

Supporting Information for

Liquid-phase synthesis of the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ -type phase in the Li–Si–P–S–Cl system

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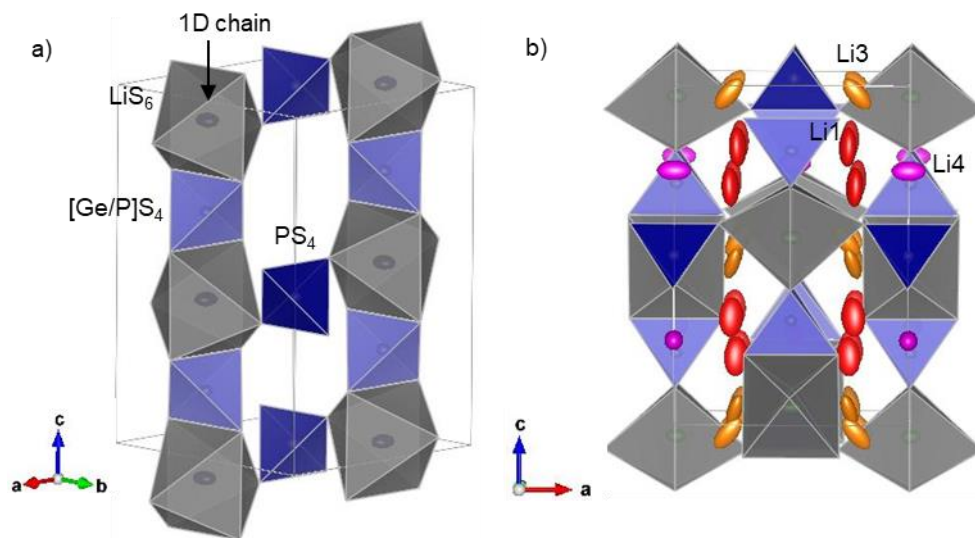


Figure S1. Crystal structure of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$.¹ a) Perspective view of the one-dimensional (1D) chains, which are formed from LiS_6 octahedra and $[\text{Ge/P}]\text{S}_4$ tetrahedra with a common edge. The chains are connected by PS_4 tetrahedra with corner sharing. b) Li ion distribution in the scaffold composed of polyhedral structural units.

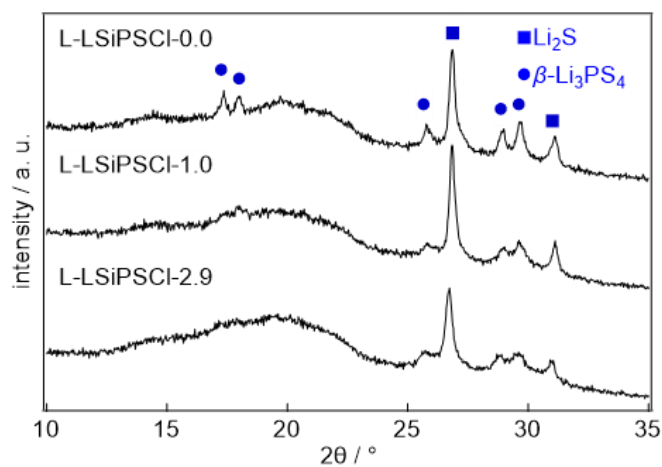


Figure S2. XRD patterns of precursor powder for the L-LSiPSCI-X ($X = 0.0, 1.0, \text{ and } 2.9$) samples.

Table S1. Lattice parameters and volume of the L-LSiPSCI- X ($X = 0.0, 1.0,$ and 2.9) and S-LSiPSCI samples.

Sample ^a	$a / \text{\AA}$	$c / \text{\AA}$	$V / \text{\AA}^3$
L-LSiPSCI-0.0	8.68774(12)	12.54775(27)	947.06(7)
L-LSiPSCI-1.0	8.71090(9)	12.56748(21)	953.62(5)
L-LSiPSCI-2.9	8.70988(10)	12.56599(23)	953.28(6)
S-LSiPSCI	8.71020(10)	12.56738(25)	953.46(6)

^a The crystal structure model for $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$ at 298K in the previous report² was considered as a reference material and used as the initial model in the refinement.

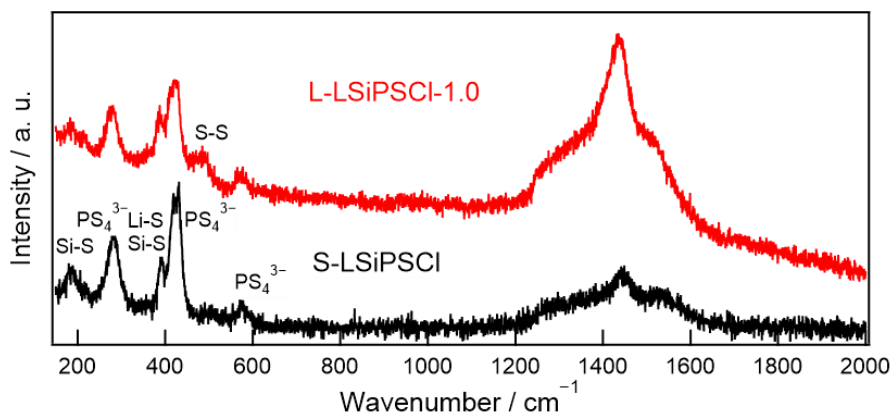


Figure S3. Micro-Raman spectra of L-LSiPSCI-1.0 and S-LSiPSCI in the range of 150–2000 cm^{-1} . The micro-Raman spectra were measured using a Lambda Vision Micro-RAM300 spectrometer at an excitation wavelength of 532 nm. The spectral peaks were assigned as follows: 280, 440, and 570 cm^{-1} (P-S bonds of the PS_4^{3-} ion),³ 190 cm^{-1} (Si-S bonds of the SiS_4 tetrahedra), and 390 cm^{-1} (Si-S bonds of the SiS_4 tetrahedra, Li-S bonds of the LiS_6 octahedra).^{4, 5} These peaks originated from the main phase crystal (LGPS-type phase), and no significant differences in the peak intensities were observed between L-LSiPSCI-1.0 and S-LSiPSCI. The peak at $\sim 480 \text{ cm}^{-1}$ was attributed only to the S-S bond of L-LSiPSCI-1.0,⁶ and so its presence was consistent with the fact that an excess of sulfur had been added during the synthetic process. In addition, the peak at $\sim 1440 \text{ cm}^{-1}$ was attributed to carbon-related bonds,⁵ and the intensity of this peak for L-LSiPSCI-1.0 was larger than that for S-LSiPSCI, suggesting that carbon-containing species were generated from the solvent used in the liquid-phase synthetic process.

References

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