld analysis using the program RIETAN-FP¹⁴. The program VESTA¹⁵ was used for drawing the crystal structures. Electron density distributions were elucidated from synchrotron powder XRD data by maximum entropy method (MEM) using the code Dysnomia¹⁶. The limited-memory Broyden-Fletcher-Goldfarb-Shanno algorithm was used for MEM analyses¹⁷. The compositional analysis except for Si of Ba₃Li₂Ta₄Zr₂Si₄O₂₆ was performed by the inductively coupled plasma atomic emission spectrometry (ICP-AES) with a HORIBA Ultima 2 ICP optical emission spectrometer. The sample solution was prepared as follows. About 1 mg of powder sample, 1 mL of concentrated nitric acid HNO₃ and 1 mL of concentrated hydrofluoric acid HF were sealed in a Teflon vessel. The samples were then heated about 170 °C and agitated ultrasonically. After the samples were dissolved, the solutions were diluted to 100 mL with distilled water. The ionic conductivity for the sintered pellets was measured by ac impedance method in the temperature range up to 1000 K over the frequency range from 20 Hz to 1 MHz using an Agilent 4284 precision LCR meter, and from 5 Hz to 13 MHz using a Yokogawa

Hewlett Packard 4192A LF Impedance Analyzer. ^7Li nuclear magnetic resonance (NMR) measurements were performed using a Bruker AVANCE III 4000WB ($B = 9.4$ T, and ^7Li Larmor frequency of 155.50 MHz) spectrometer with magic-angle spinning (MAS) at 5 kHz. Measurement conditions were 90° pulses of $1\ \mu\text{s}$ length and 10 s relaxation delays. Chemical shifts were externally referenced to a solid LiCl ($\delta = -1.19$ ppm).

3. Calculation

In order to understand the bulk properties of $A_3\text{Li}_x\text{Ta}_{6-x}\text{Zr}_x\text{Si}_4\text{O}_{26}$ ($A = \text{Sr}$ and Ba ; $x = 1.0$), theoretical analysis was performed using first-principles calculations. We employed the projector augmented planed wave method (PAW_VASP)¹⁸⁻²³ and the nudged elastic band method (NEB)²⁴ with the generalized gradient approximation, GGA (PBE)²⁵. The cut off energy was 550 eV. And as for the Brillouin zone integration, the Monkhorst-Pack special k points set 4x4x4 (36K points) was used. Based on these conditions, we identified the stable position of Li in new crystal structures.

In the initial structure for the calculation, Li ion was ignored and one Zr ion was substituted for one of six Ta ions. After initial structure calculation, single Li ion was put at the each $1a$, $1b$, and $3g$ site shown in Fig. 1 in each calculation, and then all ions

were allowed to move so as to search for the lowest-energy positions.

Using the VTST code combined with the PAW_VASP, we estimated the barrier height energy of Li ion diffusion in our new crystal structure. The details of the NEB method are similar to those in a previous paper^{26,27}.

In order to ascertain Li diffusion path, the first-principles molecular dynamics (FPMD) was carried out. In this situation, the Brillouin zone integration was approximated by Γ point sampling in order to save the computational costs. The time step was 1 fs. We carried out FPMD simulations without space group symmetry. The trajectories of Li were analyzed by visualization. The trajectories were visualized by the Fujitsu SCIGRESS ME 2.2 software package. By using this method, we obtained the stable positions of Li for the site with fractional occupancy due to the space group.

4. Results

4-1. Synthesis and structure

The powder XRD patterns for $A_3\text{Li}_x\text{Ta}_{6-x}\text{Zr}_x\text{Si}_4\text{O}_{26}$ ($A = \text{Sr}$ and Ba) are shown in Fig. 2(a) and 2(b), respectively.

1.5-column Fig. 2 Composition dependencies of X-ray diffraction patterns for $A_3Li_xTa_{6-x}Zr_xSi_4O_{26}$ at various x values. $A = Sr$ and Ba for (a) and (b), respectively.

