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**Synthesis, structure and ionic conductivity of lithium ion conductors
with perovskite and pyrochlore structures**

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Introduction

Battery is an electronic device, which converts stored chemical energy into electrical energy. Nowadays, the rechargeable battery plays important role as the power source for electronic devices such as laptops and mobile phones. In addition, it has been developed for use in hybrid vehicle and aircraft, which requires larger scale and higher energy and power densities. The lithium contained liquid electrolyte exhibits high conductivity and is compatible with the battery voltage operation window. However, limitations of narrow temperature operation range, leakage, and the safety problem due to the flammable of the solvents. Liquid-free batteries that utilize solid-state lithium ion conductors are expected to exhibit the major advantages and eliminate the safety problem.

The use of Li-ion conductors as solid electrolytes in all-solid-state batteries has attracted a good deal of interest because they have the potential to provide batteries with improved stability, safety, and reliability compared with conventional liquid-electrolyte-based Li batteries. Among the proposed solid electrolyte materials, solid oxides containing Li are of particular interest because of their high ionic conductivities and good chemical stabilities over a wide range of operating temperature. Lithium lanthanum titanates, $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$, shows their highest conductivities in the perovskite structure [1]. However, there is electrochemical stability issue due to reduction of tetravalent titanium between solid electrolyte and Li metal anode. The substitution of Ti by Ta indicated that $\text{LiSr}_{1.65}\text{Zr}_{1.3}\text{Ta}_{1.7}\text{O}_9$ was a particularly stable Li conductor [2]. Therefore, the Li-Sr-Ta-M-O system ($M = \text{Al}, \text{Ga}$) was postulated to be an ideal candidate for the achievement of high ionic conductivity with perovskite structure. The mechanism of Li-ion conduction in the perovskite structure reveals that lithium ions migrate in the tunnel surrounded by eight BO_6 octahedral. In this regard, there is a similar tunnel in pyrochlore structure

and this structure still remained an unexplored area of research as a Li-ion conducting oxide. In the present study, the Li-Sr-Ta/Nb-O-F system was investigated for the lithium ionic conductor with the pyrochlore structure.

Chapter 2. Experimental

Solid solutions were synthesized either solid-state reaction with ball-milling pre-treatment in air at 900-1350 °C or by a two-step synthesis method, i.e. simple solid-state reaction followed by high-pressure solid-state reaction method at 1 GPa of pressure and 800 °C. Powder sample were subjected to X-ray, synchrotron X-ray and powder neutron diffraction analyses for structure determination. Diffraction data was analyzed by Rietveld refinement method using Rietan-FP and GSAS programs. Ionic conductivity was measured by the AC impedance method using frequency response analyzers (NF Corp. FRA5097 and Solartron 1260); the samples were placing under flowing Ar gas, and the measurements were performed over the temperature range from 25 to 350 °C and the frequency range 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.

Chapter 3. Syntheses, structures, and ionic conductivities of perovskite-structured lithium-strontium aluminum/gallium-tantalum-oxides

In Chapter 3, the lithium containing double oxides, $(\text{Li}_x\text{Sr}_{1-x})(\text{M}_{(1-x)/2}\text{Ta}_{(1+x)/2})\text{O}_3$ ($M = \text{Al}, \text{Ga}$) were investigated based on the cubic perovskite structural model with the $Pm-3m$ space group. The partial substitution of the smaller Ga^{+3} for Ta^{+5} resulted in new compositions because the larger Ga than Al at the *B*-site offers a comparatively larger bottleneck through an increase in the *B*–O bond length.

Therefore, greater conductivity was observed upon Ga substitution. On the basis of the Ga-substituted system, the combination with different ionic radius and aliovalence cations of $\text{Sr}^{2+} / \text{Li}^{+}$ at *A*-site is to modify the crystal structure and Li composition and

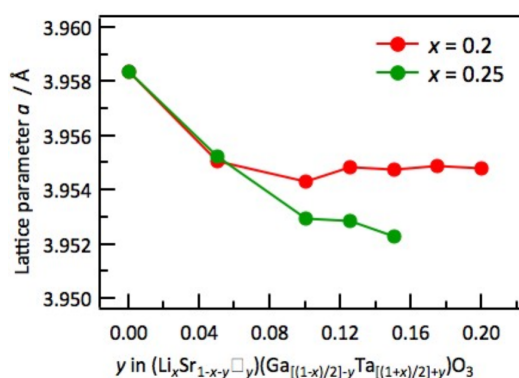


Figure 1. Composition dependence of the lattice parameter for $(\text{Li}_x\text{Sr}_{1-x-y})(\text{Ga}_{[(1-x)/2]-y}\text{Ta}_{[(1+x)/2]+y})\text{O}_3$.

A-site vacancy with compositions $(\text{Li}_x\text{Sr}_{1-x-y}\square_y)(\text{Ga}_{[(1-x)/2]-y}\text{Ta}_{[(1+x)/2]+y})\text{O}_3$, where the composition range of $0 \leq y \leq 0.20$ was examined for $x = 0.2$ and 0.25 . It was determined that changes in lattice parameters (Figure 1) associated with vacancy insertion indicate the formation of solid solutions. The highest conductivity, $1.85 \times 10^{-3} \text{ S cm}^{-1}$ at 250°C , was obtained for $(\text{Li}_{0.25}\text{Sr}_{0.625}\square_{0.125})(\text{Ga}_{0.25}\text{Ta}_{0.75})\text{O}_3$ ($x = 0.25$, $y = 0.125$). Enhanced ionic conductivities were achieved by the introduction of vacancies and amounts of Li at the *A*-sites.

