Paper

Synthesis and Lithium-Ion Conductivity of $\text{LiSrB}_2\text{O}_6\text{F}$ ($B = \text{Nb}^{5+}, \text{Ta}^{5+}$) with a Pyrochlore StructureThanya PHRAEWPHIPHAT^{1,2}, Muhammad IQBAL³, Kota SUZUKI^{1,3}, Masaaki HIRAYAMA^{1,3} and Ryoji KANNO^{1,3*}¹Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta, Midori, Yokohama 226-8502, Japan.²National Metal and Materials Technology Center, National Science and Development Agency, 114 Thailand Science Park, Paholyothin Road, Klong 1, Klong Luang, Pathum Thani 12120, Thailand.³Department of Chemical Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, 4259 Nagatsuta, Midori, Yokohama 226-8502, Japan.

ABSTRACT

This study investigated the conductivity of lithium ions in new pyrochlore materials. A two-step synthesis method, comprising a simple solid-state reaction followed by a high-pressure solid-state reaction was used to synthesize single-phase undoped $\text{LiSrB}_2\text{O}_6\text{F}$ (where $B = \text{Nb}^{5+}$ or Ta^{5+}). The samples were doped with the lower valent cation, Zr^{4+} , which replaced Nb^{5+} or Ta^{5+} at B -sites in $\text{LiSrB}_2\text{O}_6\text{F}$ and similarly, A -site point defects were introduced by reducing the amount of Sr in the sample. The crystal structure was determined by Rietveld analysis of the X-ray synchrotron diffraction data. Ionic conductivities of the samples were evaluated using electrochemical impedance spectroscopy. Sr^{2+} deficient samples showed better conductivity ($8.21 \times 10^{-6} \text{ S cm}^{-1}$ for Nb-containing samples and $6.38 \times 10^{-6} \text{ S cm}^{-1}$ for Ta-containing samples at 300°C) than that of Zr^{4+} -doped samples ($5.58 \times 10^{-6} \text{ S cm}^{-1}$ for Nb-containing samples and $3.58 \times 10^{-6} \text{ S cm}^{-1}$ for Ta-containing samples at 300°C).

KEY WORDS

lithium ion conductor, pyrochlore structure, all-solid-state battery, oxy-fluorides

1. Introduction

Lithium-ion conductors have attracted much attention as solid electrolytes in all-solid-state batteries, which should have improved energy density and reliability compared to conventional lithium batteries. Among the proposed solid-electrolyte materials, lithium containing solid oxides hold particular interest for their chemical stability over a wide range of operating temperatures¹⁻³). However, discovering novel materials is still necessary to satisfy the strict demands of electrochemical devices. In this regard, pyrochlore-structured materials remain an unexplored area of research as a lithium-ion conducting oxide. Pyrochlores are considered to have a flexible structure and have reportedly been used as semiconductors, dielectric materials, photocatalysts, sensors, and solid electrolytes in high-temperature fuel cells⁴⁻⁷). Similarly lithium-ion-containing pyrochlore oxides, such as $\text{Li}_3\text{Sm}_{3-x}\text{Bi}_x\text{Ti}_7\text{Nb}_2\text{O}_{25}$, have also been reported with microwave dielectric properties⁸). However, such materials have not been examined as lithium-ion conductors.

The pyrochlore structure has the general formula $A_2B_2O_7$, where the A -sites are occupied by a larger cation with a coordination number (CN) of 8 and B -sites contain a smaller cation with a CN of 6 (an octahedral site). The A cation is generally an alkali

earth metal or a lanthanide, and the B cation is usually a transition metal. There are two oxygen sites, O (48f) sites (referred to as O sites), and O' (8b) sites (referred to as O prime sites). This structure can be briefly described as a three-dimensional network of BO_6 octahedra sharing all their corners, which thus creates large hexagonal tunnels where A cations and O' sites are located.

