Synthesis and Lithium-Ion Conductivity of LiSrB\(_2\)O\(_4\)F (B = Nb\(^{5+}\), Ta\(^{5+}\)) with a Pyrochlore Structure

Thanya PHRAEWPHIPHAT\(^{1,2}\), Muhammad IQBAL\(^3\), Kota SUZUKI\(^{1,3}\), Masaaki HIRAYAMA\(^{1,3}\) and Ryoji KANNO\(^{1,3}\)*

\(^{1}\)Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta, Midori, Yokohama 226-8502, Japan.
\(^{2}\)National Metal and Materials Technology Center, National Science and Development Agency, 114 Thailand Science Park, Paholyothin Road, Klong 1, Klong Luang, Pathum Thani 12120, Thailand.
\(^{3}\)Department 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 LiSrB\(_2\)O\(_4\)F (where B = 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 LiSrB\(_2\)O\(_4\)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 × 10\(^{-6}\) S cm\(^{-1}\)) for Nb-containing samples and 6.38 × 10\(^{-5}\) S cm\(^{-1}\) for Ta-containing samples at 300°C) than that of Zr\(^{4+}\)-doped samples (5.58 × 10\(^{-6}\) S cm\(^{-1}\) for Nb-containing samples and 3.58 × 10\(^{-5}\) 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 temperatures\(^{1-3}\). 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 cells\(^{4,5}\). Similarly, lithium-ion-containing pyrochlore oxides, such as Li\(_2\)Sm\(_2\)O\(_7\), Li\(_2\)Ti\(_2\)O\(_7\), and Li\(_2\)NbO\(_3\), have also been reported with microwave dielectric properties\(^{6}\). 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 \(A_2^+B_2^{4+}\)O\(_7\) (+3, +4) and \(A_2^+B_2^{5+}\)O\(_7\) (+2, +5) pyrochlores has attracted a good deal of interest, especially in the case of (+3, +4) pyrochlores, as the atomic radius between A and B sites is suitable for the formation of pyrochlore structures\(^9\). 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 structure\(^{12-14}\).

Pyrochlore-type oxy-fluorides, where one oxygen O’ site is occupied with F and having the general formula \(AA'B_2O_6F\), have
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 8h 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+. KCaNb2O6F19, LiCaNb2O6F19, LiLa0.5xY0.5x, and Li1.12La0.56Y1.17Nb2O6F17 have been successfully synthesized with a cubic pyrochlore structure. Additionally, A’SrNb2O6F, where A-sites are occupied by Li and Na, were obtained as a Dion-Jacobson-type layered perovskite by a solid-state ion exchange reaction19. These compounds could transform to cubic pyrochlore oxides with an A’SrNb2O6 composition by heating at 600°C for 24 h in air.

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 O2−; 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 Sr2+ at the A and A’ sites, respectively, and Nb5+ or Ta5+ at the B-sites forming an AA’BB’O6F 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 was employed to synthesize LiSr(Nb/Ta)2O6F and its solid solutions with a stable cubic pyrochlore structure. Furthermore, LiSr(Nb/Ta)2O6F was tailored by creating Li- and F-site defects 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 Hebb20 and Wagner21. 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 LiSrB2O6F

Fig. 1 shows the X-ray diffraction patterns for stoichiometric LiSrB2O6F (B = Nb5+ and Ta5+) sample, which are similar to that of the pyrochlore KCaNb2O6F19. The diffraction patterns can be indexed as a cubic cell of the Fd-3m space group (No. 227). The lattice parameters and R/R2 ratios are listed in Table 1. The cubic

![Image](image-url)

**Fig. 1** X-ray diffraction patterns of pyrochlore-type oxyfluorides with B = Nb5+ and Ta5+ (a) Nb-based and (b) Ta-based compounds.
The pyrochlore phase was accessible via the high-pressure method although the $R_A/R_B$ ratio (1.6–1.7) of LiSr$_2$B$_2$O$_6$F was beyond the range (1.55) expected to yield stable pyrochlore structures\(^9\). 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 ($\Delta EN$). 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 samples\(^24\).