Here, the sample with $A = Sr$ and $x = 2.0$ was sintered at 1250 °C, while the samples with $A = Sr$ except for $x = 2.0$ were sintered at 1300 °C. All samples with $A = Ba$ were sintered at 1250°C. $A_3Li_xTa_{6-x}Zr_xSi_4O_{26}$ ($A = Sr$ and Ba ; $x = 0.5 - 3.0$) crystallize in a hexagonal structure with space group $P\bar{6}2m$. In the composition range of $x = 1.0 - 1.5$ and $x = 1.0 - 2.0$ for $A = Sr$ and Ba , respectively, almost a single phase sample was obtained. According to ICP analyses, the amount of Li loss during heating in $Ba_3Li_2Ta_4Zr_2Si_4O_{26}$ were 0 %, 30 % and 41 % for samples sintered at 1000 °C, 1250 °C and 1350 °C, respectively. On the other hand, the losses of Ba, Ta and Zr were not observed during heating. Composition dependences of lattice parameters for $A_3Li_xTa_{6-x}Zr_xSi_4O_{26}$ ($A = Sr$ and Ba) are shown in Fig. 3(a) and 3(b), respectively.

1.5-column Fig. 3 Composition dependencies of lattice constants for $A_3Li_xTa_{6-x}Zr_xSi_4O_{26}$ at various x values. $A = Sr$ and Ba for (a) and (b), respectively.

The sintering conditions of samples were the same ones of the samples used for XRD measurements. The values of lattice parameters for the compounds with $x = 0$ are taken from ICSD #15936²⁸ and #18317²⁹. The lattice parameters increase with an increase of x value up to $x = 3.0$ in the sample with $A = Ba$. The composition of resultant compounds did not correspond to that of starting mixtures in high x region due to formation of impurity phases (see Fig. 2). Therefore the lattice parameters did not change in a linear fashion for the compound with $A = Ba$. On the other hand, in the sample with $A = Sr$, the lattice parameter of a turned to decrease at $x = 1.5$, though little impurity phase are observed from XRD (see Fig. 2(a)). This result suggests means that Li ions substitute different site between $x = 1.0$ and 1.5 in the compounds with $A = Sr$. Structural refinements by Rietveld analysis for $x = 1.0$ samples were performed on the basis of the

structure of $A_3Ta_6Si_4O_{26}$ ($A = Sr^{28}, Ba^{29}$; see Fig. 1), which corresponds to $x = 0$ in $A_3Li_xTa_{6-x}Zr_xSi_4O_{26}$. Zr^{4+} is substituted for Ta^{5+} , and Li^+ was ignored in our structure model due to its small scattering factor. Figure 4(a) and 4(b) show the calculated, observed, and difference synchrotron X-ray diffraction patterns for $A_3LiTa_5ZrSi_4O_{26}$ ($A = Sr$ and Ba), respectively.

single-column Fig. 4 Observed (crosses), calculated (solid line), and difference (bottom) X-ray diffraction patterns for $Sr_3LiTa_5ZrSi_4O_{26}$ (a) and $Ba_3LiTa_5ZrSi_4O_{26}$ (b) after refinement in space group $P\bar{6}2m$. Peak positions of $Sr_3LiTa_5ZrSi_4O_{26}$ (up) and $ZrSiO_4$ (bottom) for (a) and $Ba_3LiTa_5ZrSi_4O_{26}$ (up) and ZrO_2 (bottom) for (b) are indicated.

The amount of impurity phases of ZrO_2 in $Ba_3LiTa_5ZrSi_4O_{26}$ and $ZrSiO_4$ in $Sr_3LiTa_5ZrSi_4O_{26}$ are estimated to be 0.6 wt% and 2.1 wt%, respectively. To the best of

our knowledge, ion-conducting compounds having this structure have not been reported until now. The refined structural parameters for $A_3\text{LiTa}_5\text{ZrSi}_4\text{O}_{26}$ ($A = \text{Sr}$ and Ba) are listed in Tables 1 and 2, respectively. The values of bond valence sums (BVS)³⁰ for A (Sr^{2+} and Ba^{2+}) cations are listed in Table 3 together with the compounds of $x = 0$ ^{28,29}. Relatively high isotropic temperature factors of A ion and oxygens in the compounds with $A = \text{Sr}$ may be attributable to spacious environment around A ion, which is indicated by low BVS value of Sr^{2+} . A relatively smaller BVS value of Sr in $\text{Sr}_3\text{LiTa}_5\text{ZrSi}_4\text{O}_{26}$ is probably related to the lower substitution limit of Li^+ and Zr^{4+} in the Sr compounds than in Ba compounds. Zr^{4+} substitution causes the expansion of lattice and, accordingly, A cation polyhedra. Sr ions of $\text{Sr}_3\text{Li}_x\text{Ta}_{6-x}\text{Zr}_x\text{Si}_4\text{O}_{26}$ are electrostatically unstable as indicated by the small BVS value. Therefore, in the compounds with $A = \text{Sr}$, further substitution of Zr cannot be accepted.

