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3 **Synthesis, structure, and electrochemical properties of crystalline Li-P-S-O solid**
4 **electrolytes: novel lithium-conducting oxysulfides of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ family**

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Abstract

Novel lithium-ion (Li^+)-conducting oxysulfides of the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ family were found in the ternary Li_2S - P_2S_5 - P_2O_5 system; $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ -type solid solutions with compositions $\text{Li}_{3+5x}\text{P}_{1-x}\text{S}_{4-z}\text{O}_z$ ($x = 0.03$ – 0.08 , $z = 0.4$ – 0.8) were confirmed. The solid solutions showed ionic conductivities from 4.14×10^{-5} to $2.64 \times 10^{-4} \text{ S cm}^{-1}$ at 298 K and a wide electrochemical window of 0–5.0 V (vs. Li/Li^+). Among the solid solutions synthesized, the purest phase had the composition $\text{Li}_{3.35}\text{P}_{0.93}\text{S}_{3.5}\text{O}_{0.5}$ ($x = 0.07$, $z = 0.5$). Structural analysis revealed that the novel oxysulfides are isostructural to the original $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ structure and the $(\text{P}/\text{Y})(\text{S}/\text{O})_4$ tetrahedra, which indicates the presence of cation defects with oxygen substitution in the crystal structure. Electrochemical stability of the oxysulfides was confirmed in the voltage range of 0–5.0 V. The solid–electrolyte interphase (SEI) resistivity and its cycle-dependence evaluation for new materials demonstrated that the oxysulfides had lower resistivities and furnished well-contacted SEI layers during the charge–discharge process.

Key words

lithium ion conductor, oxysulfide, $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, crystal structure, interfacial reaction

1. Introduction

Lithium-ion (Li^+)-conducting materials are key components of all-solid-state batteries because the stability and ionic conductivity of the solid electrolyte determines the battery performance [1-3]. Among several Li^+ -conductors, crystalline sulfides have attracted much attention because of their higher conductivities than oxide-based materials [4-9]. Especially, thio-LISICON (Lithium SuperIonic CONductor) provides a variety of compositions and conductive properties [4-6, 10, 11]. On the other hand, $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) is a promising material as the solid electrolyte in solid-state batteries because of its prominent room-temperature ionic conductivity of $>10 \text{ mS cm}^{-1}$ [7]. In addition, its solid solution system, $\text{Li}_{10+\delta}\text{Ge}_{1-\delta}\text{P}_{2-\delta}\text{S}_{12}$ ($\delta = 0.35$), provided the highest Li^+ conductivity of 14 mS cm^{-1} [8], indicating that conductivity of LGPS system can be further improved by controlling its composition. However, in terms of electrochemical stability, chemical stability, and moisture sensitivity, germanium (Ge)- and sulfur (S)-free materials are more advantageous than the original LGPS-type materials. Constituent elements are also issues to be considered in terms of cost and resources for practical application of the electrolytes in large-scale batteries. Cation site modifications were previously investigated for the substitution of Ge^{4+} by isovalent cations such as Si^{4+} and Sn^{4+} [9, 12-14]. On the other hand, simulation studies have revealed that for $\text{Li}_{10\pm1}\text{MP}_2\text{X}_{12}$ ($\text{M} = \text{Ge, Si, Sn, Al, P}$ and $\text{X} = \text{O, S, Se}$) [15], substitutions at the anion sites might also influence conductivities and electrochemical stabilities of the materials, which were not achieved by practical synthesis. In the present study, anion substitution of the LGPS-type structure was examined and the possibility of designing metal-free framework for lithium diffusion based on the $\text{Li}_9\text{P}_3\text{S}_{12}$ is revealed. Oxide-based $\text{Li}_{10\pm1}\text{MP}_2\text{O}_{12}$ materials might be thermodynamically unstable [15] and complete substitution of S by O might be difficult, although high electrochemical stability is expected for these materials. Expanding the oxide-based LGPS family could provide a larger electrochemical window to the solid electrolyte. The present study focused on metal-free oxysulfides of the LGPS family.