Chapter 4. Synthesis, structure and ionic conductivity of pyrochlore-structured $\text{LiSrB}_2\text{O}_6\text{F}$ ($B = \text{Nb}^{+5}, \text{Ta}^{+5}$).

In chapter 4, lithium ion conduction in new pyrochlore-type oxyfluorides materials, $\text{LiSrB}_2\text{O}_6\text{F}$ ($B = \text{Nb}^{+5}$ or Ta^{+5}) and their solid solutions, have been investigated. Extra Li interstitial were introduced in the lattice by doping lower oxidation state cation Zr^{+4} at the *B*-site, $\text{Li}_{1.1}\text{SrB}_{1.9}\text{Zr}_{0.1}\text{O}_6\text{F}$, and the absence of Sr and F created vacancies composition, $\text{LiSr}_{0.9}\text{B}_2\text{O}_6\text{F}_{0.8}$. Figure 2 shows the crystal structures, which have been clarified by X-ray and synchrotron diffraction techniques at room temperature using a structural model of a cubic pyrochlore-type material with *Fd-3m* symmetry. However, small amount of impurity phases were observed in the solid solutions. The conductivity increased with the introduction of interstitial Li ions and vacancies. The highest conductivity of was achieved for $\text{LiSr}_{0.9}\text{B}_2\text{O}_6\text{F}_{0.8}$, $8.21 \times 10^{-6} \text{ S cm}^{-1}$ and $6.38 \times 10^{-6} \text{ S cm}^{-1}$ at 300°C for Nb and Ta, respectively. The Li^{+1} cations migrate in pyrochlore structure through hexagonal tunnels as shown in Figure 3 and the existence F, which is located at *8b*-site, is an obstacle for migration pathway confirmed by MEM analysis at room temperature. The decrease in the *8b*-site

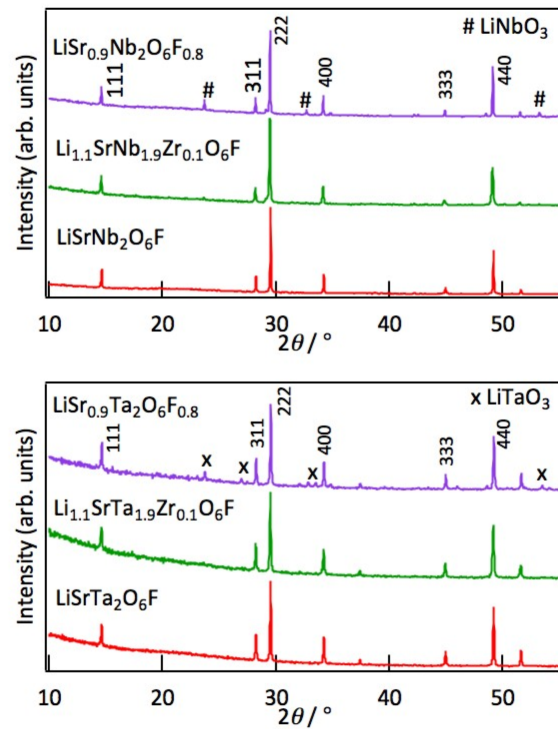


Figure 2. X-ray diffraction patterns for Nb and Ta compounds

occupation parameter (vacancies at F-site) can improve the Li-ion migration in the structure. Therefore, relation among the structural characteristics revealed that Li ion migration pathway could be affected by vacancies in *A*- and F-sites more than Li interstitial.

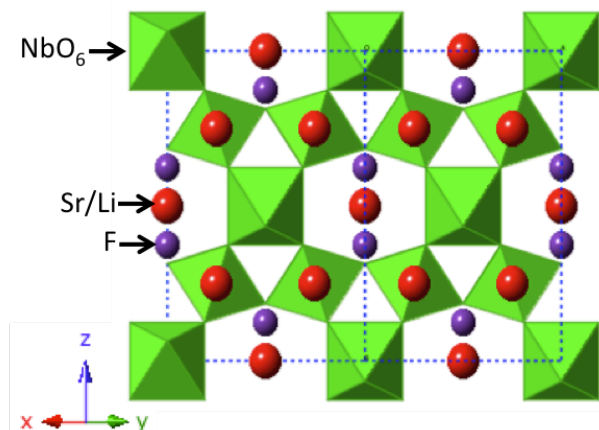


Figure 3. Representation of the structure of the LiSrNb₂O₆F based on synchrotron Rietveld analysis.

Chapter 5. Summary

In this study following results have been concluded.

1. The lithium containing double oxides, $(\text{Li}_x\text{Sr}_{1-x-y}\square_y)(\text{Ga}_{[(1-x)/2]-y}\text{Ta}_{[(1+x)/2]+y})\text{O}_3$, has been synthesized and found to exhibit a conductivity of $1.85 \times 10^{-3} \text{ S cm}^{-1}$ at 250 °C. Enhanced ionic conductivities were achieved by the introduction of vacancies and amounts of Li at the *A*-sites.
2. New Li-ion conducting oxides of pyrochlore structure, $\text{LiSrB}_2\text{O}_6\text{F}$ ($B = \text{Nb}^{+5}$ or Ta^{+5}) and their solid solutions, have been synthesized and their conductivity values were clarified. The highest conductivity value of $8.21 \times 10^{-6} \text{ Scm}^{-1}$ at 300 °C with the introduction of vacancies.
3. The introduction of vacancies at *A*-site and the change in the Li concentration affect the conductivity in these perovskite and pyrochlore structures.

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