The general combination of $A_2^{3+}B_2^{4+}O_7$ (+3, +4) and $A_2^{2+}B_2^{5+}O_7$ (+2, +5) pyrochlores has attracted a good deal of interest, especially in the case of (+3, +4) pyrochlores, as the ionic radius between A and B sites is suitable for the formation of pyrochlore structures⁹). The requirement for a stable cubic pyrochlore structure is a cation size ratio (R_A/R_B) residing at A and B sites that exists within a certain range. Normally, the R_A/R_B ratio required to create a stable cubic pyrochlore is about 1.40–1.55. However, drastic synthesis conditions like high pressure and high temperature may extend this ratio up to 2.3^{10,11}). This indicates that materials with pyrochlore structures have a wide range of structural flexibility to accommodate aliovalent cation doping and structural defects. In addition, pyrochlore structured materials with defects, such as vacancies at A or O' sites, were found to allow for the migration of cations or anions through vacancies in the structure¹²⁻¹⁴).

Pyrochlore-type oxy-fluorides, where one oxygen O' site is occupied with F and having the general formula $AA'B_2O_6F$, have

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been a recent focus of research. The structure of these systems can be dependent on the size of A and A' atoms, where the A cation is an alkali metal and the A' cation is an alkali earth metal. The presence of a fluorine anion at the $8b$ site influences the charge balance; thus, the substitution of alkali metals containing a +1 charge at A -sites satisfies charge neutrality. Cation combinations for the A - and A' -sites have been proposed that allow for the formation of a cubic pyrochlore structure, which is favorable for small A cations such as Li^+ . $\text{KCaNb}_2\text{O}_6\text{F}^{15}$, $\text{LiCaNb}_2\text{O}_6\text{F}^{16}$, $\text{LiLa}_{0.67}\text{V}_{1.33}^{\text{x}}\text{Ta}_2\text{O}_6\text{F}$, and $\text{Li}_{1.25}\text{La}_{0.58}\text{V}_{1.17}^{\text{x}}\text{Nb}_2\text{O}_6\text{F}^{17}$ have been successfully synthesized with a cubic pyrochlore structure. Additionally, $\text{ASrNb}_2\text{O}_6\text{F}$, where A -sites are occupied by Li and Na, were obtained as a Dion-Jacobson-type layered perovskite by a solid-state ion exchange reaction¹⁸. These compounds could transform to cubic pyrochlore oxides with an $\text{ASrNb}_2\text{O}_{6.5}$ composition by heating at 600°C for 24 h in air¹⁹.

Pyrochlore-type oxy-fluorides provide the possibility of Li substitution at A -sites, potentially creating a lithium ion conductor. Additionally, the presence of F^- at the $8b$ site could offer less Coulomb interaction for Li^+ than that of the O^{2-} ; therefore, faster lithium migration in the structure can be expected. Based on these variable structural characteristics, a new lithium ion conductor with a pyrochlore structure is expected to be obtained from oxy-fluorides with Li^+ and Sr^{2+} at the A and A' sites, respectively, and Nb^{5+} or Ta^{5+} at the B -sites forming an $AA'B_2\text{O}_6\text{F}$ compound. For simplicity, sites in the lattice containing fluorine are referred to as fluorine sites (F-sites). In this study, a high-pressure synthesis route has been employed to synthesize $\text{LiSr}(\text{Nb}/\text{Ta})_2\text{O}_6\text{F}$ and its solid solutions with a stable cubic pyrochlore structure. Furthermore, $\text{LiSr}(\text{Nb}/\text{Ta})_2\text{O}_6\text{F}$ was tailored by creating Li- and F-site defects by using a Sr^{2+} -deficient composition while interstitial lithium doping was examined by substituting the lower-valent cation Zr^{4+} for Nb^{5+} or Ta^{5+} sites in the structure. The crystal structures and ionic conductivities of the solid solutions were investigated and the lithium ion conduction mechanism in the pyrochlore structure was elucidated.

