Supporting Information

Native defects in Li₁₀GeP₂S₁₂ and their effect on lithium diffusion

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Computational details

Potential sets

The Vienna *Ab initio* simulation package (VASP)¹ potential set of Li (PAW_PBE Li_sv 10Sep2004), Ge (PAW_PBE Ge_d 03Jul2007), P (PAW_PBE P 06Sep2000), S (PAW_PBE S 06Sep2000) was used for total energy calculation. And, the VASP potential set of Li (PAW_PBE Li 17Jan2003), Ge (PAW_PBE Ge 05Jan2001), P (PAW_PBE P 06Sep2000), S (PAW_PBE S 06Sep2000) was used for high-cost calculations such as *ab initio* molecular dynamics (AIMD) simulations, nudged elastic band (NEB) calculations, and hybrid functional calculations.

Phase stability of Li₁₀GeP₂S₁₂

 $Li_{10}GeP_2S_{12}$ phase was predicted to be unstable at 0 K and to be decomposed into Li_4GeS_4 and Li_3PS_4 as in the following reaction.

$$Li_{10}GeP_2S_{12} \rightarrow Li_4GeS_4 + 2Li_3PS_4, \tag{1}$$

The calculated reaction energy of equation (1) is -13 meV/atom. This value of reaction energy is in a great agreement with the result by Du *et al.*,² which was -0.32 eV/f.u. (-13 meV/atom). However, this result does not exactly coincide with Mo *et al.*³ and Ong *et al.*,⁴ they calculated the decomposition energy as -25 meV/atom. The reason for this discrepancy is probably because they could not consider the Li4 sites, which was not revealed at the time of the initial report.⁵

Allowed range of chemical potentials in Li₁₀GeP₂S₁₂ phase

The chemical potentials of each element are important factors affecting the defect

formation energy and represent the experimental conditions.^{6, 7} In a given chemical space, the chemical potentials of $Li_{10}GeP_2S_{12}$ are subject to various thermodynamic limits. First, the sum of chemical potentials of corresponding stoichiometry should be equal to the energy of the $Li_{10}GeP_2S_{12}$.

$$10\mu_{Li} + \mu_{Ge} + 2\mu_P + 12\mu_S = E(Li_{10}GeP_2S_{12}), \tag{2}$$

where $E(Li_{10}GeP_2S_{12})$ indicates the energy of $Li_{10}GeP_2S_{12}$. Second, in order to prevent precipitation of the elements, the chemical potential of each element should be lower than the elemental chemical potential.

$$\mu_i \le \mu_i^0 \ (i = Li, Ge, P, S),\tag{3}$$

Third, to avoid the formation of other phases, the stoichiometric sum of chemical potentials for other stable phases in Li–Ge–P–S chemical space should be lower than the energy of those phases. For example, for stable phases Li₂GeS₃ and Li₂PS₃:

$$2\mu_{Li} + \mu_{Ge} + 3\mu_S \le E(Li_2 GeS_3), \tag{4}$$

$$2\mu_{Li} + \mu_P + 3\mu_S \le E(Li_2 PS_3), \tag{5}$$

where, $E(Li_2GeS_3)$ and $E(Li_2PS_3)$ indicate the energy of Li₂GeS₃ and Li₂PS₃, respectively. In this way, the range of allowed chemical potentials of each element in Li₁₀GeP₂S₁₂ could be determined if the Li₁₀GePS₁₂ was calculated as a stable phase.

However, $Li_{10}GeP_2S_{12}$ is unstable at 0 K and only stabilized with the help of entropic effect at elevated temperature.² Therefore, we corrected the energy of the $Li_{10}GeP_2S_{12}$ by reducing the decomposition energy to zero as suggested by Zhu *et al.*⁸ This correction implies tri-phasic equilibrium with Li_4GeS_4 , Li_3PS_4 and $Li_{10}GeP_2S_{12}$. From the assumed tri-phasic

equilibrium two constraints are introduced as follows:

$$4\mu_{Li} + \mu_{Ge} + 4\mu_S = E(Li_4 GeS_4), \tag{6}$$

$$3\mu_{Li} + \mu_P + 4\mu_S = E(Li_3 PS_4), \tag{7}$$

Then, the equation (2) becomes a linear combination of equation (6) and (7). Four variables with two constraints implies that all variables can be determined by two independent variables. Taking additional thermodynamic constraints such as equation (3), (4) and (5) into account, the allowed chemical potential range of Li₁₀GeP₂S₁₂ can be defined in terms of $\Delta \mu_{Li}$ and $\Delta \mu_S$ ($\Delta \mu_i = \mu_i - \mu_i^0$).