The ternary composition diagram of the $\text{Li}_2\text{S}-\text{P}_2\text{S}_5-\text{P}_2\text{O}_5$ system is shown in Figure 1, illustrating the representative composition examined in this study. Although the tie-line between Li_3PS_4 and Li_3PO_4 was previously reported by Takada *et al.* [16], existence of the LGPS-type structure was not elucidated. In this study, partial substitution of S by O was examined for $\text{Li}_{3+5x}\text{P}_{1-x}\text{S}_4$ in terms of the composition z in

$\text{Li}_{3+5x}\text{P}_{1-x}\text{S}_{4-z}\text{O}_z$. Structural and electrochemical properties of the new oxysulfides of the LGPS family were also investigated.

2. Experimental

The powdered $\text{Li}_{3+5x}\text{P}_{1-x}\text{S}_{4-z}\text{O}_z$ samples were synthesized by a melt-quenching method using Li_2S (Kojyundo Chemical Laboratory Co., Ltd., 99% purity), P_2S_5 (Aldrich, 99% purity), and P_2O_5 (Kojyundo Chemical Laboratory Co., Ltd., 99.99% purity) as the starting materials. They were weighed in appropriate molar ratios in an Ar-filled glove box, and were ground by a vibrating mill (CMT, TI-100) for 30 min. The ground powders were pressed into pellets and were then sealed in a carbon-coated quartz tube at 10 Pa. The pellets were heated to 973–1073 K at a heating rate of 2 K min^{-1} ; after 1 h the pellets were cooled to ~300 K using water bath. X-ray diffraction data of the samples were collected by X-ray diffractometer (Rigaku SmartLab) with $\text{CuK}\alpha$ radiation over $2\theta = 10\text{--}40^\circ$ with step-width = 0.03° . Synchrotron X-ray diffraction was conducted using the BL02B2 beamline at SPring-8 for structural analysis at 298 K. The X-rays were monochromated using a Si(111) double-crystal system and the selected X-ray had a wavelength of 0.6 Å. Synchrotron X-ray Rietveld analysis was performed to determine the structural parameters using Rietan-FP [17].

The prepared sample was subjected to scanning electron microscopy–energy-dispersive X-ray spectroscopy (SEM/EDX, JEOL JSM-7800F) to analyze its chemical composition. The obtained powder was pressed into a pellet and was transferred from the Ar-filled glove box to the SEM observation room using an Ar-filled container to prevent exposure of the sample to air.

Ionic conductivity was measured by the alternating current (ac)-impedance method in an Ar gas flow over a temperature (T) range of 298–378 K with applied frequencies in the 1–10 MHz range using a Solartron 1260 frequency response analyzer. For impedance measurements, the sample was pressed into a pellet (diameter = 10.2 mm; thickness = 1–2 mm), which was then Au-coated to form electrodes. Electrochemical stability of the sample was evaluated by cyclic voltammetry (CV) using a Au electrode and a Li electrode as the working and a counter/reference electrodes, respectively. A potential was swept between –0.5 V and 5.0 V at a scan rate of 1 mV s^{-1} using a Solartron 1287 electrochemical interface. Interfacial reaction of the materials in an all-solid-state battery was also evaluated by symmetric cell

charge–discharge and impedance methods with a Li-Sn alloy ($\text{Li}_{0.4}\text{Sn}$, ~ 0.8 V vs. Li/Li^+) [18]. The preparation methods for the symmetric cell, the $\text{Li}_{4-k}\text{Ge}_{1-k}\text{P}_k\text{S}_4$ (LGPS $_k$) solid electrolytes, and the experimental procedures are reported in the literature [2, 3, 8].

3. Results and discussions

3.1 Phase determination and structure analysis

Phases in the obtained powders were determined by X-ray diffraction (XRD) studies. The diffraction patterns of $\text{Li}_{3.35}\text{P}_{0.93}\text{S}_{4-z}\text{O}_z$ ($x = 0.07$, $z = 0\text{--}1.0$) are shown in Figure 2. At $z = 0\text{--}0.3$, diffraction peaks due the LGPS-type structure are not clearly observed, although the peaks indexed by the $\gamma\text{-Li}_3\text{PS}_4$ phase are clearly seen around $2\theta = 20^\circ$ and 23° . In addition, existence of the Li_7PS_6 impurity phase was confirmed by the presence of the diffraction peak at $2\theta \approx 30^\circ$. The $\gamma\text{-Li}_3\text{PS}_4$ peak intensities decrease with decreasing z value and the diffraction lines due to the LGPS-type phase become more apparent. Although the Li_7PS_6 peaks exist, LGPS-type phase was the main phase for $z = 0.4\text{--}0.6$. Further increase of z up to 0.8 reveals additional unknown peaks around $2\theta \approx 22^\circ$. These results indicate that the LGPS-type oxysulfide solid solution exists in $\text{Li}_{3.35}\text{P}_{0.93}\text{S}_{4-z}\text{O}_z$ around $z = 0.5$. Other compositions of $\text{Li}_{3+5x}\text{P}_{1-x}\text{S}_{4-z}\text{O}_z$ were also investigated and it was revealed that the LGPS-type solid solution exists over a range of $x = 0.03\text{--}0.08$ and $z = 0.4\text{--}0.8$.