2. Experimental

Stoichiometric amounts of SrCO_3 (Aldrich, 99.9%), ZrO_2 (Kanto Chem., 99.9%), Nb_2O_5 (Wako, 99.9%), and Ta_2O_5 (Kanto Chem., 99.95%) were mixed in acetone and ball-milled for 8 h. After evaporation of acetone, the mixtures were calcined at 1100°C for 4 h and then cooled down to room temperature. The powders were mixed with LiF (Wako, 99.9%), and Li_2O (Kojundo, 99.0%) with 100% Li excess in an argon filled glove box. The mixed sample was encapsulated in a gold capsule and further subjected to high-pressure at 1 GPa at 800°C for 30 min.

The reaction products were characterized by X-ray diffraction (XRD; Rigaku Smart Lab and Miniflex 300, Rigaku) using $\text{Cu-K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation. The lattice constants were determined

using Si (SRM 640d) as an internal standard for calibration. Synchrotron X-ray diffraction patterns were recorded using BL19B2 and BL02B2 beam lines at SPring-8, operating with a wavelength of 0.5 and 0.6 $\text{\AA}$, respectively. All the diffraction data were collected at 298 K. Rietveld analysis was conducted for refinement of the structural parameters using diffraction data collected at each 0.02° step width over a 2θ range from 10 to 70° . The RIETAN-FP program was used for Rietveld refinement²⁰.

Ionic conductivity was measured by the AC impedance method using frequency response analyzers (Solartron 1260). The samples were placed under flowing argon gas, and the measurements were performed at temperatures ranging from 25 to 350°C and at frequencies ranging from 0.1 Hz to 10 MHz . Gold paste was used for the blocking electrodes and was painted onto both sides of each sample for the measurements. The electronic conductivity of each sample was measured *via* the polarization cell method, as developed by Hebb²¹ and Wagner²². Platinum sheets were used for the blocking electrodes on both sides of the pellet. The voltage, controlled with a potentiostat (Solartron 1287), was applied from 0.1 to 1.6 V . The resulting current due to the electronic contribution was evaluated.

3. Results and discussion

3.1. Synthesis and structural characterization of $\text{LiSrB}_2\text{O}_6\text{F}$

Fig. 1 shows the X-ray diffraction patterns for stoichiometric $\text{LiSrB}_2\text{O}_6\text{F}$ ($B = \text{Nb}^{5+}$ and Ta^{5+}) sample, which are similar to that of the pyrochlore $\text{KCaNb}_2\text{O}_6\text{F}^{15}$. The diffraction patterns can be indexed as a cubic cell of the $Fd\bar{3}m$ space group (No. 227). The lattice parameters and R_A/R_B ratios are listed in Table 1. The cubic

Fig. 1 X-ray diffraction patterns of pyrochlore-type oxyfluorides with $B = \text{Nb}^{5+}$ and Ta^{5+} (a) Nb-based and (b) Ta-based compounds.

Table 1 Lattice parameters and R_A/R_B ratios for all samples synthesized with a cubic pyrochlore structure.

Composition	Lattice parameter $a/\text{\AA}$	R_A/R_B ratio
LiSrNb ₂ O ₆ F	10.48371(5)	1.70
LiSr _{0.9} Nb ₂ O ₆ F _{0.8}	10.4951(2)	1.60
Li _{1.1} SrNb _{1.9} Zr _{0.1} O ₆ F	10.48854(6)	1.68
LiSrTa ₂ O ₆ F	10.46919(5)	1.70
LiSr _{0.9} Ta ₂ O ₆ F _{0.8}	10.4737(3)	1.60
Li _{1.1} SrTa _{1.9} Zr _{0.1} O ₆ F	10.46992(9)	1.68

pyrochlore phase was accessible *via* the high-pressure method although the R_A/R_B ratio (1.6–1.7) of LiSrB₂O₆F was beyond the range (1.55) expected to yield stable pyrochlore structures⁹⁾. The Ta-containing phases showed relatively smaller a values than those of Nb-containing phases. Observed lattice parameter modification occurred even though the size of the B -site cations, Nb and Ta, are the same (0.64 Å, CN = 6)²³⁾ and was explained as originating from the difference in their electronegativity values (ΔEN). The larger electronegativity difference between Ta and O ($\Delta EN = 1.9$) as compared to Nb and O ($\Delta EN = 1.8$) makes the Ta – O bond stronger and as a result shortens the lattice parameter of Ta-based samples compared to that of Nb-based samples²⁴⁾.