Table 1 Structural parameters of Ba₃LiTa₅ZrSi₄O₂₆.

atom	site	<i>g</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> / Å ²
Ba	3 <i>f</i>	1	0.60106(15)	0	0	0.67(2)
Ta	6 <i>i</i>	0.8333	0.23906(7)	0	0.25568(12)	0.253(9)
Zr		0.1667				
Si	4 <i>h</i>	1	1/3	2/3	0.2949(7)	0.64(11)
O1	2 <i>d</i>	1	1/3	2/3	1/2	0.56(8)
O2	3 <i>g</i>	1	0.2779(13)	0	1/2	<i>B</i> (O1)
O3	6 <i>i</i>	1	0.8177(9)	0	0.2600(13)	<i>B</i> (O1)
O4	12 <i>l</i>	1	0.1790(6)	0.4899(8)	0.2212(8)	<i>B</i> (O1)
O5	3 <i>f</i>	1	0.22712(15)	0	0	<i>B</i> (O1)

Hexagonal, space group $P\bar{6}2m$ (No. 189), $Z = 1$, $a = 9.0495(2)$ Å, $c = 7.8198(1)$ Å, $V = 554.593(16)$ Å³; $R_{\text{wp}} = 5.02$ %, $R_{\text{p}} = 3.78$ %, $R_{\text{e}} = 2.84$ %, $S = 1.77$, $R_{\text{B}} = 1.11$ %, $R_{\text{F}} = 0.44$ %.

Table 2 Structural parameters of $\text{Sr}_3\text{LiTa}_5\text{ZrSi}_4\text{O}_{26}$.

atom	site	g	x	y	z	$B / \text{\AA}^2$
Sr	$3f$	1	0.59720(16)	0	0	1.11(3)
Ta	$6i$	0.8333	0.23964(5)	0	0.25354(10)	0.397(5)
Zr		0.1667				
Si	$4h$	1	1/3	2/3	0.2942(5)	0.70(2)
O1	$2d$	1	1/3	2/3	1/2	1.70(3)
O2	$3g$	1	0.2769(11)	0	1/2	$B(\text{O1})$
O3	$6i$	1	0.8075(7)	0	0.2533(13)	$B(\text{O1})$
O4	$12l$	1	0.1766(5)	0.4965(5)	0.2121(6)	$B(\text{O1})$
O5	$3f$	1	0.2297(12)	0	0	$B(\text{O1})$

Hexagonal, space group $P\bar{6}2m$ (No. 189), $Z = 1$, $a = 8.9234(1) \text{ \AA}$, $c = 7.6990(1) \text{ \AA}$, $V = 530.915(8) \text{ \AA}^3$; $R_{\text{wp}} = 3.24 \%$, $R_p = 2.32 \%$, $R_e = 2.68 \%$, $S = 1.21$, $R_B = 1.52 \%$, $R_F = 0.90 \%$.

Table 3 Bond valence sums for $\text{A}_3\text{Li}_x\text{Ta}_{6-x}\text{Zr}_x\text{Si}_4\text{O}_{26}$ ($A = \text{Sr}$ and Ba).

x	Sr	Ba
0	1.75	2.03
1.0	1.68	2.00

A conventional Rietveld refinement using XRD data gives us little information on Li position. Therefore, we tried to elucidate the position of Li using maximum entropy method (MEM) and bond valence sum calculation. The three candidate sites, *1a*, *1b* and *3g* site, were picked up among interstitial space (see Fig. 1). Both of the *1a* and *1b* sites are surrounded by six TaO₆ octahedra. The *1a* and *1b* sites are located in the A cation containing layer and A cation vacant layer, respectively. The *3g* site is located in the A cation vacant layer and is surrounded by SiO₄ tetrahedra and TaO₆ octahedra. An *x* position of *3g* site was fixed at the same as that of A cation, i.e. the center of the cage formed by TaO₆ and SiO₄. Fractional coordinates and BVSs of Li⁺ for each candidate sites are listed in Table 4. The BVSs of *1a* sites for Sr₃LiTa₅ZrSi₄O₂₆ and Ba₃LiTa₅ZrSi₄O₂₆, are 0.90 and 0.88, respectively, which are close to nominal charge of Li⁺, indicating that *1a* site is electrostatically stable for Li⁺. On the other hand, those of *1b* and *3g* sites were much smaller than the values expected from nominal charge, indicating that these sites are too large for Li⁺.

