



Synthesis and structure of novel lithium-ion conductor $\text{Li}_7\text{Ge}_3\text{PS}_{12}$



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ABSTRACT

The novel lithium-ion conductor $\text{Li}_7\text{Ge}_3\text{PS}_{12}$ was synthesized by slow cooling from the ternary $\text{Li}_2\text{S}-\text{GeS}_2-\text{P}_2\text{S}_5$ system, and was shown to exhibit a cubic argyrodite-type structure. The phase composition was determined by varying the ratio of starting materials; the observed monophasic properties were close to those for the $\text{Li}_7\text{Ge}_3\text{PS}_{12}$ composition. The lattice parameter ($a = 9.80192(3) \text{ \AA}$) of $\text{Li}_7\text{Ge}_3\text{PS}_{12}$ was slightly smaller than that of Li_7PS_6 ($a = 9.993 \text{ \AA}$), indicating that substitution of a Li cation by the smaller Ge cation contracted the cubic lattice. In addition, the novel structure consisted of a framework composed of four isolated (Ge/P) S_4 tetrahedra. Li^+ ions occupied tetrahedral sites within the framework, forming a three-dimensional conduction pathway. Finally, $\text{Li}_7\text{Ge}_3\text{PS}_{12}$ exhibited a high ionic conductivity of $1.1 \times 10^{-4} \text{ S cm}^{-1}$ at $25 \text{ }^\circ\text{C}$ and an activation energy of 25 kJ mol^{-1} .

1. Introduction

Lithium-ion conductors are of great interest for use as solid electrolytes in lithium-ion batteries, as they have the potential to allow operation under significantly more severe conditions than those suitable for current battery systems [1,2]. In particular, the development of stable and non-flammable electrolytes could improve battery reliability, with solid electrolytes being promising candidates for this purpose. However, a number of issues remain, including the search for novel solid electrolytes exhibiting high lithium-ion conductivity combined with high electrochemical and chemical stabilities [2–5]. Thus, the discovery and development of new lithium-ion conducting solids is important to provide additional materials for all-solid-state battery systems.

One example of a crystalline superionic conductor is $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, which exhibits an extremely high lithium-ion conductivity of $1.2 \times 10^{-2} \text{ S cm}^{-1}$ at $27 \text{ }^\circ\text{C}$ and a high electrochemical stability $> 5 \text{ V}$ versus lithium [1]. This material exists in the $\text{Li}_2\text{S}-\text{GeS}_2-\text{P}_2\text{S}_5$ system, which also includes a number of other lithium-ion conductors with high ionic conductivities. Examples include $\text{Li}_4\text{GeS}_4-\text{Li}_3\text{PS}_4$ solid solutions with the LISICON-type structure [6,7], Li_7PS_6 with the argyrodite-type structure [8,9], and $\text{Li}_7\text{P}_3\text{S}_{11}$ glass ceramics [10]. Indeed, previous reports have indicated that this quasi-ternary system could provide various novel materials exhibiting high lithium-ion conducting characteristics, with a number of materials potentially remaining un-

explored.

Among the various ionic conductors reported to date, materials exhibiting an argyrodite-type structure can be considered interesting candidates because they allow anion/cation substitution in their crystal structure [11]. The term *argyrodite* is derived from the mineral Ag_8GeS_6 . Various atomic substitutions in the structure of this mineral have provided a wide range of argyrodite-type materials suitable for the ionic conduction of monovalent cations, including Ag^+ and Cu^+ [12,13]. However, to date, only a few argyrodite-type materials had been reported as lithium-ion conductors in the anion/cation substituted Li_7PS_6 system. For example, halogen-substituted compounds such as $\text{Li}_6\text{PS}_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) have cubic argyrodite-type structures and exhibit a lithium-ion conductivity of $10^{-4} \text{ S cm}^{-1}$ at room temperature [14,15]. The argyrodite structure consists of 136 tetrahedral sites in a unit cell, including four isolated PS_4 tetrahedra in a tetrahedrally close-packed anion array, in which 24 lithium ions occupy sites within the remaining 132 empty tetrahedral sites [11]. This distribution of lithium ions, which contributes to ionic diffusion, is characteristic of the argyrodite structure.

Thus, we herein report the development of a novel lithium-ion conducting crystalline material, focusing on the ternary $\text{Li}_2\text{S}-\text{GeS}_2-\text{P}_2\text{S}_5$ system, examining a previously un-synthesized composition. A systematic materials search will be carried out to identify any novel crystalline materials, and the relationship between structure and ionic conductivity will be investigated.

