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**Ionic Conduction Mechanism of a Lithium Superionic Argyrodite in the Li-Al-Si-S-O System**

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We report the conduction mechanism in oxygen-substituted lithium conductors composed of the $\text{Li}_{x}\text{Al}_{1-x}\text{Si}_{1+x}\text{S}_{3-x}\text{O}_4$ (LASSO) system, which is a novel member of the argyrodite-type family and has superionic conductivities, making it suitable for all-solid-state batteries. The crystal structures, ionic conductivities, and electrochemical properties of these systems were examined using powder X-ray and neutron diffractometry combined with impedance spectroscopy and cyclic voltammetry measurements. The optimal $\text{Li}_{0.35}\text{Al}_{0.65}\text{Si}_{1.35}\text{S}_{2.65}\text{O}_4$ (x = 0.6) material exhibited a high ionic conductivity of 1.24 mS cm$^{-1}$ at 25 °C with a low activation energy of 36.6 kJ mol$^{-1}$. Rietveld refinement and maximum-entropy-method analysis using neutron diffraction data revealed a unique interstitial Li$^+$ and O$^2-/S^2-$ site disorder, which led to a flatter energy landscape for migrating Li$^+$ ions and, thus, a low percolation threshold for three dimensional (3D) Li$^+$ ion diffusion. Oxygen substitution also stabilized the structure, and a wide electrochemical window from −0.1 V to 5 V vs. Li/Li$^+$ was achieved. The significant improvements in the ionic conductivity and stability owing to structural changes after cation and anion substitutions reveal an important strategy toward the development of argyrodite-type superionic conductors.

**Introduction**

All-solid-state batteries have attracted considerable attention because of their potentials to tremendously improve device safety by replacing highly flammable liquid electrolytes with solid-state inorganic ionic conductors. 1,2 Lithium ion conductors that could be used as solid electrolytes are the key materials for the all-solid-state devices.3,4 Despite significant research efforts, the number of candidates for the electrolytes with high ionic conductivities (> 1 mS cm$^{-1}$) is still limited, with only thio-LISICONs5-8 lithium argyrodites,9-13 Li10GeP2S12 (LGPS)-type materials,14,17 and Li$_2$P$_2$S$_11$ glass-ceramics18,19 showing good potential. However, most of these are thiophosphates that are highly volatile at high temperatures, posing challenges for their synthesis.20 Additionally, the multiplicity of phosphorus oxidation states in thiophosphates is one of the reasons for their high chemical instabilities toward electrode materials.21-24 Thus, it is of great interest to search for phosphorus-free lithium ion conductors with high ionic conductivities and chemical stabilities, which must also use low-cost and abundant materials for practical applications.

Recently, phosphorus-free argyrodite-type materials have been discovered that consist of low-cost and earth-abundant materials, such as Li$_2$S-Al$_2$Si$_2$S$_2$ (LASS).25 By replacing the P$^{5+}$ cations with Al$^{3+}$/Si$^{4+}$ in order to introduce more Li$^+$ into the argyrodite structure, these materials exhibit superior ionic conductivity in the order of 10$^{-4}$ S cm$^{-1}$ at room temperature, which is three orders of magnitude higher than those of the thio-LISICON phases of the Li$_2$S-Al$_2$Si$_2$S$_2$ system.7 In classical lithium argyrodites, such as Li$_8$P$_5$S$_x$ (x = Cl, Br, I),9,13 two distinct Li$^+$ positions have been identified, namely the 48h and 24g Wyckoff sites that form lithium diffusion cages. However, our group found a unique interstitial Li$^+$ site at the 16e Wyckoff site between the cages of the Li-rich LASS argyrodite structure,25 comparable to those found in Ag and Cu argyrodite analogs, such as γ-Ag$_2$P$_2$S$_6$ and γ-Cu$_2$P$_2$Se$_6$.27 The effect of this interstitial Li$^+$ on lithium ionic conductivity has not yet been discussed comprehensively. Another issue to be solved is the effect of the inclusion of oxygen in the material, which was detected in the synthesized sample in our previous report.25 Oxygen doping can enhance the electrochemical stability of lithium ion conductors against lower reduction potentials as suggested by recent studies.28,29