### 3.2. Synthesis and structural characterization of LiSr$_{1-x}$B$_x$O$_6$F$_{1-2x}$ and Li$_{1+y}$Sr$_{x}$B$_{1-y}$Zr$_y$O$_6$F

Introductions of vacancies at the A- and F-sites and interstitial lithium were examined using the composition formulas of LiSr$_{1-x}$B$_x$O$_6$F$_{1-2x}$ and Li$_{1+y}$Sr$_x$B$_{1-y}$Zr$_y$O$_6$F. 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 $Fd-3m$. A small amount of impure phases (LiBO$_3$) were observed in both Li$_{1.1}$SrNb$_{1.9}$Zr$_{0.1}$O$_6$F and Li$_{1.1}$SrTa$_{1.9}$Zr$_{0.1}$O$_6$F 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 Zr$^{4+}$ was doped at the B site of LiSrBO$_4$F ($B = $ Ta$^{5+}$, Nb$^{5+}$) using the same synthetic procedure. Doping with Zr$^{4+}$ also expanded the pyrochlore lattice, indicating that Zr$^{4+}$ make a solid solution in the structure. It was also observed that excessive doping (higher than 10%) appears as a ZrO$_2$ impurity in the materials. Charge compensation might be achieved by induction of extra Li$^+$ in Zr-doped LiSrBO$_4$F ($B = $ Ta$^{5+}$, 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.

$$\sigma = \frac{\sigma_0}{1 + \frac{E}{k_B T}}$$

where $\sigma$, $\sigma_0$, $E$, and $k_B$ are the total conductivity, absolute temperature, pre-exponential factor, activation energy, and Boltzmann constant.
The DC polarization measurements indicated that the contribution obtained as a function of the applied voltage at 300°C and 350°C. The steady state currents shown in Fig. 4 were expanding the bottleneck for Li-ion diffusion in the structure.

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

<table>
<thead>
<tr>
<th>Composition</th>
<th>Conductivity at 300°C ( \sigma / \text{S cm}^{-1} )</th>
<th>Activation energy ( E_a / \text{kJ mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiSrNb_2O_6F</td>
<td>1.08 \times 10^{-6}</td>
<td>58.32</td>
</tr>
<tr>
<td>LiSr_{1.1}Nb_{0.9}O_6F</td>
<td>8.21 \times 10^{-6}</td>
<td>68.45</td>
</tr>
<tr>
<td>Li_{1.1}Sr_{0.9}Zr_{0.1}O_6F</td>
<td>5.58 \times 10^{-6}</td>
<td>59.97</td>
</tr>
<tr>
<td>LiSrTa_2O_6F</td>
<td>1.12 \times 10^{-6}</td>
<td>58.29</td>
</tr>
<tr>
<td>LiSr_{1.1}Ta_{0.9}F_{0.8}</td>
<td>6.38 \times 10^{-6}</td>
<td>72.32</td>
</tr>
<tr>
<td>Li_{1.1}Sr_{0.9}Zr_{0.1}F</td>
<td>3.58 \times 10^{-6}</td>
<td>66.87</td>
</tr>
</tbody>
</table>

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 \( \text{Sr}^{2+} \) deficient compound, \( \text{LiSr}_{1.1}\text{B}_0\text{F}_{0.8} \) 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 \( \text{LiSr}_{1.1}\text{B}_0\text{F}_{0.8} \) 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 \( 1.24 \times 10^{-7} - 9.25 \times 10^{-8} \text{ S cm}^{-1} \) 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.

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 \( Fd\text{-}3m \) symmetry. The initial atomic positions for the structural refinement models were as follows: Li and Sr at 16\( d \) (1/2, 1/2, 1/2), Nb, Ta, and Zr at 16c (0, 0, 0), O at 48\( f \) (x, 0, 0) and F at 8\( b \) (3/8, 3/8, 3/8). This initial structure model is based on the previous report that analyzed the crystal structure of \( \text{LiCaTa}_2\text{O}_6\text{F} \): \( \text{LiCa} \) at site 16\( d \), Ta at 16c site, O at 48\( f \) site and F at 8b site. During the refinements, the occupancy factors of 16\( c \) (0, 0, 0) (Nb and Ta) and 48\( f \) (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 \( (R_p, R_w) \) confirmed that the structure model proposed for the diffraction data is reasonable. The synchrotron diffraction data for \( \text{LiSr}_{0.9}\text{B}_0\text{F}_{0.8} \) and \( \text{Li}_{1.1}\text{Sr}_{0.9}\text{Zr}_{0.1}\text{F}_{0.8} \) samples were refined with a two-phase model using the \( Fd\text{-}3m \) and \( R3\text{c} \) space group for pyrochlore and \( \text{LiBO}_3 \) 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 \( \text{LiSr}_{1.1}\text{B}_0\text{F}_{0.8} \) and constrained to be 1-gt(Sr) for \( \text{Li}_{1.1}\text{Sr}_{0.9}\text{Zr}_{0.1}\text{O}_6\text{F} \). During \( \text{LiSr}_{0.9}\text{B}_0\text{F}_{0.8} \) refinements, the occupancy \( (g) \) values for F at 8b sites was refined to be 0.91(3) and 0.90(9) for \( \text{LiSr}_{0.9}\text{Nb}_{0.1}\text{F}_{0.8} \) and \( \text{LiSr}_{0.9}\text{Ta}_{0.1}\text{F}_{0.8} \), respectively. Further, relatively low occupancy \( (g) \) values for Sr at 16\( d \) sites are confirmed.
3.5. Relationship between the structure and conductivity