Electron density distribution of Ba₃LiTa₅ZrSi₄O₂₆ calculated by MEM analysis was shown in Fig. 5.

2-column Fig. 5 Equidensity maps of electron density distributions for $\text{Ba}_3\text{LiTa}_5\text{ZrSi}_4\text{O}_{26}$. The iso surface density levels are $0.25 \text{ e}\text{\AA}^{-3}$. Three-dimensional map (a) and part of electron density along $z = 0.25 - 0.73$ (b) are shown.

Very small maximums of electron density were observed at $1b$ and $3g$ sites. The electron density maximum at $3g$ site was not located at the center of cage, but shifted to TaO_6 octahedra, indicating that Li^+ does not prefer a center of cage as indicated as BVS value at $3g$ site.

Table 4 Fractional coordinates and bond valence sums of the candidate sites for Li⁺.

<i>A</i>	site	<i>x</i>	<i>y</i>	<i>z</i>	BVS
Sr	1 <i>a</i>	0	0	0	0.90
	1 <i>b</i>	0	0	1/2	0.50
	3 <i>g</i>	0.59720	0	1/2	0.17
	3 <i>g</i> (relaxed) ^a	0.7619	0	1/2	0.84
Ba	1 <i>a</i>	0	0	0	0.88
	1 <i>b</i>	0	0	1/2	0.54
	3 <i>g</i>	0.60106	0	1/2	0.15
	3 <i>g</i> (relaxed) ^a	0.7737	0	1/2	0.79

^a The positions of 3*g*(relaxed) are obtained by first principles calculation.

Figure 6 shows the ⁷Li MAS-NMR spectra of A₃LiTa₅ZrSi₄O₂₆ (*A* = Sr and Ba).

single-column Fig. 6 ${}^7\text{Li}$ MAS NMR spectra for $\text{A}_3\text{Li}_x\text{Ta}_{6-x}\text{Zr}_x\text{Si}_4\text{O}_{26}$.

NMR patterns were fitted with a mixture of Gaussian and Lorentzian line shape. Decomposed patterns and resulting chemical shift δ , integrated intensity, and line width for individual resonances are shown in Fig. S1 - S3 and Table S3 - S5 in the supporting information. An asymmetric peak for the sample with $A = \text{Sr}$ means that Li^+ ions are probably distributed into several different sites in this compound. On the other hand, single peaks were observed for the samples with $A = \text{Ba}$, indicating that almost all Li^+ ions are at a single site. In the compound with $A = \text{Sr}$, the main peak appears at small chemical shift value at 0.99 ppm, indicating that most of Li ions are relatively strongly shielded. The peak at 0.99 ppm may be assigned to Li ions at $1a$ site because Li ion at $1a$ site is more covalent than others [due to relatively shorter Li-O bond lengths, which is](#)

also indicated by high BVS value (Table 3). However, x position of 3g site is variable and thus the possibility of Li ion residing in 3g site cannot be excluded. In the compound with $A = \text{Ba}$, large chemical shift value about 5 ppm was observed, indicating that most of Li ions are more ionic than those in the compound with $A = \text{Sr}$. There is little difference of BVS values between the compounds with $A = \text{Sr}$ and Ba, indicating that the ionicity of Li at each site are close between the compounds with $A = \text{Sr}$ and Ba. Therefore, the main peak in the compounds with $A = \text{Ba}$ at about 5 ppm may originate from Li ion at 1b site or 3g site.

The stability for Li^+ at each candidate site was examined by the first principles calculation. After structure relaxation, Li^+ ion at 3g site was shifted in the direction of Ta/ZrO₆ octahedra. The shift direction was opposite to that obtained by MEM analysis, but we do not as yet have satisfactory explanation for this. Resulted Li^+ position at 3g site is shown in Fig. 7 and Table 4.

single-column Fig. 7 Li position in 3g site refined by first principles calculation.