Herein, the effectiveness of substituting Al$^{3+}$/Si$^{4+}$ for P$^{5+}$ (cation substitution) and O$^{2-}$ for S$^{2-}$ (anion substitution) when tailoring and optimizing material properties is considered. We synthesized the solid-solution Li$_{0.15}$Al$_{0.85}$Si$_{1.35}$S$_{2.65}$O$_4$ (LASSO) to clarify its structure-property-composition relationships, with the goal of improving our understanding of the ionic conduction mechanism for phosphorus-free argyrodite-type materials using a combination of Rietveld refinement and maximum-entropy-method (MEM) analysis. On the basis of the results, we...
observe that: 1) the interstitial Li-ions at structural joints with nearby Li-ions allow for concerted diffusion, which is suggested to lead to a flatter energy landscape for the migrating Li-ions; and 2) oxygen substitution creates anion site disorder, resulting in a low percolation threshold for 3D Li-ion diffusion. Both effects synergistically help to increase Li-ion conductivity to above 1 mS cm\(^{-1}\) in the optimal material, making \(Li_{x}Si_{15}Al_{15}SiS_{x}O_{6}\) (\(x = 0.6\)) among the best phosphorus-free superionic conductors reported so far.

### Experimental

Li\(_2\)S (Mitsuwa Chemical Co., Ltd., >99.9% purity), Al\(_2\)S\(_3\) (Kojundo Chemical Laboratory Co., Ltd., >98% purity), Si\(_2\)S\(_3\) (Mitsuwa Chemical Co., Ltd., >99% purity), and Li\(_2\)O (Kojundo Chemical Laboratory Co., Ltd., >99% purity) were the starting materials used to synthesize \(Li_{0.15}Al_{15}Si_{13.5}S_{x}O_{6}\) (LASSO). These powders were weighed in stoichiometric ratios in an Ar-filled glovebox and then mechanically mixed in a sealed stainless steel pot for 30 min at 370 rpm using a vibration milling apparatus (CMT Co., Ltd., Ti-100). The obtained mixtures were pelletized, placed in a carbon tube, and sealed at 15 Pa in a carbon-coated quartz tube, followed by annealing at 1000 °C for 1 h, after which they were quenched in iced water.

Powder X-ray diffraction (XRD) patterns of the synthesized samples were obtained using a Rigaku Smartlab X-ray diffractometer with CuK\(_\alpha\) radiation. Synchrotron XRD experiments were performed on the BL19B2 beamline at the SPring-8 facility (Japan) at a wavelength of 0.5 Å. Specimens were sealed under Ar in quartz capillaries (diameter: 0.3 mm), and a Debye–Scherrer diffraction camera was used to acquire data. Neutron diffraction data were acquired using the SPICA time-of-flight (TOF) neutron-powder diffractometer at the J-PARC facility (Japan). Samples (~0.5 g) were placed in cylindrical vanadium cells (diameter: 6 mm; height: 55 mm). Lattice and structural parameters were refined using the Z-Rietveld software (Ver.1.1.0).\(^{30}\) Nuclear density distributions were calculated by MEM analysis using crystal structure factors, and standard deviations were obtained by Rietveld refinement. All MEM calculations were performed using the Z-MEM algorithm in the Z-Code software package,\(^{31}\) which employs the conventional Sakata-Sato algorithm with a zeroth-order single-pixel approximation.\(^{32}\) The Z-three-dimensional algorithm was used to generate the nuclear density maps of the structures.\(^{33}\) The MEM analysis data were visualized with the VESTA software package.\(^{34}\)

The ionic conductivity of each sample was determined by the AC-impedance method. The samples used were pelletized (diameter: 10.1 mm; thickness: ~1 mm) at 91 MPa. The pellet was then pressed at 181 MPa and 400 °C for 2 h, followed by natural cooling to room temperature. Conductivities were measured using frequency-response analyzers (Solartron 1260 and 1287) with an applied voltage of 10 mV in the 1 Hz to 10 MHz frequency range, at temperatures of between −45 and 110 °C. All the processes were conducted in an Ar atmosphere.