Fig. 6 shows the structural model obtained by Rietveld refinement for the synchrotron data. The B (B = Ta<sup>5+</sup> or Nb<sup>5+</sup>) 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 $[BO_6]^{2-}$ and $[(Li, Sr)F]^+$ 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 $[(Li, Sr)_4F]^2$. Thus, the size of these tunnels, numbers of F and Sr vacancies and nature of $8b$-site anions can

![Fig. 5](image)

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

<table>
<thead>
<tr>
<th></th>
<th>LiSr&lt;sub&gt;2&lt;/sub&gt;B&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt;F</th>
<th>LiSr&lt;sub&gt;1.4&lt;/sub&gt;B&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt;F</th>
<th>Li&lt;sub&gt;1.1&lt;/sub&gt;Sr&lt;sub&gt;1.9&lt;/sub&gt; Nb&lt;sub&gt;0.1&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt;F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameter $a$ (Å)</td>
<td>10.48171 (9)</td>
<td>10.46401 (5)</td>
<td>10.48564 (4)</td>
</tr>
<tr>
<td>$x$</td>
<td>0.3183 (3)</td>
<td>0.31556 (3)</td>
<td>0.3182 (7)</td>
</tr>
<tr>
<td>$g$ (Sr)</td>
<td>0.5036 (18)</td>
<td>0.499 (2)</td>
<td>0.479 (5)</td>
</tr>
<tr>
<td>$g$ (Li)</td>
<td>= $g$ (Sr)</td>
<td>= $g$ (Sr)</td>
<td>= 1-$g$ (Sr)</td>
</tr>
<tr>
<td>$g$ (F)</td>
<td>1.0</td>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>$R_p$</td>
<td>0.73%</td>
<td>1.49%</td>
<td>1.18%</td>
</tr>
<tr>
<td>$R_{wp}$</td>
<td>3.88%</td>
<td>11.36%</td>
<td>4.11%</td>
</tr>
<tr>
<td>$S$</td>
<td>1.21</td>
<td>3.89</td>
<td>2.24%</td>
</tr>
</tbody>
</table>

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.
Synthesis and Lithium-Ion Conductivity of LiSr\(_2\)O\(_6\)F (B = Nb\(^{5+}\), Ta\(^{5+}\)) with a Pyrochlore Structure

3.5.1 Stoichiometric LiSr\(_2\)O\(_6\)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 (Li/Sr)\(_4\)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 (Li/Sr)\(_4\)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.

Fig. 6  Representation of the structure of LiSrNb\(_2\)O\(_6\)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 Li\(^+/\)Sr\(^{2+}\) cations as shown in the [Li\(_2\)Sr\(_2\)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 \(\text{Ta}^{5+}\).
3.5.2 LiSr$_{1−x}$B$_x$O$_6$F$_{0.8}$ and Li$_{1.1}$Sr$_{0.9}$B$_{2−y}$Zr$_y$O$_6$F systems

For Sr deficient compositions ($x = 0.1$), the highest conductivity is confirmed in each system ($8.21 \times 10^{-6}$ S cm$^{-1}$ for Nb compound and $6.38 \times 10^{-5}$ 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 Li$_{1.1}$Sr$_{0.9}$B$_{2−y}$Zr$_y$O$_6$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$^−$ or F$^−$) might be possible to the observed ionic conductivity. However, the conductivity increased with a composition of Li$_{1.1}$Sr$_{0.9}$B$_{2−y}$Zr$_y$O$_6$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 LiSr$_{1−x}$B$_x$O$_6$F$_{0.8}$ is slightly larger than that of LiSrB$_2$O$_6$F and Li$_{1.1}$Sr$_{0.9}$B$_{2−y}$Zr$_y$O$_6$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 LiSr$_{1−x}$B$_x$O$_6$F$_{0.8}$ could also be a result of the absences of Sr and F, especially in LiSr$_{1−x}$Nb$_2$O$_6$F$_{0.8}$. These results indicate that further enhancement of lithium conductivity in the pyrochlore structure may require the modification of (Li/Sr)$_4$F$_7$ tetrahedral units rather than introducing extra lithium at interstitial sites in the structure.

4. Conclusions

The LiSr$_{1−x}$B$_x$O$_6$F ($B = \text{Nb}^{5+}$, $\text{Ta}^{4+}$) 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, $\text{Zr}^{4+}$. 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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