Dashed open circles show the Li position before refinement.

Table 5 lists the total energies for various Li^+ sites in $\text{A}_3\text{LiTa}_5\text{ZrSi}_4\text{O}_{26}$ ($\text{A} = \text{Sr}$ and Ba).

The total energies of Li^+ at $1a$ site are set as zero for purposes of comparison. $3g-1$ and $3g-2$ sites are distinguished by nearest neighbor cations. $3g-1$ sites are surrounded by only Ta^{5+} ions, while $3g-2$ sites are surrounded by Ta^{5+} ions and Zr^{4+} ion. There are little differences between $1a$, $3g-1$ and $3g-2$ sites for both the compounds. It is likely that Li^+ ions are distributed into these sites.

Table 5 The total energy of $\text{A}_3\text{LiTa}_5\text{ZrSi}_4\text{O}_{26}$ ($\text{A} = \text{Sr}$ and Ba) for various Li^+ site.

A	$1a$	$3g-1$	$3g-2$	$1b$
Sr	0 eV	0.094 eV	0.013 eV	0.56 eV
Ba	0 eV	0.14 eV	0.064 eV	0.50 eV

The BVS and first principles calculations suggest that in both the compounds, Li ions prefer to occupy $1a$ site. However, NMR and MEM analysis showed that Li ions little occupy $1a$ site for $\text{Ba}_3\text{LiTa}_5\text{ZrSi}_4\text{O}_{26}$. We are not entirely sure about the difference between calculation and experimental result with respect to Li sites at this time.

Structural refinement using neutron diffraction should be a future work.

Figure 8(a), 8(b), 8(c), and 8(d) show the powder XRD patterns and composition dependences of lattice parameters for A-site deficient type $A_{3-y/2}Li_{1+y}Ta_5ZrSi_4O_{26}$ ($A = Sr$ and Ba ; $y = 0 - 2.0$), respectively.

2-column Fig. 8 Composition dependences of X-ray diffraction patterns and lattice constants for $A_{3-y/2}Li_{1+y}Ta_5ZrSi_4O_{26}$ at various y values. XRD pattern and lattice parameter for $A = Sr$ are (a) and (b), respectively, and $A = Ba$ are (c) and (d), respectively.

Impurity phases appear in both the compounds above $y = 1.0$. There is no change of lattice parameters above $y = 1.0$ and 1.5 for $A = Sr$ and Ba , respectively, indicating that substitution limits for $A = Sr$ and Ba are $y = 0.5$ and up to 1.0 , respectively.

4-2. Ionic conductivity

Figure 9(a) shows Arrhenius plots for total (bulk + grain-boundary) ionic conductivity for $A_3LiTa_5ZrSi_4O_{26}$ ($A = Sr$ and Ba) sintered at $1300^\circ C$ and $1250^\circ C$, respectively.

single-column Fig. 9 Ionic conductivities for $A_{3-y/2}Li_{1+y}Ta_{6-x}Zr_xSi_4O_{26}$. Arrhenius plots of $A_3LiTa_5ZrSi_4O_{26}$ ($A = Sr, Ba$) (a), Arrhenius plots for $Ba_3Li_xTa_{6-x}Zr_xSi_4O_{26}$ at various x values (b), that for $Ba_3Li_2Ta_4Zr_2Si_4O_{26}$ synthesized at various temperatures (c), that for $Ba_{3-y/2}Li_{1+y}Ta_5ZrSi_4O_{26}$ at various y values (d), and ionic conductivities at 500 K and activation energy for $Ba_3Li_xTa_{6-x}Zr_xSi_4O_{26}$ at various x values (e) are shown.