Element distribution in the sample was investigated by SEM/EDX observation. Figure 3 shows the obtained results for the $\text{Li}_{3.35}\text{P}_{0.93}\text{S}_{3.5}\text{O}_{0.5}$ powder, which agreed well with the XRD pattern showing the purest characteristics. In the layered image, overlapping of P and S in the entire region is confirmed, while segregation of O is indicated at specific regions; a small amount of C is also observed, probably derived from the carbon coating on the silica tube wall. On the other hand, the separated images revealed O distribution in the entire sample, indicating that the $\text{Li}_{3.35}\text{P}_{0.93}\text{S}_{3.5}\text{O}_{0.5}$ main phase contains a small amount of O in the structure. O-rich regions could have an oxygen-excess composition of $\text{Li}_{3.35}\text{P}_{0.93}\text{S}_{4-z}\text{O}_z$ ($z > 0.5$) because homogeneous distribution of P and S (to a lesser extent) is confirmed in these regions.

To characterize the LGPS-type oxysulfide structure, the $\text{Li}_{3.35}\text{P}_{0.93}\text{S}_{3.5}\text{O}_{0.5}$ ($x = 0.07$, $z = 0.5$) was analyzed by synchrotron XRD. The structural parameters were refined by Rietveld refinement using synchrotron XRD (Figure 4 and Table 1). The space group $P4_2/nmc$ was used for the refinement, and the initial parameters were taken

from a structural model reported for the LGPS phase [8]. Atomic positions and occupancies for the Li atoms were fixed at the values reported for the neutron diffraction data with a composition of $\text{Li}_{10.05}\text{Ge}_{1.05}\text{P}_{1.95}\text{S}_{12}$ ($\text{Li}_{3.35}\text{Ge}_{0.35}\text{P}_{0.65}\text{S}_4$) at 300 K, which has the same Li composition as in the LGPS-type structure [8]. The incident beam wavelength was calibrated to 0.59866 Å using a NIST SRM Ceria 640b CeO_2 standard.

Good fitting results were obtained for the two-phase model of the LGPS-type and Li_7PS_6 (impurity) phases. The remaining difference between the raw diffraction data and the simulation results could be due to the formation of another LGPS phase with a slightly different composition in the samples because formation of oxygen-rich phases at specific regions in the sample was confirmed by SEM/EDX studies. The XRD pattern reflects the average structure of the samples, therefore any slightly different structural parameter of the oxygen-rich phases present in the sample could prevent good fitting. Therefore, the atomic displacement parameters B of all the S sites were constrained because B is strongly related to the occupancies of the S sites. Lattice parameters of $\text{Li}_{3.35}\text{P}_{0.93}\text{S}_{3.5}\text{O}_{0.5}$ ($x = 0.07$, $z = 0.5$) were $a = 8.3702(3)$ and $c = 12.3023(6)$ Å, smaller than those of the original LGPS, $a = 8.71771(5)$ and $c = 12.63452(10)$ Å, due to substitution by smaller ions (P^{5+} (0.17 Å) < Ge^{4+} (0.39 Å), O^{2-} (1.4 Å) < S^{2-} (1.84 Å)). Lower ionic conductivity of this material ($9.1 \times 10^{-5} \text{ S cm}^{-1}$) could be attributed to its smaller lattice volume than the original LGPS phase. Three-dimensional framework and the Li(1) and Li(3) atoms of $\text{Li}_{3.35}\text{P}_{0.93}\text{S}_{3.5}\text{O}_{0.5}$ ($x = 0.07$, $z = 0.5$) and the original LGPS phase [7] are illustrated in Figure 5. The (Ge/P) S_4 tetrahedron, which shares a common edge with the LiS_6 octahedron forming a one-dimensional chain along the c axis, was replaced by the PS_4 tetrahedron. The (P/Y)(S/O) $_4$ tetrahedron connects the chains with corner sharing in the oxysulfide, indicating the preferred defect formation and anion substitution at the P(2) and the S(1) sites, respectively. The calculated composition was $\text{Li}_{3.35}\text{P}_{0.93}\text{S}_{3.56}\text{O}_{0.44}$, which was nominally the same as $\text{Li}_{3.35}\text{P}_{0.93}\text{S}_{3.5}\text{O}_{0.5}$, indicating that an LGPS-type oxysulfide structure was synthesized. The defect at the P(2) site corresponds to the aliovalent cation substitution, $\text{P}^{5+} \leftrightarrow 5\text{Li}^+$, according to the x value in the composition $\text{Li}_{3+5x}\text{P}_{1-x}\text{S}_{4-z}\text{O}_z$ [11]. The slightly lower oxygen content compared to the nominal composition could be due to the formation of oxygen-rich phases, which incorporates more oxygen in the structure.