3.2. Synthesis and structural characterization of LiSr_{1-x}B₂O₆F_{1-2x} and Li_{1+y}SrB_{2-y}Zr_yO₆F

Introductions of vacancies at the A - and F -sites and interstitial lithium were examined using the composition formulas of LiSr_{1-x}B₂O₆F_{1-2x} and Li_{1+y}SrB_{2-y}Zr_yO₆F. The XRD patterns with a composition of $x = 0.1$ and $y = 0.1$ are shown in Fig. 1. In both Nb and Ta systems, the main diffraction peaks are indexed as cubic pyrochlore phases with a space group of $Fd\bar{3}m$. A small amount of impure phases (LiBO₃) were observed in both Li_{1.1}SrNb_{1.9}Zr_{0.1}O₆F and LiSr_{0.9}B₂O₆F_{0.8} due to the increase of the Li/Sr ratio. Diffraction lines of the main phase shifted to lower angles with Sr deficiencies ($x = 0.1$) and B -site substitutions ($y = 0.1$), indicating lattice expansion, which is also presented in Table 1. The Sr deficiencies (A - and F - site vacancies) created a solid solution and increased the lattice parameter of the pyrochlore structure. In Sr-deficient materials, charge compensation might occur due to vacancies at the F -sites in the structure.

Similarly, lower valent cation Zr⁴⁺ was doped at the B site of LiSrBO₆F ($B = \text{Ta}^{5+}, \text{Nb}^{5+}$) using the same synthetic procedure. Doping with Zr⁴⁺ also expanded the pyrochlore lattice, indicating that Zr⁴⁺ make a solid solution in the structure. It was also observed that excessive doping (higher than 10%) appears as a ZrO₂ impurity in the materials. Charge compensation might be achieved by induction of extra Li⁺ in Zr-doped LiSrBO₆F ($B = \text{Ta}^{5+}, \text{Nb}^{5+}$) samples and this extra Li might be provided by the excess Li present in the precursor.

3.3. Li-ion conductivity

Ionic conductivities were determined from impedance plots by calculating the intercept of the semicircular plot with the x -axis.

Fig. 2 Complex impedance plots obtained at 300°C in a dry Ar atmosphere for the (a) Nb-based compounds and (b) Ta-based compounds.

Fig. 2 shows typical complex impedance plots for all compounds at temperatures of 300°C under a gas flow of argon. The impedance plot is composed of a semicircle at higher frequencies and a spike at lower frequencies, which correspond to the contributions of the bulk/grain boundary and electrode resistances, respectively. A semicircle with a capacitance value on the order of 10^{-11} F indicates a total resistance that consists of a mixed (bulk and grain boundary) contribution. The temperature dependence of the conductivity in Fig. 3 can be fitted by an Arrhenius equation using the following expression:

$$\sigma T = \sigma_0 \exp(-E_a/k_B T)$$

where σ , T , σ_0 , E_a and k_B are the total conductivity, absolute temperature, pre-exponential factor, activation energy, and Boltzmann constant,

Fig. 3 Arrhenius plots showing the temperature dependence of the conductivity for (a) Nb-based compounds and (b) Ta-based compounds.

Table 2 Ionic conductivity and activation energy for all cubic pyrochlore samples.