The Nyquist plots obtained at 780 K for these compounds are shown in Fig. S4(a) in the supporting information. These compounds show almost the same activation energy, 0.76 eV and 0.79 eV for $A = Sr$ and Ba , respectively. On the other hand, the sample with $A = Ba$ exhibited relatively greater conductivity of $6.9 \times 10^{-8} \text{ S cm}^{-1}$ at 500 K than that with $A = Sr$ (e.g. $3.2 \times 10^{-8} \text{ S cm}^{-1}$ at 500 K). Figure 9(b) shows Arrhenius plots for total ionic conductivity of $Ba_3Li_xTa_{6-x}Zr_xSi_4O_{26}$ sintered at 1250 °C at various x values. Figure 9(c) shows Arrhenius plots for total ionic conductivities of $Ba_3Li_2Ta_4Zr_2Si_4O_{26}$ ($x = 2.0$ samples) sintered at various temperatures. These samples show the same activation energy, E_a , of 0.79 eV. The sample sintered at 1250 °C exhibited the highest ionic conductivity. The finding suggests that the grain boundary resistance decreases with an increase in sintering temperature due to grain growth, but too high sintering temperature reduces ionic conductivity because of Li vaporization as shown by ICP-AES measurement. Arrhenius plots of A-site deficient type $Ba_{3-y/2}Li_{1+y}Ta_5ZrSi_4O_{26}$ sintered at 1300 °C are shown in Fig. 9(d). Nyquist plots of the sample of $y = 0.5$ at various temperatures are shown in Fig. S4(b) in the supporting information. The sample with $y =$

0.5 exhibit the best conductivity of $4.1 \times 10^{-7} \text{ S cm}^{-1}$ at 500 K and low activation energy of 0.72 eV in $\text{Ba}_{3-y/2}\text{Li}_{1+x+y}\text{Ta}_{6-x}\text{Zr}_x\text{Si}_4\text{O}_{26}$ system. Composition dependences of conductivity at 500 K and activation energies for $\text{Ba}_3\text{Li}_x\text{Ta}_{6-x}\text{Zr}_x\text{Si}_4\text{O}_{26}$ are shown in Fig. 9(e). The conductivity increases as x increases up to 2.5, implying that conductive species are Li^+ ions. The activation energies were not significantly changed, indicating that the conduction mechanism for $\text{Ba}_3\text{Li}_x\text{Ta}_{6-x}\text{Zr}_x\text{Si}_4\text{O}_{26}$ is the same in this composition region.

The ionic conductivities of $\text{A}_3\text{Li}_x\text{Ta}_{6-x}\text{Zr}_x\text{Si}_4\text{O}_{26}$ ($A = \text{Sr}$ and Ba) are discussed in terms of crystal structure. The possible diffusion paths of Li^+ are from $1a$ to $1b$ site, which is parallel to c axis, from $1b$ to $3g$ site, and from $3g$ to other $3g$ sites, both of which are vertical to c axis, and vice versa. Schematics of the diffusion path along c axis and in ab plane are shown in Fig. 10(a) and 10(b), respectively.

single-column Fig. 10 Ionic diffusion paths for $\text{A}_3\text{Li}_x\text{Ta}_{6-x}\text{Zr}_x\text{Si}_4\text{O}_{26}$ ($A = \text{Sr}, \text{Ba}$).

Diffusion paths along c axis (a), in ab plane (b) are shown. The bottlenecks between $1a$ and $1b$ site (c), $1b$ and $3g$ sites (d), and $3g$ and other $3g$ sites (e) are shown.

All of these paths includes bottlenecks formed by $(\text{Ta}, \text{Zr})\text{O}_6$ octahedra and SiO_4 tetrahedra. Figure 10(c), 10(d), and 10(e) and Fig. 11 show the schematics of bottlenecks for each path and those sizes, respectively.

single-column Fig. 11 Bottleneck sizes of $\text{A}_3\text{LiTa}_5\text{ZrSi}_4\text{O}_{26}$ ($\text{A} = \text{Sr}, \text{Ba}$). Enclosed alphanumerics 1 - 5 denote positions shown in Fig. 10(c) - (e).

Li^+ is unlikely to diffuse along c axis due to the small bottleneck size in-between $1a$ and $1b$ site. This suggestion was confirmed by a first principles calculation. Figure 12(a) and 12(b) show minimum energy paths of Li ion diffusing from $1a$ to $1b$ site and $1b$ to $3g$ sites in $\text{Sr}_3\text{LiTa}_5\text{ZrSi}_4\text{O}_{26}$, respectively.

single-column Fig. 12 Relative barrier height energies ΔE of Li diffusion between 1a and 1b in $\text{Sr}_3\text{LiTa}_5\text{ZrSi}_4\text{O}_{26}$ are illustrated in (a), where 1a site is chosen as the origin of ΔE . There appears a maximum barrier height energy with 2.97 eV. At this maximum configuration, Li locates at the center of the vacant space of three connected octahedrons which include Ta or Zr. (b) shows relative barrier height energies of Li diffusion in $\text{Sr}_3\text{LiTa}_5\text{ZrSi}_4\text{O}_{26}$ from 1b to 3g-1 through 3g-2 site. The maximum barrier height energy of Li along this path is 0.69 eV.