AIMD simulations for diffusivity calculations

From the range where the diffusivity converges, the diffusivity can be calculated from the following relation as implemented in python materials genomics (pymatgen)⁹ open-source library as in previous studies:^{3,4}

$$D = \frac{1}{2dt} \langle [\Delta \mathbf{r}(t)]^2 \rangle, \tag{8}$$

where *D* is the diffusivity, *d* is the dimension of the diffusion (*i.e.* d = 3 for Li₁₀GeP₂S₁₂ structure), *t* is the time, $\langle [\Delta r(t)]^2 \rangle$ is the mean square displacement (MSD) which is calculated as:

$$\langle [\Delta \mathbf{r}(t)]^2 \rangle = \frac{1}{N} \sum_i \langle [\mathbf{r}_i(t+t_0) - \mathbf{r}_i(t_0)]^2 \rangle_{t_0}, \tag{9}$$

where N is the total number of lithium ions participating in the diffusion, $r_i(t)$ is the position of i^{th} lithium ion at time t. It should be noted that MSD is also an ensemble averaged value over time t_0 . Then, the diffusivity can be calculated by performing a linear

fitting of the MSD *vs.* 2*dt*. From the *D* values of high temperature (500 K to 1300 K), the activation energy and diffusivity at 300 K (D_{300K}) were obtained by extrapolation of the Arrhenius relationship:

$$D = D_0 exp(-\frac{E_A}{k_B T}),\tag{10}$$

where D_0 is the prefactor, E_A is the activation energy, respectively. The ionic conductivity at room temperature (σ_{300K}) can be derived from the Nernst–Einstein equation:

$$\sigma_{300K} = \frac{\rho z^2 F^2}{RT} D_{300K},\tag{11}$$

where ρ is the molar density of lithium ions, z is the charge of lithium ions (+1), F is the Faraday constant, R is the gas constant, respectively.

	Neutral defects		Charged defects
Notation	Description	Notation	Description
Pa	Parallel Ge/P1 arrangement along ab-direction	p+	Removal of electron
Pc	Parallel Ge/P1 arrangement along c-direction	e ⁻	Addition of electron
V _{Li} ⁰	Vacancy of Li	V_{Li}^{-}	Vacancy of Li ⁺
V _{Ge}	Vacancy of Ge	V_{Ge}^{4-}	Vacancy of Ge ⁴⁺
$V_{P_1}^0$	Vacancy of P1	$V_{\mathtt{P1}}^{\mathtt{5-}}$	Vacancy of P15+
V _{P2} ⁰	Vacancy of P2	V _{P2} ⁵⁻	Vacancy of P25+
Vso	Vacancy of S	V_S^{2+}	Vacancy of S ²⁻
Li ⁰	Additional Li at interstitial sites	Li ⁺	Additional Li ⁺ at interstitial sites
Ge ⁰	Additional Ge at interstitial sites	Ge ⁴⁺	Additional Ge4+ at interstitial sites
P_i^0	Additional P at interstitial sites	P_i^{5+}	Additional P ⁵⁺ at interstitial sites
Ge_{Li}^0	Substitution of Li by Ge	Ge_{Li}^{3+}	Substitution of Li^+ by Ge^{4+}
P_{Li}^0	Substitution of Li by P	P_{Li}^{4+}	Substitution of $Li^{\scriptscriptstyle +}$ by $P^{\scriptscriptstyle 5+}$
Li ⁰ _{Ge}	Substitution of Ge by Li	Li ^{3–}	Substitution of Ge^{4+} by Li^+
Li ⁰ _{P1}	Substitution of P1 by Li	Li ⁴⁻	Substitution of $P1^{5+}$ by Li^+
Li ⁰ _{P2}	Substitution of P2 by Li	Li ⁴⁻	Substitution of $P2^{5+}$ by Li^+
Ge_{P1}^0	Substitution of P1 by Ge	Ge_{P1}^{-}	Substitution of P1 ⁵⁺ by Ge ⁴⁺
Ge ⁰ _{P2}	Substitution of P2 by Ge	Ge_{P2}^{-}	Substitution of $P2^{5+}$ by Ge^{4+}
P_{Ge}^{0}	Substitution of Ge by P	P_{Ge}^+	Substitution of Ge^{4+} by P^{5+}

Table S1. Descriptions of considered defects in this study.