Composition	Conductivity at 300°C $\sigma/\text{S cm}^{-1}$	Activation energy $E_a/\text{kJ mol}^{-1}$
$\text{LiSrNb}_2\text{O}_6\text{F}$	1.08×10^{-6}	58.32
$\text{LiSr}_{0.9}\text{Nb}_2\text{O}_6\text{F}_{0.8}$	8.21×10^{-6}	68.45
$\text{Li}_{1.1}\text{SrNb}_{1.9}\text{Zr}_{0.1}\text{O}_6\text{F}$	5.58×10^{-6}	59.97
$\text{LiSrTa}_2\text{O}_6\text{F}$	1.12×10^{-6}	58.29
$\text{LiSr}_{0.9}\text{Ta}_2\text{O}_6\text{F}_{0.8}$	6.38×10^{-6}	72.32
$\text{Li}_{1.1}\text{SrTa}_{1.9}\text{Zr}_{0.1}\text{O}_6\text{F}$	3.58×10^{-6}	66.87

respectively. Table 2 summarizes the ionic conductivities measured at 300°C and the activation energies E_a , for the compounds. For samples with stoichiometric compositions, Nb and Ta-systems showed comparable conductivity and activation energy. An increase in conductivity is observed for samples containing both Sr deficiencies ($x = 0.1$) and B-site substitutions ($y = 0.1$) compared to that of stoichiometric $\text{LiSrB}_2\text{O}_6\text{F}$. The highest conductivity value was observed for the Sr^{2+} deficient compound, $\text{LiSr}_{0.9}\text{B}_2\text{O}_6\text{F}_{0.8}$ yielding conductivities of $8.21 \times 10^{-6} \text{ S cm}^{-1}$ and $6.38 \times 10^{-6} \text{ S cm}^{-1}$ at 300°C for Nb- and Ta-based compounds, respectively. The increased conductivities observed for Sr-deficient compounds might be due to the existence of vacancies at Sr- and F- sites in the pyrochlore structure. In addition, the largest observed lattice parameter of $\text{LiSr}_{0.9}\text{B}_2\text{O}_6\text{F}_{0.8}$ also may have enhanced the ionic conductivity by expanding the bottleneck for Li-ion diffusion in the structure.

To investigate the electronic contribution to the total conductivity, DC polarization measurements were carried out for $\text{LiSrTa}_2\text{O}_6\text{F}$ and $\text{LiSrNb}_2\text{O}_6\text{F}$. The steady state currents shown in Fig. 4 were obtained as a function of the applied voltage at 300°C and 350°C. The DC polarization measurements indicated that the contribution of the electronic conductivity, which was $1.24 \times 10^{-7} - 9.25 \times 10^{-7} \text{ S cm}^{-1}$ at 300°C, was negligible because it was ten times less than the total conductivity. Therefore, the conductivity observed in these samples is mainly attributed to lithium ion diffusion.

Fig. 4 Steady-state current as a function of the applied voltage at 300°C and 350°C in dry Ar atmosphere for $\text{LiSrTa}_2\text{O}_6\text{F}$ and $\text{LiSrNb}_2\text{O}_6\text{F}$.

3.4. Crystal structure analysis

The structures of the pyrochlores were determined by synchrotron diffraction data obtained at room temperature using a structural model of a cubic pyrochlore-type material with $Fd\bar{3}m$ symmetry. The initial atomic positions for the structural refinement models were as follows: Li and Sr at $16d$ ($1/2, 1/2, 1/2$), Nb, Ta, and Zr at $16c$ ($0, 0, 0$), O at $48f$ ($x, 0, 0$) and F at $8b$ ($3/8, 3/8, 3/8$). This initial structure model is based on the previous report that analyzed the crystal structure of $\text{LiCaTa}_2\text{O}_6\text{F}^{(6)}$: Li/Ca at site $16d$, Ta at $16c$ site, O at $48f$ site and F at $8b$ site. During the refinements, the occupancy factors of $16c$ ($0, 0, 0$) (Nb and Ta) and $48f$ ($x, 0, 0$) (Oxygen) were fixed to the same value as the nominal composition. Also, oxygen and fluorine positions are fixed since X-ray analysis is difficult to identify oxygen and fluorine separately due to the similarity of atomic number.