The activation energy of route from 1a to 1b site, which is along to *c*-axis, is calculated to be 2.97 eV. Trajectory plots of $\text{Sr}_3\text{LiTa}_5\text{ZrSi}_4\text{O}_{26}$ from [001] and [110] direction at 1400 K during 1980 ps are shown in Fig. 13(a) and 13(b), respectively. Li ion spends almost time at 3g sites, corresponding to the total energy calculation (Table 4).

single-column Fig. 13(a) Trajectory from [001] direction of atoms in $\text{Sr}_3\text{LiTa}_5\text{ZrSi}_4\text{O}_{26}$. The whole simulation time is 1980 ps with time step 1 fs. The 3000 snap shots are chosen equally during 1980 ps. Each atom at every snapshot is connected by lines and form the trajectories in the cell. (b) stands for the trajectories from [110] direction. The initial position of Li is located at 1b site.

Diffusion of Li ions from A cation deficient layer to A cation containing layer was not observed. Therefore, Li ion diffuses two dimensionally on A cation deficient layer. Li^+ diffusion path from 3g to other 3g sites (Fig. 10(b) and 10(e)) probably dominate the ionic conductivity in $\text{A}_3\text{Li}_x\text{Ta}_{6-x}\text{Zr}_x\text{Si}_4\text{O}_{26}$ ($\text{A} = \text{Sr}$ and Ba) because of the narrowest bottleneck in this structure. For comparison, bottleneck sizes are $1.79 - 2.22 \text{ \AA}$ ³¹ for perovskite-type LLTO ($E_a = 0.4 \text{ eV}$)⁶, and $1.94 \text{ \AA}$ ³² and $2.15 \text{ \AA}$ ³³ for NASICON-type $\text{LiGe}_2(\text{PO}_4)_3$ ($E_a = 0.6 \text{ eV}$) and $\text{LiHf}_2(\text{PO}_4)_3$ ($E_a = 0.33 \text{ eV}$)³⁴, respectively. The

activation energy of route from 3g to other 3g sites derived from nudged elastic band calculation (Fig. 12(b)) is 0.69 eV in $\text{Sr}_3\text{LiTa}_5\text{ZrSi}_4\text{O}_{26}$, which is in agreement with the experimental value of 0.76 eV. Two maximum points were observed in this route. One of maximum point is attributable to bottleneck and the other is oversized polyhedron of 3g sites, that is lack of stabilization which originates from ionic bonding between Li^+ and O^{2-} . These results suggest that ionic conductivity could not be improved by just expanding the bottleneck in A cation deficient layer. A-site deficient $\text{Ba}_{3-y/2}\text{Li}_y\text{Ta}_5\text{ZrSi}_4\text{O}_{26}$ exhibited high conductivity and low excitation energy, indicating that new ionic diffusion paths from A deficient site to 3g site along *c*-axis were formed. Further improvement of ionic conductivity could be attained to form a three dimensional diffusion path.

5. Conclusions

We synthesized $\text{A}_3\text{Li}_x\text{Ta}_{6-x}\text{Zr}_x\text{Si}_4\text{O}_{26}$ (*A* = Sr and Ba) solid oxide electrolyte. These compounds have hexagonal structure with space group $P\bar{6}2m$, and are first ion conductors with this structure. Li ions diffuse in *ab* plane through lattice interstice sites, but oversized interstice in these structures acts as potential barrier. To improve ionic conductivity, forming a new diffusion path is necessary.

