

Supporting Information

Conduction mechanism of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ -type lithium superionic conductors in a Li-Sn-Si-P-S system

Makoto Inagaki,^a Kota Suzuki,^{a,b,c,d} Satoshi Hori,^c Kazuhiro Yoshino,^b Naoki Matsui,^b Masao Yonemura,^e Masaaki Hirayama,^{a,b,c} and Ryoji Kanno^{a,b,c}*

^a Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan

^b Department of Chemical Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan

^c All-Solid-State Battery Unit, Institute of Innovative Research, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

^d Japan Science and Technology Agency (JST), Precursory Research for Embryonic Science and Technology (PRESTO), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

^e Neutron Science Laboratory (KENS), Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), 203-1 Shirakata, Tokai, Ibaraki 319-1106, Japan

Table S1. Rietveld refinement results for sample (i) with $\delta = 0.2$, $y = 0.8$, $x = 0.6$ in $\text{Li}_{10+\delta}[\text{Sn}_y\text{Si}_{1-y}]_{1+\delta}\text{P}_2-\delta\text{S}_{12}$ ($\text{Li}_{4-x}[\text{Sn}_y\text{Si}_{1-y}]_{1-x}\text{P}_x\text{S}_4$) at 300 K

Atom	Site	g	x	y	z
Li(1)	16 <i>h</i>	0.425(4)	0.2533(3)	0.2705(4)	0.1826(3)
Li(2)	4 <i>d</i>	1	0	0.5	0.9491(3)
Li(3)	8 <i>f</i>	0.877(8)	0.2411(2)	= x (Li(3))	0
Li(4)	4 <i>c</i>	0.645(3)*	0	0	0.2466(3)
Sn(1)	4 <i>d</i>	0.39	0	0.5	= x (P(1))
Si(1)	4 <i>d</i>	0.26	0	0.5	= x (P(1))
P(1)	4 <i>d</i>	0.35	0	0.5	0.68753(6)
P(2)	2 <i>b</i>	1	0	0	0.5
S(1)	8 <i>g</i>	1	0	0.18798(10)	0.40900(9)
S(2)	8 <i>g</i>	1	0	0.28667(14)	0.09885(13)
S(3)	8 <i>g</i>	1	0	0.69897(14)	0.78740(11)

*6-0.35-4× g (Li(1))- g (Li(2))-2× g (Li(3))

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Li(1)	4.1(3)	4.7(2)	16.3(4)	1.46(16)	-1.5(3)	-5.6(3)
Li(2)	8.9(2)	9.0(2)	15.6(3)	0	0	0
Li(3)	10.5(2)	= B_{11} (Li(3))	31.2(6)	-4.9(2)	9.01(18)	= - B_{13} (Li(3))
Li(4)	3.4(3)	12.3(4)	6.7(3)	0	0	0
Sn(1)	= B_{11} (P(1))	= B_{22} (P(1))	= B_{33} (P(1))	= B_{12} (P(1))	= B_{13} (P(1))	= B_{23} (P(1))
Si(1)	= B_{11} (P(1))	= B_{22} (P(1))	= B_{33} (P(1))	= B_{12} (P(1))	= B_{13} (P(1))	= B_{23} (P(1))
P(1)	4.81(6)	3.13(5)	3.94(6)	0	0	0
P(2)	3.29(4)	= B_{11} (P(2))	5.43(10)	0	0	0
S(1)	4.93(7)	3.29(7)	4.48(8)	0	0	-0.07(6)
S(2)	2.26(6)	6.73(8)	4.92(8)	0	0	-0.80(6)
S(3)	5.16(8)	5.90(7)	3.71(8)	0	0	1.90(7)

Space group $P4_2/nmc$; $a = 8.74128(3)$ Å, $c = 12.75215(7)$ Å, $V = 974.391$ Å³; $R_{\text{WP}} = 2.01\%$, $R_e = 0.28\%$, $R_p = 1.52\%$, goodness of fit $S = R_{\text{WP}}/R_e = 7.18$, $R_B = 2.27\%$, $R_F = 3.35\%$; and secondary phase: Li_3PO_4 (~1.0 mass%).