Fig. 5 shows the Rietveld refinement patterns and the results are presented in Table 3. All the diffraction peaks of $\text{LiSrB}_2\text{O}_6\text{F}$ were assigned to a single cubic-phase pyrochlore structure. The values of reliability factors (R_p and R_{wp}) confirmed that the structure model proposed for the diffraction data is reasonable. The synchrotron diffraction data for $\text{LiSr}_{0.9}\text{B}_2\text{O}_6\text{F}_{0.8}$ and $\text{Li}_{1.1}\text{SrB}_{1.9}\text{Zr}_{0.1}\text{O}_6\text{F}$ samples were refined with a two-phase model using the $Fd\bar{3}m$ and $R3ch$ space group for pyrochlore and LiBO_3 phases, respectively. The occupancies of A-sites were constrained to have the same values for $\text{LiSrB}_2\text{O}_6\text{F}$. Li occupancy was fixed to the same value as the nominal composition for $\text{LiSr}_{0.9}\text{B}_2\text{O}_6\text{F}_{0.8}$ and constrained to be $1-g(\text{Sr})$ for $\text{Li}_{1.1}\text{SrB}_{1.9}\text{Zr}_{0.1}\text{O}_6\text{F}$. During $\text{LiSr}_{0.9}\text{B}_2\text{O}_6\text{F}_{0.8}$ refinements, the occupancy (g) values for F at $8b$ sites was refined to be 0.91(3) and 0.90(9) for $\text{LiSr}_{0.9}\text{Nb}_2\text{O}_6\text{F}_{0.8}$ and $\text{LiSr}_{0.9}\text{Ta}_2\text{O}_6\text{F}_{0.8}$, respectively. Further, relatively low occupancy (g) values for Sr at $16d$ sites are confirmed.

Fig. 5 Synchrotron Rietveld analysis results for all pyrochlore-type oxyfluorides. Solid lines overlaying the data were obtained with a single-phase Rietveld refinement for (a) and (d). Vertical markers below the patterns indicate positions of possible Bragg reflections of $Fd-3m$ space group for cubic pyrochlore. Solid lines overlaying the data were obtained via two-phase Rietveld refinements for (b), (c), (e), and (f). Vertical markers below the patterns indicate positions of possible Bragg reflections of $Fd-3m$ and $R3ch$ space groups for cubic pyrochlore and LiBO_3 , respectively.

Table 3 Crystallographic data of pyrochlores with $Fd-3m$ space group.

	$\text{LiSrB}_2\text{O}_6\text{F}$		$\text{LiSr}_{0.9}\text{B}_2\text{O}_6\text{F}_{0.8}$		$\text{Li}_{1.1}\text{SrB}_{1.9}\text{Zr}_{0.1}\text{O}_6\text{F}$	
	Nb	Ta	Nb	Ta	Nb	Ta
Lattice parameter a (Å)	10.48171 (9)	10.46401 (5)	10.4909 (3)	10.4687 (4)	10.48564 (4)	10.46491 (14)
x	0.3183 (3)	0.31556 (3)	0.3143 (5)	0.3138 (17)	0.3182 (7)	0.31475 (3)
g (Sr)	0.5036 (18)	0.499 (2)	0.466 (6)	0.467 (8)	0.479 (5)	0.483 (4)
g (Li)	= g (Sr)	= g (Sr)	0.5	0.5	= $1-g$ (Sr)	= $1-g$ (Sr)
g (F)	1.0	1.0	0.91 (3)	0.90 (9)	1.0	1.0
R_p	0.73%	3.88%	1.49%	11.36%	1.18%	4.11%
R_{wp}	1.32%	5.82%	2.35%	16.46%	2.24%	6.82%
S	0.51	1.12	1.21	3.89	0.82	1.20

Atomic positions, $16d$ (1/2, 1/2, 1/2) for Li/Sr, $16c$ (0, 0, 0) for Nb and Ta, $48f$ (x , 1/8, 1/8) for O and $8b$ (3/8, 3/8, 3/8) for F.