The electrochemical windows were evaluated by cyclic voltammetry measurement. Experiments involving the Li/Solid electrolyte (SE)/Al cells were conducted between 0.1 and 5.0 V and at 25 °C using a lithium reference electrode and at a scan rate of 1 mV s\(^{-1}\).

All-solid-state batteries were constructed using our samples as the SE, a mixture of LiNO\(_2\)-coated LiCoO\(_2\) and LGPS\(^{14}\) as the composite cathode (7:3 weight ratio), and In-Li as the anode. The anode (lithium foil [thickness: 0.1 mm, diameter: 5 mm], indium foil [thickness: 0.1 mm, diameter: 10 mm] with a Cu mesh current collector), and the composite cathode with Al mesh and Al foil current collectors were pressed onto opposite sides of the solid electrolyte pellet. The electrochemical properties of the cells were evaluated using a TOSCAT-3100 battery tester (Toyo System). Cycling was performed between 1.9 and 3.6 V vs. the In-Li anode (≈0.6 V vs. Li/Li\(^+\)) at an applied current of 0.2 C and 25 °C.

### Results and discussion

#### Material Synthesis

The mono-phasic region of the argyrodite structure was searched based on the formation diagram for the Li-Al-Si-S-O system. A schematic composition diagram of the Li-Al-Si-S-O system is depicted in Fig. 1. Nominal oxygen substitution of the argyrodite-type structure (cubic argyrodite, space group F-43m) was determined to be beneficial, where \(x\) ranged from 0.4 to 0.6. Within this range, the reproducibility of the argyrodite phase was much higher than that of the Li-Al-Si-S system,\(^{25}\) which required careful control of both the composition and the cooling process. This strongly implies that oxygen substitution can further stabilize the argyrodite structure, thereby increasing the reproducibility of the argyrodite phase at room temperature.

![Schematic composition diagram of the Li-Al-Si-S-O system (found between the pseudo-ternary Li\(_2\)O-SiO\(_2\)-Li\(_2\)O, and Li\(_2\)S-Si\(_2\)S\(_3\)-Al\(_2\)S\(_3\) diagrams). The argyrodite-type phase appears in a narrow region, as indicated by dashed cylinder. Samples with the Li\(_{1.2}\)Al\(_{1.5}\)Si\(_{1.5}\)S\(_{0.6}\)O\(_6\) (LASSO) (0.4 ≤ x ≤ 0.9) composition were synthesized.](image)
A representative X-ray diffraction pattern for Li$_{6.15}$Al$_{0.15}$Si$_{1-2x}$O$_{0.6}$ is shown in Fig. 2(a); the pattern can be indexed as an argyrodite phase using the Li$_7$PS$_6$ reference (ICSD#421130, also shown in Fig. 2(a)). Fig. 2(b) shows the lattice parameters of solid solutions with the formula Li$_{6.15}$Al$_{0.15}$Si$_{1-2x}$O$_{0.6}$ as a function of the nominal oxygen content $x$. The lattice data for $x = 0$ are taken from the literature.\textsuperscript{21}

Ionic conductivity

Figure 3(a) shows the lithium ion conductivity of LASSO as a function of the nominal oxygen content $x$. The oxygen-substituted samples showed significant improvement over previous results (where $x = 0$)$^{25}$, with ionic conductivities up to five times higher. The maximum ionic conductivity of Li$_{6.15}$Al$_{0.15}$Si$_{1-2x}$O$_{0.6}$ was observed at $x = 0.6$. This conductivity-composition dependence corresponds to the phase purity of the argyrodite: when the oxygen content is too low, an amorphous phase exists within the sample, while secondary phases exist when the oxygen content is too high. Fig. 3(b) displays the complex impedance (Nyquist) and the Arrhenius plots of Li$_{6.15}$Al$_{0.15}$Si$_{1-2x}$O$_{0.6}$ ($x = 0.6$), which exhibited the highest ionic conductivity, as determined at temperatures between 45 and 110°C. Ionic conductivities were calculated from the impedance plots, which are characteristic of pure ionic conductors; they each consist of a semicircle and a spike, which corresponds to contributions from the bulk/grain boundaries and the electrode, respectively. As the bulk and grain boundaries cannot be deconvoluted; hence, the conductivity was obtained by summing the grain boundary and bulk resistances. The ionic conductivity was 1.24 x 10$^{-3}$ S cm$^{-1}$ with an activation energy of 36.6 kJ mol$^{-1}$ for Li$_{6.15}$Al$_{0.15}$Si$_{1-2x}$O$_{0.6}$ at 25°C, almost four orders of magnitude higher than that for the thio-LiSICONs in the Li$_4$Al$_{1-2x}$S$_4$ system,\textsuperscript{7} which is among the highest value among the phosphorus-free silicon sulfides.