Table S2. Rietveld refinement results for sample (ii) with $\delta = 0.5$, $y = 0.2$, $x = 0.5$ in $\text{Li}_{10+\delta}[\text{Sn}_y\text{Si}_{1-y}]_{1+\delta}\text{P}_{2-\delta}\text{S}_{12}$ ($\text{Li}_{4-x}[\text{Sn}_y\text{Si}_{1-y}]_{1-x}\text{P}_x\text{S}_4$) at 300 K

Atom	Site	g	x	y	z
Li(1)	16 <i>h</i>	0.515(5)	0.2504(4)	0.2610(4)	0.1913(3)
Li(2)	4 <i>d</i>	1	0	0.5	0.9434(3)
Li(3)	8 <i>f</i>	0.726(10)	0.2431(3)	= x (Li(3))	0
Li(4)	4 <i>c</i>	0.738(4)**	0	0	0.2454(4)
Sn(1)	4 <i>d</i>	0.15	0	0.5	= x (P(1))
Si(1)	4 <i>d</i>	0.6	0	0.5	= x (P(1))
P(1)	4 <i>d</i>	0.25	0	0.5	0.68978(8)
P(2)	2 <i>b</i>	1	0	0	0.5
S(1)	8 <i>g</i>	1	0	0.18814(15)	0.40817(13)
S(2)	8 <i>g</i>	1	0	0.29602(14)	0.10102(15)
S(3)	8 <i>g</i>	1	0	0.69543(17)	0.78651(12)

** $6 - 0.25 - 4 \times g(\text{Li}(1)) - g(\text{Li}(2)) - 2 \times g(\text{Li}(3))$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Li(1)	6.7(3)	2.5(3)	17.8(8)	2.34(17)	-2.2(3)	-4.6(3)
Li(2)	8.2(3)	9.1(3)	8.4(3)	0	0	0
Li(3)	8.8(3)	= $B_{11}(\text{Li}(3))$	22.9(8)	-4.9(3)	4.7(2)	= $-B_{13}(\text{Li}(3))$
Li(4)	9.6(5)	11.6(5)	10.0(4)	0	0	0
Sn(1)	= $B_{11}(\text{P}(1))$	= $B_{22}(\text{P}(1))$	= $B_{33}(\text{P}(1))$	= $B_{12}(\text{P}(1))$	= $B_{13}(\text{P}(1))$	= $B_{23}(\text{P}(1))$
Si(1)	= $B_{11}(\text{P}(1))$	= $B_{22}(\text{P}(1))$	= $B_{33}(\text{P}(1))$	= $B_{12}(\text{P}(1))$	= $B_{13}(\text{P}(1))$	= $B_{23}(\text{P}(1))$
P(1)	2.57(7)	2.56(7)	2.42(6)	0	0	0
P(2)	4.40(6)	= $B_{11}(\text{P}(2))$	4.39(11)	0	0	0
S(1)	4.41(9)	4.34(9)	4.26(9)	0	0	0.26(10)
S(2)	4.29(9)	4.78(9)	4.26(8)	0	0	-0.20(7)
S(3)	3.96(8)	3.93(9)	3.74(9)	0	0	0.06(8)

Space group $P4_2/nmc$; $a = 8.71240(3)$ Å, $c = 12.64584(7)$ Å, $V = 959.894$ Å³; $R_{\text{WP}} = 2.13\%$, $R_c = 0.34\%$, $R_p = 1.64\%$, goodness of fit $S = R_{\text{WP}}/R_c = 6.26$, $R_B = 2.67\%$, $R_F = 3.38\%$; and secondary phase: Li_3PO_4 (~3.8 mass%).