3.5. Relationship between the structure and conductivity

Fig. 6 shows the structural model obtained by Rietveld refinement structure analysis for the synchrotron data. The B ($B = \text{Ta}^{5+}$ or Nb^{5+}) atom is bonded with six O atoms forming the BO_6 octahedron, while Sr, Li, and F are located in large hexagonal tunnels created by the corner-sharing pattern of BO_6 octahedra. If we neglect Li/Sr–O interactions, this oxy-fluoride pyrochlore structure can be simply

described by the existence of two different polyhedral networks consisting of $[\text{BO}_6]^{2-}$ and $[(\text{Li}, \text{Sr})_4\text{F}]^{2+}$ units. The corner shared B -site octahedra are connected in such a way that formulates a three-dimensional network of hexagonal tunnels all over the lattice. In these hexagonal tunnels, (Li/Sr) cations are positioned and forming $[(\text{Li}, \text{Sr})_4\text{F}]$ tetrahedra. Thus, the size of these tunnels, numbers of F and Sr vacancies and nature of $8b$ -site anions can

Fig. 6 Representation of the structure of $\text{LiSrNb}_2\text{O}_6\text{F}$ based on synchrotron Rietveld analysis, showing Li/Sr (blue spheres), F (green spheres) and NbO_6 octahedra. The hexagonal tunnels and empty trigonal tunnels can be observed in the $[1\ 1\ 0]$ direction. The fluoride ions are in tetrahedral coordination with the $\text{Li}^+/\text{Sr}^{2+}$ cations as shown in the $[(\text{Li}_2\text{Sr}_2)\text{F}]$ tetrahedron.

Fig. 7 Composition dependence of (a) the lattice parameter, (b) the conductivities at 300°C, (c) O-O bond length, (d) B-O-B bond angle, (e) B-O bond length, and (f) A-F bond length with $B = \text{Nb}^{5+}$ and Ta^{5+} .

affect A -site cation migration in the pyrochlore structure.

3.5.1 Stoichiometric $\text{LiSrB}_2\text{O}_6\text{F}$ system

The stoichiometric samples show comparable conductivity while clear differences in the lattice parameters are confirmed as shown in Fig. 7 with the Nb-system having a larger a value than the Ta-system. This fact indicates there are other structural parameters affecting lithium migration in the pyrochlore structure. As described in Fig. 6, the local environment of the octahedra could be related to the conductivity since these octahedra form hexagonal tunnels for lithium migration. Further, the local structure of $(\text{Li/Sr})_4\text{F}$ tetrahedra could be related to the conductivity because of Coulomb

interactions between Li and F. These local structural parameters are also summarized in Fig. 7. Three parameters, O-O bond length, B-O-B bond angle, and B-O bond length, determine the size of the hexagonal channels with larger parameters expanding the channels. On the other hand, the A-F bond length is the dominant parameter for $(\text{Li/Sr})_4\text{F}$ tetrahedra. According to the parameters related to the size of the hexagon, the Ta-system may have larger hexagonal channels while having a smaller lattice parameter than the Nb-system. Therefore, the large hexagonal channels in the Ta-system could be a reason for the comparable ionic conductivities of the stoichiometric system.