3.2 Electrochemical properties of Li-P-S-O solid electrolyte

Ionic conductivity of the $\text{Li}_{3+5x}\text{P}_{1-x}\text{S}_{4-z}\text{O}_z$ was measured by ac-impedance spectroscopy over $T = 298\text{--}378$ K. Figure 6 shows the impedance plots and the Arrhenius plots of $\text{Li}_{3.35}\text{P}_{0.93}\text{S}_{3.5}\text{O}_{0.5}$ ($x = 0.07$, $z = 0.5$). The impedance plots show one semicircle with spikes at all measured temperatures. The capacitance of the semicircle was $\sim 10^{-10}$ F, which might be due to the bulk/grain boundary of the samples. Therefore, component separation for the bulk and the grain boundary could not be achieved. The conductivity was calculated from the semicircle as a total resistance (bulk resistance + grain boundary resistance). A conductivity of $9.1 \times 10^{-5} \text{ S cm}^{-1}$ was observed at 298 K, which is smaller than those of the other LGPS phases, probably because of the smaller lattice volumes of the oxysulfides. The activation energy of 36.6 kJ mol^{-1} is larger than those of other LGPS phases [7-9, 13].

CV measurements were carried out using an asymmetric cell with a configuration of $\text{Li}/\text{Li}_{3+5x}\text{P}_{1-x}\text{S}_{4-z}\text{O}_z$ ($x = 0.07$, $z = 0.5$ and $x = 0.07$, $z = 0.8$)/Au. Figure 7 illustrates a representative CV curve. Except for the currents near 0 V vs. Li/Li^+ redox potential, no significant current peak was observed. The oxysulfides were stable in the voltage range of 0–5 V (vs. Li/Li^+). Smaller current compared to that of the LGPS phase [7] could be due to the low ionic conductivity of this material. The excellent electrochemical stability of the oxysulfide can be applied to solid-state batteries with wide voltage ranges.

Charge–discharge tests were carried out with symmetric cells ($\text{Li}_{0.4}\text{Sn}/\text{Li}_{3+5x}\text{P}_{1-x}\text{S}_{4-z}\text{O}_z$ ($x = 0.07$, $z = 0, 0.4, 0.8$), LGPS_k ($k = 0.5, 0.65$)/ $\text{Li}_{0.4}\text{Sn}$) by applying a constant current of 1.38 mA cm^{-2} for 20 min, followed by applying the same amount of current in the opposite direction. Redox voltage of the $\text{Li}_{0.4}\text{Sn}$ alloy is ~ 0.8 V (vs. Li/Li^+) [18]. The ac-impedance of the cell was measured after each charge–discharge cycle. All the electrochemical experiments were carried out at 298 K. The solid–electrolyte interphase (SEI) resistance was calculated using a semicircle in the high-frequency region of the obtained impedance plots [2, 3, 19]. The SEI resistances and their cycle-dependence are shown in Figure 8. At the initial cycle, the LGPS_k system showed lower resistance than the $\text{Li}_{3+5x}\text{P}_{1-x}\text{S}_{4-z}\text{O}_z$ system, probably due to the intrinsic higher ionic conductivity of the LGPS_k system. On the other hand, the SEI resistance of the LGPS_k system increased while that of the $\text{Li}_{3+5x}\text{P}_{1-x}\text{S}_{4-z}\text{O}_z$ system