Conduction mechanism based on structural analysis

In order to understand the conduction mechanism, the crystal structure of the composition with the highest conductivity, namely Li$_{6.15}$Al$_{0.15}$Si$_{1-2x}$O$_{0.6}$, was refined by the Rietveld method using neutron-diffraction data obtained at 25°C. The refined neutron-diffraction patterns of Li$_{6.15}$Al$_{0.15}$Si$_{1-2x}$O$_{0.6}$ are shown in Fig. 4. The structure of HT-Li$_{1.5}$Al$_{0.5}$Si$_{0.5}$S$_2$ (space group: F43m, No. 216) was used as a model for the initial values during refinement (Li in the 48h and 16e sites, Si(Al)/Si in the 48h, 16e, and 4b sites, and S/O in the

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Figure 2 (a) X-ray diffraction pattern for Li$_{6.15}$Al$_{0.15}$Si$_{1-2x}$O$_{0.6}$ along with the pattern of argyrodite Li$_7$PS$_6$ (ICSD: 421130), which is indexed as the cubic argyrodite phase. (b) Lattice parameter for Li$_{6.15}$Al$_{0.15}$Si$_{1-2x}$O$_{0.6}$ as a function of the nominal oxygen content $x$. The lattice data for $x = 0$ are taken from the literature.\textsuperscript{21}

Figure 3. (a) Lithium ion conductivity of LASSO as a function of the nominal $x$, as obtained by impedance spectroscopy at 25°C. The conductivity data for $x = 0$ was obtained from the literature.\textsuperscript{25} (b) Impedance plots for conductivity data between -45 and 130°C (insets) and the Arrhenius plot for Li$_{6.15}$Al$_{0.15}$Si$_{1-2x}$O$_{0.6}$. Conductivities were obtained by summing the grain-boundary and bulk resistances.

Figure 4. The structure of HT-Li$_{1.5}$Al$_{0.5}$Si$_{0.5}$S$_2$ (space group: F43m, No. 216) was used as a model for the initial values during refinement (Li in the 48h and 16e sites, Si(Al)/Si in the 48h, 16e, and 4b sites, and S/O in the
16e, 4c, and 4a sites). After the refinement, an agreement factor $R_{wp}$ of 1.1610% (goodness of fit $S = 1.83$) was finally obtained, indicating that the refinement was satisfactory for the structural models employed in this study. Table S1 lists the refined lattice and structural parameters for Li$_{x}$Al$_{0.15}$Si$_{1.35}$S$_{6}O$_{25} (x = 0, x = 0.8) are indicated in the Supporting Information (Table S2, S3).