3.5.2 $\text{LiSr}_{1-x}\text{B}_2\text{O}_6\text{F}_{1-2x}$ and $\text{Li}_{1+y}\text{SrB}_{2-y}\text{Zr}_y\text{O}_6\text{F}$ systems

For Sr deficient compositions ($x = 0.1$), the highest conductivity is confirmed in each system ($8.21 \times 10^{-6} \text{ S cm}^{-1}$ for Nb compound and $6.38 \times 10^{-6} \text{ S cm}^{-1}$ for Ta compound). This enhancement could be due to the increase in lattice parameter and expansion of the hexagonal channel for lithium diffusion especially as for these systems, the largest lattice parameter, O–O bond length, and B–O–B bond angle were confirmed. Zr doped compositions ($y = 0.1$) also show relatively higher conductivity compared to the stoichiometric compositions. Slightly larger lattice parameters and hexagonal channels could be the reason for high conductivity. In addition, the increase in the conductivity in $\text{Li}_{1.1}\text{SrB}_{1.9}\text{Zr}_{0.1}\text{O}_6\text{F}$ might also be due to the existence of interstitial lithium ions. There are two possible locations for interstitial lithium ions in this structure. Li-ions might be located at hexagonal tunnels or between O- and F-sites due to the increase in O–O bond length.

Additional contribution from anions (O^{2-} or F^-) might be possible to the observed ionic conductivity. However, the conductivity increased with a composition of $\text{Li}_{1+y}\text{SrB}_{2-y}\text{Zr}_y\text{O}_6\text{F}$ including lithium interstitial. In this composition, anion composition is stoichiometric (i.e., no vacancy and no excess anion). Also, O–O bond length increased with $x = 0.1$ and $y = 0.1$ while the conductivity increased. Increase in the bond length may provide a negative effect at least oxygen ion conduction. Therefore, we concluded that the dominant charge carrier could be Li^+ .

Finally, the highest conductivity of the Sr deficient compositions ($x = 0.1$) could be due to the absence of Sr and F atoms which provides vacant sites for lithium migration and smaller Coulomb interactions with lithium ions. As the Rietveld refinement confirmed the presence of A- and F- site defects, it was found that Sr deficient compositions introduced structural defects in the pyrochlore. The A–F bond length in $\text{LiSr}_{0.9}\text{B}_2\text{O}_6\text{F}_{0.8}$ is slightly larger than that of $\text{LiSrB}_2\text{O}_6\text{F}$ and $\text{Li}_{1.1}\text{SrB}_{1.9}\text{Zr}_{0.1}\text{O}_6\text{F}$. This increase in the average Li/Sr–F bond length was most likely due to the local absence of Sr and F sites. The significant decrease in the B–O bond length in $\text{LiSr}_{0.9}\text{B}_2\text{O}_6\text{F}_{0.8}$ could also be a result of the absences of Sr and F, especially in $\text{LiSr}_{0.9}\text{Nb}_2\text{O}_6\text{F}_{0.8}$. These results indicate that further enhancement of lithium conductivity in the pyrochlore structure may require the modification of $(\text{Li}/\text{Sr})_4\text{F}$ tetrahedral units rather than introducing extra lithium at interstitial sites in the structure.

4. Conclusions

The $\text{LiSrB}_2\text{O}_6\text{F}$ ($B = \text{Nb}^{5+}$, Ta^{5+}) systems were prepared *via* solid-state reaction followed by high-pressure solid-state reaction. The materials were tailored by creating samples with Sr-deficient compositions, which were used to create A-site point defects in the materials. Similar tailoring was achieved by doping B-sites with the lower valent cation, Zr^{4+} . The X-ray diffraction patterns of Nb and Ta compounds indicate that the main phase is a cubic pyrochlore structure. The lattice parameters for Nb-based compounds were

larger than that of the corresponding Ta-based compounds for all compositions. In addition, Sr-deficient compounds offer the largest lattice parameters in both stoichiometric as well as Zr-doped systems. Conductivities slightly increase with Zr doping in the material, however, significant increases in conductivity were observed with Sr-deficient compositions. Charge balance in the Sr-deficient compounds might be done with the introduction of vacancies at A-sites and vacancies at the F-site. This might be the reason for better ion conduction in the Sr-deficient system. Rietveld refinement structural analyses also indicated that Li-ion diffusion occurs inside the hexagonal tunnels formed by the corner sharing arrangement of Ta/Nb-site octahedra.

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