decreased with cycling. Sakuma *et al.* reported [3] that the Ge content in the structure strongly influences the SEI resistance. For example, a Ge-rich phase with the composition $\text{Li}_{3.55}\text{Ge}_{0.5}\text{P}_{0.5}\text{S}_4$ ($k = 0.5$) showed the highest resistivity (over 1000 Ω). On the other hand, the $\text{Li}_{3+5x}\text{P}_{1-x}\text{S}_{4-z}\text{O}_z$ system showed significant decrease in resistance from 600–1000 Ω to 30–110 Ω , indicating a formation of a stable and well-contacted SEI layer. Ge-free $\text{Li}_{3+5x}\text{P}_{1-x}\text{S}_{4-z}\text{O}_z$ ($x = 0.07$, $z = 0.0$) phase with its low resistance is advantageous for the formation of an SEI layer suitable for battery reactions. Furthermore, the composition $\text{Li}_{3+5x}\text{P}_{1-x}\text{S}_{4-z}\text{O}_z$ ($x = 0.07$, $z = 0.4$) showed the lowest SEI resistance, indicating that oxygen substitution could form a well-contacted SEI layer during the charge–discharge process. The SEI layer formed in the oxysulfide structure could provide a better interface than Li-Ge-P-S system, which suppresses further electrolyte decomposition and contributes to better Li^+ diffusion and facilitates charge transfer. Since larger amount of impurity phases are contained in the as-prepared samples, the single $\text{Li}_{3+5x}\text{P}_{1-x}\text{S}_{4-z}\text{O}_z$ ($x = 0.07$, $z = 0.8$) phase might provide a slightly smaller SEI resistance. The electrochemical evaluations demonstrated that the novel LGPS-type oxysulfides (Li-P-S-O) without any metallic element in the framework could be a good candidate for the solid electrolyte in an all-solid-state lithium battery using low-redox-potential anode materials, and could enhance the energy density of the all-solid-state battery.

4. Conclusion

Novel Li^+ -conducting oxysulfides with LGPS-type structure were developed, and their structures and electrochemical properties were evaluated. Formation of an LGPS-type phase with a composition of $\text{Li}_{3+5x}\text{P}_{1-x}\text{S}_{4-z}\text{O}_z$ ($x = 0.03$ – 0.08 and $z = 0.4$ – 0.8) was confirmed. Structural analysis of $\text{Li}_{3.35}\text{P}_{0.93}\text{S}_{3.5}\text{O}_{0.5}$ ($x = 0.07$, $z = 0.5$) revealed that the novel oxysulfide is isostructural with the original LGPS phase and the $(\text{P/Y})(\text{S/O})_4$ tetrahedra, indicating the presence of cation defects with oxygen substitution in the crystal structure. Lower ionic conductivity ($9.1 \times 10^{-4} \text{ S cm}^{-1}$) and larger activation energy (36.6 kJ mol^{-1}) of the $\text{Li}_{3.35}\text{P}_{0.93}\text{S}_{3.5}\text{O}_{0.5}$ ($x = 0.07$, $z = 0.5$) phase compared to the original LGPS phase could be due to lattice contraction and the contained impurity phases. Electrochemical stability was confirmed in a voltage range of 0–5.0 V. The SEI resistivity and its cycle-dependence evaluation demonstrated that the novel LGPS-type oxysulfides (Li-P-S-O) provide low resistivity and a well-contacted SEI layer during the

charge–discharge process. These results indicate that the novel oxysulfides could be a good candidate as the solid electrolyte in all-solid-state lithium batteries using low-redox-potential anode materials, and could enhance the energy density of the batteries.

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FIGURE CAPTIONS

Figure 1. Ternary diagram and composition of Li_2S - P_2S_5 - P_2O_5 system. Representative reported materials are also plotted. The triangles indicate representative compositions investigated in this study.

Figure 2. XRD patterns of $\text{Li}_{3.35}\text{P}_{0.93}\text{S}_{4-z}\text{O}_z$ ($x = 0.07$) for $z = 0$ – 1.0 . The XRD patterns of γ - Li_3PS_4 (ICSD #180318) and $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (ICSD #248307) are also illustrated.

Figure 3. SEM and EDX mapping images for the pressed pellet of the $\text{Li}_{3.35}\text{P}_{0.93}\text{S}_{3.5}\text{O}_{0.5}$ powder. SEM images with layered elemental maps (a) and corresponding elemental maps via EDX mapping for (b) sulfur, (c) oxygen, (d) phosphorous and (e) carbon. Scale bar of the images for (b–e) are the same as shown in (b).