			Lattice P	arameters			
a (Å)	b (Â)	c (Å)	α (°)	β	(°)	γ (°)
8.740	8.7	40	12.862	90.00	90	.00	90.47
			Atomic	positions			
Element	а	b	С	Element	а	b	С
Li	0.000	0.003	0.261	S	0.998	0.192	0.407
Li	0.003	0.000	0.739	S	0.002	0.811	0.405
Li	0.333	0.287	0.252	S	0.308	0.493	0.909
Li	0.287	0.333	0.748	s	0.695	0.508	0.910
Li	0.669	0.716	0.251	s	0.508	0.695	0.090
Li	0.264	0.742	0.826	s	0.493	0.308	0.091
Li	0.740	0.260	0.826	s	0.192	0.998	0.593
Li	0.260	0.740	0.174	s	0.811	0.002	0.595
Li	0.742	0.264	0.174	s	0.002	0.307	0.098
Li	0.716	0.669	0.749	S	0.001	0.695	0.097
Li	0.250	0.250	0.000	s	0.213	0.496	0.587
Li	0.752	0.752	0.000	S	0.788	0.506	0.588
Li	0.252	0.748	0.498	S	0.506	0.788	0.412
Li	0.748	0.252	0.502	S	0.496	0.213	0.413
Li	0.245	0.245	0.500	S	0.307	0.002	0.902
Li	0.756	0.756	0.500	S	0.695	0.001	0.903
Li	0.004	0.502	0.942	s	0.993	0.704	0.792
Li	0.000	0.500	0.441	s	0.011	0.297	0.791
Li	0.500	0.000	0.559	S	0.811	0.486	0.283
Li	0.502	0.004	0.058	S	0.191	0.518	0.284
Ge	0.001	0.501	0.684	S	0.518	0.191	0.716
Ge	0.501	0.001	0.316	S	0.486	0.811	0.717
Р	0.001	0.501	0.189	S	0.704	0.993	0.208
Р	0.501	0.001	0.811	s	0.297	0.011	0.209
Р	0.001	0.001	0.500				
Р	0.501	0.501	0.000				

Table S2. Detailed information about relaxed ground-state atomic configuration of pristine structure obtained from hybrid functional calculation.

Defect	overall (averaged)	ab-plane	c-channel
type	σ [mS/cm]	σ [mS/cm]	σ [mS/cm]
w/o	410	177	875
Pa	635	246	1414
Pc	595	250	1283
P_{Ge}^+	528	215	1153
V_{Li}^{-}	329	199	589
Li ⁺	618	243	1370

Table S3. Lithium ionic conductivity (σ) at 500 K of structures with and without defects.



Figure S1. Three types of Ge/P1 configurations in unit cell of $Li_{10}GeP_2S_{12}$ structure. (a) Z configuration, (b) Pa configuration, (c) Pc configuration, respectively.



Figure S2. Local structures of bridge sites. For the case of Li4 sites, it has two corner-shared Ge/P1 tetrahedra. Then, the notations for Li4 sites can be designated by the ions that is corner-shared with it. On the other hand, the nomenclature for Li2 sites depends on the Ge/P1 arrangement. In Z and Pa configurations, the two edge-shared Ge/P1 sites are occupied by different ions and the Li2 sites can be notated by the ion that is pointed out such as Li2_Ge or Li2_P. In Pc configuration, however, the criterion for naming the Li2 sites is different. The two Ge/P1 sites edge-shared with Li2 site are identical in Pc configuration. So, the notation for Li2 sites is designated by the kinds of edge-sharing Ge/P1 sites.



Figure S3. Local structures of channel sites. Two Li1 sites are identical in Z and Pc configuration, whereas they are in different local environment in Pa configuration. On the other hand, two Li3 sites are symmetrically distinctive only in Z configuration. Note that this linkage between the local structure and the notation based on the coordinates of *c*-axis might be exchanged because there are other arrangements with Z configurations in the given unit cell of $Li_{10}GeP_2S_{12}$ structure.



Figure S4. Interactions between channels investigated by NEB calculations. (a) Calculated relative energy curves for each condition and a table for summarizing the activation energies. (b) Relative locations of considered channels. The dotted square indicates the size $1 \times 1 \times 1$ supercell. The colors in (b) indicate the corresponding conditions in (a). One additional Li ion was introduced to form the defected channel.

In this study, we used a $2 \times 2 \times 1$ supercell of Li₁₀GeP₂S₁₂ that is four times larger than that used in previous studies.^{3, 4} The use of smaller supercells is beneficial in terms of computational cost, but there are important problems that shouldn't be ignored in this study. As pointed out by Bhandari *et al.*,¹⁰ the $1 \times 1 \times 1$ supercell of Li₁₀GeP₂S₁₂ is not large enough to eliminate the artificial interactions between the periodic images. We also found the interactions between neighboring *c*-channels that cannot be resolved within the range of $1 \times 1 \times 1$ supercells. In particular, the activation barrier for cooperative migration¹¹ along *c*channels is gradually restored to its non-defected value (0.22 eV) as it moves away from the defected channel. Therefore, we chose a $2 \times 2 \times 1$ supercell, which is the largest possible supercell within computational resources, to better explain the diffusion phenomena in $Li_{10}GeP_2S_{12}$. Moreover, a larger supercell is required to describe the directly affected region and the rest by a point defect P_{Ge}^+ .