In the argyrodite structure, the doublet and intra-cage jumps occur within a local lithium diffusion cage, while the inter-cage jumps link adjacent cages to enable long-range diffusion, which is considered the rate-limiting step and, consequently, determines the macroscopic lithium ion conductivity. Compared with classical argyrodite structure, the doublet and intra-cage jumps (solid line), intra-cage (dashed line), and inter-cage (dotted line). The tetrahedra represent the MS$^{4+}$ units that form the argyrodite framework, and the equi-contour surfaces of the lithium nuclear density distribute in the crystal structures. Fig. 7 shows the nuclear distribution maps for Li$_{x}$Al$_{0.15}$Si$_{1.35}$S$_{6}O$_{25} (a) x = 0.6 and (b) x = 0. The tetrahedra represent the MS$_{4}$ (M = Al$_{0.15}$Si$_{1.35}$) units that form the argyrodite framework, and the equi-contour surfaces of the lithium nuclear density distribute in the structure. At an iso-surface level of $-2$ fm Å$^{-3}$, Li$^{+}$ at the 48h and 16e sites can be identified in both the oxygen-doped (x = 0.6) and un-doped (x = 0) samples based on the scattering amplitude distribution map. The oxygen-doped sample shows a higher Li$^{+}$ nuclear density than the non-doped sample. As the iso-surface level is increased to $-0.1$ fm Å$^{-3}$, the Li$^{+}$ sites in the oxygen-doped sample tend to connect with one another, while those in the non-doped sample remain isolated. When the iso-surface level is further increased to $-0.025$ fm Å$^{-3}$, 3D lithium diffusion is evident in the oxygen-doped sample, including the doublet,
intra-cage, and inter-cage jumps, while the non-doped sample only shows local diffusion pathways at this level. This analysis shows that oxygen doping in the structure of Li-argyrodite \( \text{Li}_{1.15}\text{Al}_{0.15}\text{Si}_{1.35}\text{S}_{5.4}\text{O}_{0.6} = 0 \) contributes to a lower percolation threshold for 3D diffusion of Li\(^+\). Similar phenomena have been observed in halogen-substituted Li-argyrodites,\(^{40} \) where Cl\(^-\) (or Br\(^-\))-substituted argyrodites exhibit much higher ionic conductivities than \( \text{I}^-\)-substituted ones. This was ascribed to the anion site-disorder created by substitution,\(^{16} \) although the latter ones have larger lattice parameters.

In our structural analysis, we found that the oxygen ions were not evenly distributed at the 4a and 4c sites. Around 20% of the oxygen ions were substituted at the 4c sites, while the remainder were found at the 4a sites, showing a high degree of anion site-disorder. This anion site-disorder in the local environment may also modify the potential energy landscape for migrating ions, leading to further dramatic increases in conductivity.\(^{12} \) When compared with the parent material, \( \text{Li}_{1.15}\text{Al}_{0.15}\text{Si}_{1.35}\text{S}_{5.4}\text{O}_{0.6} \) the oxygen substitution in \( \text{Li}_{1.15}\text{Al}_{0.15}\text{Si}_{1.35}\text{S}_{5.4}\text{O}_{0.6} \) lowers the activation energy from 40 kJ mol\(^{-1}\) to 36.6 kJ mol\(^{-1}\) (see Fig. 3(b)), which is consistent with the large improvement in ionic conductivity (up to a five-fold increase after oxygen doping). Although more experimental and theoretical work is needed to further evaluate the effects of anion site-disorder, it is suggested that \( \text{O}^{2-}/\text{S}^{2-} \) site-disorder may have a similar effect as seen for the halogen-containing analogues, where the activation energy (percolation threshold) for the migrating \( \text{Li}^+ \) is lowered leading to significant improvement in ionic conductivity.

**Thermal and electrochemical stability**

The thermodynamic evolution of \( \text{Li}_{6.15}\text{Al}_{0.15}\text{Si}_{1.35}\text{S}_{5.4}\text{O}_{0.6} \) was evaluated by in-situ high-temperature synchrotron X-ray diffractometry. Minor structural changes were observed during the heating process, but the argyrodite structure was maintained after annealing at 500 °C (Fig. 8(a)). The major phase was a cubic argyrodite-type phase even at 600 °C, where its non-oxygen doped HT-Li\(_4\)Al\(_{0.15}\)Si\(_{0.9}\)S\(_4\) counterpart had already decomposed completely into \( \text{Li}_2\text{SiS}_4 \) and \( \text{Li}_2\text{S} \) secondary phases (see Fig. S2).\(^{25} \) This result again indicates that oxygen substitution can significantly improve the thermal stabilities of sulfide-based electrolytes, providing improved safety even when applications require high-temperature working environments.