Figure 4. Synchrotron X-ray Rietveld refinement patterns for $\text{Li}_{3.35}\text{P}_{0.93}\text{S}_{3.5}\text{O}_{0.5}$ ($x = 0.07$, $z = 0.5$). Observed data points are indicated by plus signs (+) and solid lines overlaying the data were obtained via Rietveld refinement analysis. Vertical markers below the patterns indicate positions of possible Bragg reflections of space group

$P4_2/nmc$ for the LGPS-type (green) and the impurity Li_7PS_6 (black) phases. Differences between observed and calculated intensities are plotted below the data on the same scale.

Figure 5. Three-dimensional framework including $\text{Li}(2)\text{S}_6$ octahedra, $\text{Li}(4)\text{S}_4$ tetrahedra, $\text{M}(1)\text{X}_4$ tetrahedra, and $\text{M}(2)\text{X}_4$ tetrahedra ($\text{M} = \text{P}, \text{Ge}, \text{X} = \text{S}, \text{O}$) with the $\text{Li}(1)$ and $\text{Li}(3)$ atoms and their comparison with $\text{Li}_{3.35}\text{P}_{0.93}\text{S}_{3.5}\text{O}_{0.5}$ ($x = 0.07, z = 0.5$) (a) and LGPS (b).

Figure 6. Nyquist plots at various temperatures for $\text{Li}_{3.35}\text{P}_{0.93}\text{S}_{3.5}\text{O}_{0.5}$ ($x = 0.07, z = 0.5$) (a) and Arrhenius plots generated using the obtained impedance data (b). The magnified Nyquist plots are also included in (a).

Figure 7. Cyclic voltammogram for the asymmetric $\text{Li}/\text{Li}_{3.35}\text{P}_{0.93}\text{S}_{3.5}\text{O}_{0.5}$ ($x = 0.07, z = 0.5$)/Au cell.

Figure 8. Cycling dependence of the SEI resistance for cells with $\text{Li}_{0.4}\text{Sn}/\text{S.E}$ interface.

Results of LGPS k ($\text{Li}_{4-k}\text{Ge}_{1-k}\text{P}_k\text{S}_4$) and $\text{Li}_{3+5x}\text{P}_{1-x}\text{S}_{4-z}\text{O}_z$ systems are plotted as a function of numbers of cycles.

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Figure 8

TABLE

Table 1. Structural parameters obtained from the Rietveld refinement analysis on synchrotron XRD data of $\text{Li}_{3.35}\text{P}_{0.93}\text{S}_{3.5}\text{O}_{0.5}$ ($x = 0.07$, $z = 0.5$) using the $P4_2/nmc$ space group.

Atom	Site	g	x	y	z	B ($\text{\AA}^2$)
P(1)	$4d$	1.0	0.0	0.5	0.6835(5)	1.09(7)
P(2)	$2b$	0.793(12)	0.0	0.0	0.5	$= B[\text{P}(1)]$
S(1)	$8g$	0.671(8)	0.0	0.1730(4)	0.4173(3)	2.55(9)
O(1)	$8g$	$= 1-g[\text{S}(1)]$	0.0	$= y[\text{S}(1)]$	$= z[\text{S}(1)]$	$= B[\text{S}(1)]$
S(2)	$8g$	1.0	0.0	0.2940(4)	0.0974(3)	$= B[\text{S}(1)]$
S(3)	$8g$	1.0	0.0	0.7023(4)	0.7804(2)	$= B[\text{S}(1)]$
Li(1)	$16h$	0.38	0.26	0.27	0.19	5.0
Li(2)	$4d$	1.0	0.0	0.5	0.95	3.0
Li(3)	$8f$	0.83	0.24	0.24	0.0	5.0
Li(4)	$4c$	0.84	0.0	0.0	0.26	5.0

Unit cell: tetragonal $P4_2/nmc$ (137); $a = 8.3702(3)$ $\text{\AA}$, $c = 12.3023(6)$ $\text{\AA}$, $V = 861.92(6)$ $\text{\AA}^3$; $R_{\text{wp}} = 7.034$, $R_{\text{p}} = 5.094$, $R_{\text{b}} = 2.115$, $R_{\text{R}} = 16.232$, $R_{\text{e}} = 4.472$, goodness of fit $S = R_{\text{wp}}/R_{\text{e}} = 1.57$; phase: Li_7PS_6 (~ 21.1 mass%).