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Table 1
Reaction products detected in the prepared Li_2S – GeS_2 – P_2S_5 system.

Sample Number	Mole fraction in starting material			Identified phases
	Li_2S	GeS_2	P_2S_5	
1	0.63	0.09	0.27	<i>Li₄P₂S₆</i> , GeS_2 , unknown ^a
2	0.62	0.25	0.13	<i>Li₃PS₄</i> , GeS_2 , unknown ^a
3	0.61	0.33	0.06	<i>Li₄GeS₄</i> , GeS_2 , unknown ^a
4	0.6	0.16	0.24	<i>Li₄P₂S₆</i> , GeS_2 , unknown ^a
5	0.5	0.2	0.3	<i>Li₄P₂S₆</i> , GeS_2
6	0.5	0.33	0.17	<i>Li₄P₂S₆</i> , GeS_2 , unknown ^a
7	0.5	0.38	0.12	<i>Argyrodite</i> ^c , <i>Li₄P₂S₆</i> , GeS_2 , unknown ^a
8	0.51	0.42	0.07	<i>Argyrodite</i> ^c , <i>Li₄P₂S₆</i>
9 ^b	0.5	0.43	0.07	<i>Argyrodite</i> ^c , <i>Li₄P₂S₆</i>
10	0.49	0.44	0.07	<i>Argyrodite</i> ^c , <i>Li₄P₂S₆</i>
11	0.46	0.47	0.07	<i>Argyrodite</i> ^c , <i>Li₄P₂S₆</i> , GeS_2
12	0.48	0.47	0.06	<i>Argyrodite</i> ^c , <i>Li₄P₂S₆</i> , GeS_2 , unknown ^a
13	0.48	0.42	0.1	<i>Argyrodite</i> ^c , <i>Li₄P₂S₆</i> , GeS_2
14	0.46	0.46	0.09	<i>Argyrodite</i> ^c , <i>Li₄P₂S₆</i> , GeS_2
15	0.44	0.49	0.07	<i>Argyrodite</i> ^c , <i>Li₄P₂S₆</i> , GeS_2
16	0.41	0.52	0.07	GeS_2 , unknown ^a
17	0.33	0.33	0.34	<i>Li₄P₂S₆</i> , GeS_2

Italic characters represent the main phase for each composition.

^a Unknown = unidentified phases.

^b Composition of number 9 is $\text{Li}_7\text{Ge}_3\text{PS}_{12}$.

^c Argyrodite = a phase exhibiting an argyrodite-type structure.

2. Materials and methods

The starting materials, Li_2S (99.9%, Nippon Chemical Industrial Co. Ltd.), GeS_2 (>99.99%, Kojundo Chemical Laboratory Co. Ltd.), and P_2S_5 (99%, Sigma-Aldrich), were mixed in the appropriate molar ratios (see Table 1) in an Ar-filled glovebox. All mixtures were pelletized, placed into carbon-coated quartz glass tubes, and sealed in a ~10 Pa vacuum. The samples were then heated at 870 °C for 8 h in a furnace and cooled slowly to 28 °C. The reaction products were characterized by powder X-ray diffraction under an argon atmosphere using a Rigaku SmartLab powder X-ray diffractometer with Cu K α radiation (45 kV, 200 mA). The diffraction data were collected at 25 °C in a 2θ range of 10–120° with a step width of 0.01°.

The synchrotron X-ray diffraction pattern of the powdered sample was obtained at 25 °C using a Debye-Scherrer camera with an imaging plate at the BL02B2 beam line, at a wavelength of 0.6 Å. All measurements were carried out at the SPring-8 facility. Synchrotron X-ray diffraction data were analyzed using the Rietveld method and the RIETAN-FP package [16].

Ionic conductivity was determined using an alternating current (ac) impedance method in the frequency range of 1–1 MHz using a Solartron 1260 frequency response analyzer. A disk-shaped sample

(thickness: ~1 mm, diameter: ~6 mm) was prepared for conductivity measurements by solidifying the melt above the melting point of the material (~570 °C). Gold paste electrodes were coated on the surfaces of the disk prior to heating under vacuum at 150 °C for 3 h. The data were collected under a flow of Ar gas between 25 and 105 °C. Differential thermal analysis (DTA) was performed using a Rigaku Thermo Plus TG 8120 system between 24 and 900 °C for the sample sealed in an evacuated quartz ampule.