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Reference

- (1) Tatsumisago, M.; Nagao, M.; Hayashi, A. *Journal of Asian Ceramic Societies***2013**, *1*, 17.
- (2) Tarascon, J. M.; Armand, M. *Nature***2001**, *414*, 359.
- (3) Ohta, S.; Kobayashi, T.; Seki, J.; Asaoka, T. *J. Power Sources***2012**, *202*, 332.
- (4) Tatsumisago, M.; Takano, R.; Tadanaga, K.; Hayashi, A. *J. Power Sources***2014**, *270*, 603.
- (5) Stramare, S.; Thangadurai, V.; Weppner, W. *Chem. Mater.***2003**, *15*, 3974.
- (6) Inaguma, Y.; Liqun, C.; Itoh, M.; Nakamura, T.; Uchida, T.; Ikuta, H.; Wakihara, M. *Solid State Commun.***1993**, *86*, 689.
- (7) García-Martín, S.; Rojo, J. M.; Tsukamoto, H.; Morán, E.; Alario-Franco, M. A. *Solid State Ionics***1999**, *116*, 11.
- (8) Kuwano, J.; West, A. R. *Mater. Res. Bull.***1980**, *15*, 1661.
- (9) Aono, H.; Sugimoto, E.; Sadaoka, Y.; Imanaka, N.; Adachi, G. y. *J. Electrochem. Soc.***1989**, *136*, 590.
- (10) Murugan, R.; Thangadurai, V.; Weppner, W. *Angew. Chem. Int. Ed.***2007**, *46*, 7778.
- (11) Bersuker, I. B. *Phys. Lett.***1966**, *20*, 589.

- (12) Nakayama, M.; Kotobuki, M.; Munakata, H.; Nogami, M.; Kanamura, K. *Phys. Chem. Chem. Phys.***2012**, *14*, 10008.
- (13) Jorgensen, C. K. *Progress in Inorganic Chemistry*; Wiley, 1970; Vol. 12.
- (14) Izumi, F.; Momma, K. *Solid State Phenom.***2007**, *130*, 15.
- (15) Momma, K.; Izumi, F. *J. Appl. Crystallogr.***2011**, *44*, 1272.
- (16) Momma, K.; Ikeda, T.; Belik, A. A.; Izumi, F. *Powder Diffr.***2013**, *28*, 184.
- (17) Noceda, J. *Math. Comp.***1980**, *35*, 773.
- (18) Vanderbilt, D. *Phys. Rev. B***1990**, *41*, 7892.
- (19) Kresse, G.; Hafner, J. *Phys. Rev. B***1993**, *47*, 558.
- (20) Blöchl, P. E. *Phys. Rev. B***1994**, *50*, 17953.
- (21) Kresse, G.; Furthmüller, J. *Phys. Rev. B***1996**, *54*, 11169.
- (22) Kresse, G.; Furthmüller, J. *Comput. Mater. Sci.***1996**, *6*, 15.
- (23) Kresse, G.; Joubert, D. *Phys. Rev. B***1999**, *59*, 1758.
- (24) Perdew, J. P. *Phys. Rev. Lett.***1985**, *55*, 1665.
- (25) Henkelman, G.; Jónsson, H. *J. Chem. Phys.***2000**, *113*, 9978.
- (26) Ikeda, M.; Yamasaki, T.; Kaneta, C. *J. Phys.: Condens. Matter***2010**, *22*, 384214.
- (27) Hayashi, K.; Sato, S.; Ikeda, M.; Kaneta, C.; Yokoyama, N. *J. Am. Chem. Soc.***2012**, *134*, 12492.
- (28) Choynet, J.; Nguyen, N.; Groult, D.; Raveau, B. *Mater. Res. Bull.***1976**, *11*, 887.
- (29) Shannon, J.; Katz, L. *J. Solid State Chem.***1970**, *1*, 399.
- (30) Brown, I. D.; Altermatt, D. *Acta Crystallogr.***1985**, *B41*, 244.
- (31) Inaguma, Y.; Katsumata, T.; Itoh, M.; Morii, Y. *J. Solid State Chem.***2002**, *166*, 67.
- (32) Alami, M.; Brochu, R.; Soubeyroux, J. L.; Gravereau, P.; Le Flem, G.; Hagenmuller, P. *J. Solid State Chem.***1991**, *90*, 185.
- (33) Losilla, E. R.; Aranda, M. A. G.; Martínez-Lara, M.; Bruque, S. *Chem. Mater.***1997**, *9*, 1678.
- (34) Martínez-Juárez, A.; Pecharrromán, C.; Iglesias, J. E.; Rojo, J. M. *J. Phys. Chem. B***1998**, *102*, 372.