The electrochemical window of our material was evaluated by cyclic voltammetry. Fig. 8(b) shows the cyclic voltammogram for a Li/ \( \text{Li}_{6.15}\text{Al}_{0.15}\text{Si}_{1.35}\text{S}_{5.4}\text{O}_{0.6}/\text{Al} \) cell. The cathodic and anodic currents at around 0 V correspond to lithium deposition and dissolution, respectively. No significant currents by side reactions were observed from -0.1 V to 5 V, indicating that no severe electrolyte decomposition occurred in this voltage range.

The \( \text{Li}_{6.15}\text{Al}_{0.15}\text{Si}_{1.35}\text{S}_{5.4}\text{O}_{0.6} \) was examined as a solid electrolyte in an all-solid-state battery. Fig. 8(c) shows the charge-discharge curves of the fabricated cell, which consisted of \( \text{Li}_{6.15}\text{Al}_{0.15}\text{Si}_{1.35}\text{S}_{5.4}\text{O}_{0.6} \) as the electrolyte, a Li-In metal anode, and a LiNbO\(_3\)-coated LiCoO\(_2\)/LGPS cathode at a charge-discharge rate of 0.2 C at 25 °C. A reversible capacity of over 120 mAh g\(^{-1}\) was observed, showing a good Coulombic efficiency that corresponds to the theoretical value for LiCoO\(_2\).
battery demonstrates feasible stable performance when employing phosphorus-free Li-argyrodite as a solid electrolyte.

Using a combination of neutron diffraction, analyzed by the Rietveld refinement and the maximum-entropy method, and impedance spectroscopy, we observed that changes in Li' occupancies and O\(^{2-}/S^{2-}\) site disorder correlate with ionic conductivity. Two impacts of conductivity on composition were discussed. Firstly, when compared with conventional Li-argyrodite, the higher Li' concentration in LASSO resulted in unique interstitial Li' sites, allowing for concerted Li' migration, possibly due to a flatter energy landscape for Li' migration. Secondly, inclusion of oxygen anions created O\(^{2-}/S^{2-}\) site disorder that lowered the percolation threshold for 3D Li' diffusion. Both of these effects modified the energy landscape for Li' migration and synergistically contributed to the improvement in ionic conductivity, which was as high as 1.24 mS cm\(^{-1}\) at 25 °C—one of the best reported values for phosphorus-free superionic conductors. Furthermore, this oxygen-substituted conductor exhibited a wide electrochemical stability window with suitable electrode materials, and an all-solid-state battery based on this solid electrolyte was successfully assembled and cycled at a 0.2 C rate. Our work shows that structural changes induced by both cation and anion substitutions can significantly improve the thermal, chemical, and electrochemical performances of solid conductors, which will prove invaluable for the optimization of existing solid conductors and the discovery of new materials, thereby facilitating their practical applications in all-solid-state batteries.

Conflicts of interest

There are no conflicts to declare.

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Figure 8. (a) Synchrotron X-ray diffraction patterns of Li\(_{6.15}\)Al\(_{0.15}\)Si\(_{1.35}\)O\(_{5.4}\) at temperatures ranging from room temperature to 500 °C. The sample examined at room temperature was obtained directly from the reaction after quenching. (b) Cyclic voltammogram for a Li/? Li\(_{6.15}\)Al\(_{0.15}\)Si\(_{1.35}\)O\(_{5.4}\)/Al cell, from –0.1 to 5 V at a scan rate of 1 mV s\(^{-1}\). (c) Charge-discharge curve of an all-solid-state battery using Li\(_{6.15}\)Al\(_{0.15}\)Si\(_{1.35}\)O\(_{5.4}\) as the electrolyte, anode, and cathode materials, respectively. The charge-discharge current rate was 0.2 C.

Conclusions

In this study, the conduction mechanism of the phosphorus-free Li\(_{6.15}\)Al\(_{0.15}\)Si\(_{1.35}\)O\(_{5.4}\) (LASSO) argyrodite-type material was investigated, which confirmed that superionic conductivity can be obtained through cation and anion substitution effects.
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