The charge and discharge characteristics of the all-solid-state battery were examined using $\text{Li}_7\text{Ge}_3\text{PS}_{12}$ as a solid electrolyte. The positive and negative electrodes were composed of a mixture of LiNbO_3 -coated LiCoO_2 and Li-In metal (thicknesses: 0.3 mm (Li) and 0.1 mm (In), diameters: 10 mm (Li and In)) [17]. The electrochemical properties of the cell were determined using a TOSCAT-3100 battery analyzer (Toyo System Co. Ltd.). A cycling test was carried out between 1.9 and 3.6 V (*vs.* Li-In: ~0.6 V *vs.* Li/Li⁺) at an applied current of 7.25 mA g⁻¹ at 25 °C.

3. Results and discussion

A materials search for lithium-ion conductors was carried out using the formation diagram of the quasi-ternary Li_2S – GeS_2 – P_2S_5 system, which is depicted in Fig. 1. In this system, intermediate crystalline compounds, such as Li_3PS_4 (thio-LISICON structure) [18], Li_7PS_6 (argyrodite structure) [9], and $\text{Li}_7\text{P}_3\text{S}_{11}$ [10] exist in the Li_2S – P_2S_5 tie line, while Li_4GeS_4 [19–22] and the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ -type $\text{Li}_{4-k}\text{Ge}_{1-k}\text{P}_k\text{S}_4$ solid-solution exist in the Li_3PS_4 – Li_4GeS_4 tie line [1,7,23]. Although other compositions have also been reported [24,25], large regions of the diagram remain unexamined. Table 1 summarizes the compositions synthesized herein along with the phase identification results obtained from X-ray diffraction measurements. For clarity, all compositions are numbered consistently throughout Figs. 1 and 2. A number of X-ray diffraction patterns of the materials synthesized in the ternary system are provided in Fig. 2, which shows that the observed phases were indexed as GeS_2 , $\text{Li}_4\text{P}_2\text{S}_6$, Li_3PS_4 , and Li_4GeS_4 , together with peaks corresponding to the new argyrodite phase. Specific analysis close to the region of formation of the new phase indicated that this novel phase could be generated with a nominal composition close to that of $\text{Li}_7\text{Ge}_3\text{PS}_{12}$ (see composition number 9 in Table 1).

Fig. 3 shows the X-ray diffraction patterns of both $\text{Li}_7\text{Ge}_3\text{PS}_{12}$ and the cubic high-temperature modification of Li_7PS_6 with the $F-43m$ space group (no. 216) (ICSD no. 421130) exhibiting an argyrodite-type structure. The two diffraction patterns are similar, indicating that the novel $\text{Li}_7\text{Ge}_3\text{PS}_{12}$ phase also exhibits a cubic argyrodite-type structure. The diffraction peaks of this new phase were indexed assuming a cubic unit cell with an $F-43m$ space group. Interestingly, the shifts of a number of peaks to higher angles compared to the Li_7PS_6 pattern indicate that the new phase contains smaller lattice parameters.

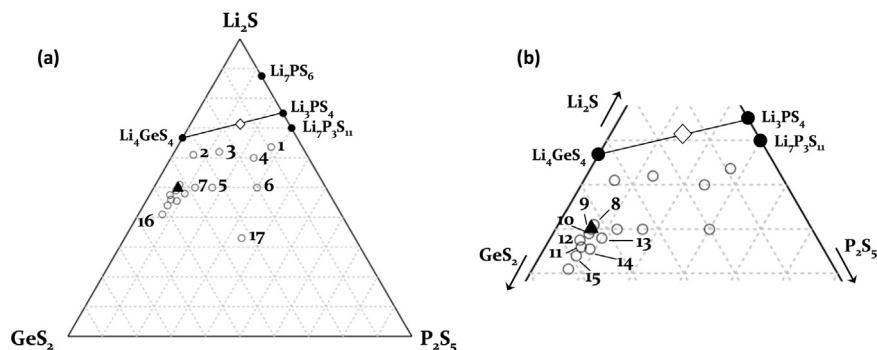


Fig. 1. Formation diagram of the Li_2S – GeS_2 – P_2S_5 quasi-ternary system. (a) The full Li_2S – GeS_2 – P_2S_5 region, and (b) the region close to the new argyrodite type phase (\blacktriangle : #9) discovered in this study. Numbered hollow circles (○) indicate the compositions synthesized in this study. The numbers correspond to those used in the XRD patterns (Fig. 2) and in the composition table (Table 1). Bold circles (●) indicate previously reported compositions for this system, and hollow diamonds (◇) depict the composition of the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ superionic conductor on the tie line of Li_4GeS_4 and Li_3PS_4 .

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