The activation energy was calculated by using the climbing image-nudged elastic band (CI-NEB)¹² method as implemented in VASP.¹ An energy cutoff of 400 eV and a $1 \times 1 \times 2$ *k*-point grid based on Monkhorst-Pack scheme¹³ was used to calculate a $2 \times 2 \times 1$ supercell structure of Li₁₀GeP₂S₁₂. The initial and final images were fully relaxed until the residual forces less than 0.02 eV/Å, whereas only internal atomic positions were relaxed for the intermediates images. The activation energy calculations were performed non-spin-polarized.



Figure S5. Chemical potential map including stable phases in Li–Ge–P–S chemical space. The gray square indicates the allowed region for Li₁₀GeP₂S₁₂ phase. Note that the data for Li phase, which is a vertical line at $\Delta \mu_{Li} = 0$, is not shown in the graph, and the data in Figure S5 is calculated by using the generalized gradient approximation (GGA) functional.¹⁴ Only the four phases effectively limiting the chemical potentials of Li₁₀GeP₂S₁₂ is recalculated with hybrid functional.



Figure S6. Defect formation energy profiles at chemical potential limit (a) A, (b) B, (c) C, and (d) D. Fermi energy indicates the energy of electron in reference to valence band maximum (VBM) and varies up to conduction band minimum (CBM), where the corresponding band gap was obtained as 3.8 eV. Hybrid functional with a denser *k*-point grid of $4 \times 4 \times 2$ was used to calculate the band gap. The neutral and charged defects are depicted with solid and dash-dot lines, respectively. The determined Fermi energy that satisfies the charged neutrality of the system is depicted in vertical dotted lines.



Figure S7. Site occupancy and hopping rate of the structures with configurational defects. Site occupancy of channel sites for structure (a) with Pa and (d) with Pc. Site occupancy of bridge sites for structure (b) with Pa and (e) with Pc. Hopping rate of bridge sites for structure (c) with Pa and (f) with Pc.



Figure S8. Site occupancy and hopping rate in the region near $((P_{Ge}^+))$ and away from $((P_{Ge}^+)^C)$ the point defect P_{Ge}^+ . Site occupancy of channel sites in the region (a) near P_{Ge}^+ and (d) away from P_{Ge}^+ . Site occupancy of bridge sites in the region (b) near P_{Ge}^+ and (e) away from P_{Ge}^+ . Hopping rate of bridge sites in the region (c) near P_{Ge}^+ and (f) away from P_{Ge}^+ .



Figure S9. Site occupancy and hopping rate of the structures with Li Frenkel defects. Site occupancy of channel sites for structure (a) with V_{Li}^- and (d) with Li_i^+ . Site occupancy of bridge sites for structure (b) with V_{Li}^- and (e) with Li_i^+ . Hopping rate of bridge sites for structure (c) with V_{Li}^- and (f) with Li_i^+ .



Figure S10. Distribution of Li4_P sites in the unit cell structure (a) in Pa configuration, (b) in Z configuration for comparison. Since the Li4_P sites that are the active hopping center for *ab*-plane diffusion are located in the same layer in Pa configuration, the lithium ions can be transported more effectively in Pa configuration than Z configuration.



Figure S11. Isosurfaces (red) of lithium ion probability density distribution $P = P_{\text{max}}/1024$ of the structure in Pc configuration at 500 K. All the Li2_P sites were contained in the PS₄ columns and other bridge sites are located away from the columns. It is shown that the lithium ions are pushed away by the PS₄ columns and agglomerated.

The probability density analysis was performed by using the pymatgen⁹ open-source library as in previous studies.^{15, 16} The probability density P is a measure of how long lithium ions stay in each grid point in a given simulation time period. The P_{max} indicates the maximum probability among all calculated grid points.



Figure S12. Illustration of (a) channel sites and (b) bridge sites classified as the region near to P_{Ge}^+ . For channel sites, 4 out of 16 channels are classified as (P_{Ge}^+) . For bridge sites, (P_{Ge}^+) consists of one Li2_Ge site, one Li2_P site, two Li4_Ge sites and two Li4_P sites. Note that there are four Li sites including two Li1 and two Li3 sites in one *c*-channel of Li₁₀GeP₂S₁₂ structure, and Li1_c3/4 and Li3_c2/4 sites in (P_{Ge}^+) were directly affected by the P_{Ge}^+ .

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