Table S3. Rietveld refinement results for sample (iii) with $\delta = 0.35$, $y = 0.2$, $x = 0.55$ in $\text{Li}_{10+\delta}[\text{Sn}_y\text{Si}_{1-y}]_{1-x}\text{P}_x\text{S}_4$ at 300 K

Atom	Site	g	x	y	z
Li(1)	16 <i>h</i>	0.501(3)	0.2495(3)	0.2642(3)	0.1918(2)
Li(2)	4 <i>d</i>	1	0	0.5	0.9449(2)
Li(3)	8 <i>f</i>	0.689(8)	0.24715(18)	= $x(\text{Li}(3))$	0
Li(4)	4 <i>c</i>	0.791(13)***	0	0	0.2453(2)
Sn	4 <i>d</i>	0.135	0	0.5	= $z(\text{P}(1))$
Si	4 <i>d</i>	0.54	0	0.5	= $z(\text{P}(1))$
P(1)	4 <i>d</i>	0.325	0	0.5	0.68999(6)
P(2)	2 <i>b</i>	1	0	0	0.5
S(1)	8 <i>g</i>	1	0	0.18834(10)	0.40969(8)
S(2)	8 <i>g</i>	1	0	0.29646(11)	0.10121(10)
S(3)	8 <i>g</i>	1	0	0.69147(13)	0.78485(8)

*** $6 - 0.325 - 4 \times g(\text{Li}(1)) - g(\text{Li}(2)) - 2 \times g(\text{Li}(3))$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Li(1)	10.4(2)	8.9(2)	14.6(4)	3.42(16)	-1.03(18)	-10.3(2)
Li(2)	13.6(2)	7.78(14)	6.89(16)	0	0	0
Li(3)	8.1(3)	= $B_{11}(\text{Li}(3))$	37.8(7)	-0.7(2)	1.75(16)	= - $B_{13}(\text{Li}(3))$
Li(4)	9.4(4)	35.7(6)	7.5(4)	0	0	0
Sn(1)	= $B_{11}(\text{P}(1))$	= $B_{22}(\text{P}(1))$	= $B_{33}(\text{P}(1))$	= $B_{12}(\text{P}(1))$	= $B_{13}(\text{P}(1))$	= $B_{23}(\text{P}(1))$
Si(1)	= $B_{11}(\text{P}(1))$	= $B_{22}(\text{P}(1))$	= $B_{33}(\text{P}(1))$	= $B_{12}(\text{P}(1))$	= $B_{13}(\text{P}(1))$	= $B_{23}(\text{P}(1))$
P(1)	5.10(7)	4.51(6)	4.40(7)	0	0	0
P(2)	3.81(5)	= $B_{11}(\text{P}(2))$	8.20(10)	0	0	0
S(1)	5.54(6)	4.71(8)	3.10(7)	0	0	0.86(6)
S(2)	4.58(7)	6.15(7)	3.88(7)	0	0	-0.04(5)
S(3)	5.14(8)	5.14(8)	3.44(7)	0	0	1.26(6)

Space group $P4_2/nmc$; $a = 8.71073(2) \text{ \AA}$, $c = 12.62060(6) \text{ \AA}$, $V = 957.610 \text{ \AA}^3$; $R_{\text{WP}} = 3.47\%$, $R_{\text{e}} = 0.37\%$, $R_{\text{p}} = 2.42\%$, goodness of fit $S = R_{\text{WP}}/R_{\text{e}} = 9.38$, $R_{\text{B}} = 3.27\%$, $R_{\text{F}} = 4.84\%$; and secondary phase: Li_3PO_4 (~1.0 mass%).

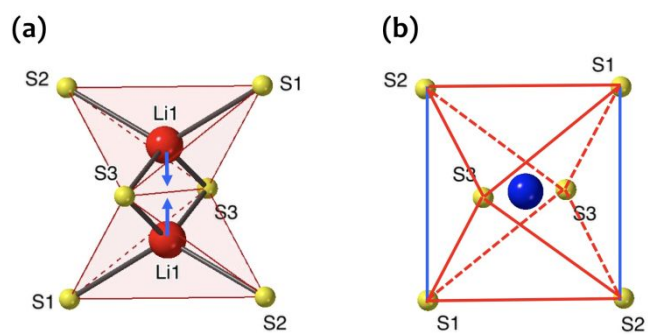


Fig. S1. Schematic illustration of the Li1S_4 tetrahedra (coordination number (C.N.): 4) (a) and the Li1S_6 octahedron (C.N.: 6).