

Site-Specific Substitution Preferences in the Solid Solutions Li₁₂Si_{7-x}Ge_x, Li_{12-v}Na_vSi₇, Na₇LiSi_{8-z}Ge_z, and Li₃NaSi_{6-v}Ge_v

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Abstract. The mixed silicide-germanides $\text{Li}_{12}\text{Si}_{7-x}\text{Ge}_x$, $\text{Na}_7\text{LiSi}_{8-z}\text{Ge}_z$, and $\text{Li}_3\text{NaSi}_{6-\nu}\text{Ge}_\nu$ which could serve as potential precursors for $\text{Si}_{1-x}\text{Ge}_x$ materials were synthesized and characterized by X-ray diffraction methods. The full solid solution series $\text{Li}_{12}\text{Si}_{7-x}\text{Ge}_x$ $(0 \le x \le 7)$ is easily accessible from the elements and features preferential occupation of the more negatively charged crystallographic tetrel positions by Ge, which is the more electronegative element. In case of $\text{Na}_7\text{LiSi}_{8-z}\text{Ge}_z$ a broad solid solution range of $1.3 \le x \le 8$ is available but the ternary silicide Na_7LiSi_8 could not be obtained by the tested

Introduction

In the global struggle to switch from fossil fuels to renewable energy sources, power generation with photovoltaic technologies can play an important role.^[1] However, commercial implementation, which is primarily based on crystalline silicon has not yet become truly economical in comparison to power generation from coal, natural gas, and petroleum.^[2] A significant increase in solar cell efficiency achieved by a disruptive technology could significantly lower costs. However, due to the indirect band structure of crystalline silicon, solar energy absorption of solar cells based on pure silicon is limited. Therefore, many other materials such as $Cu_2ZnSnS_{4-r}Se_r^{[3]}$ and organic-inorganic perovskites^[4] are currently being investigated. Alternatively, the advantages of silicon (abundant, low price, non-hazardous) can be combined with higher efficiencies in new silicon-based materials such as Si_{1-x}Ge_x.^[5] In such materials, silicon and germanium form a solid solution, whose electronic properties are tunable by stoichiometry.^[6]

Alkali metal silicides and germanides have been established as precursors for novel Si and Ge materials and allotropes. Partial oxidation of Na_4Si_4 and K_4Si_4 with gaseous HCl or H₂O leads to Si-rich clathrate structures^[7] and thermal decomposition of Na_4Si_4 under vacuum even yields the guest-free clathrate $\Box_{24}Si_{136}$.^[8] The analogous Ge clathrate $\Box_{24}Ge_{136}$ can be prepared by oxidation of Na_4Ge_9 in ionic liquids.^[9] A varimethods of synthesis. The solubility of Ge in $\rm Li_3NaSi_{6-\nu}Ge_\nu$ is highly limited to a maximum of $\nu\approx 0.5$, and again the formally more negatively charged tetrel positions are preferred by Ge. Additionally, the two crystallographic Li positions in $\rm Li_{12}Si_7$ with unusually large displacement parameters can be partially substituted by Na in $\rm Li_{12-\nu}Na_{\nu}Si_7$ with $0\leq y\leq 0.6$. The statistical mixing of Li and Na in this solid solution contrasts the typical ordering of Li and Na in most ternary tetrelides.

ety of alkali metal tetrelides comprising tetrahedral [Si₄]⁴⁻ and $[Ge_4]^{4-}$ anions have been shown to be efficient precursors for nanocrystalline Si and Ge^[10] and hexagonal mesoporous Ge can be synthesized by comproportionation of K₄Ge₉ and GeCl₄ or by oxidation of ${}^{1}_{\infty}[\text{Ge}_{9}^{2-}]$ with ferrocenium hexafluorophosphate.^[11] In 1982, single crystals of allo-Ge were obtained in a topochemical reaction of Li7Ge12 crystals with benzophenone.^[12] A similar reaction of microcrystalline Li₇Ge₁₂ yielded slightly different *m-allo-Ge*, whose structure was established in 2010.^[13] It consists of the two-dimensional sheets present in Li_7Ge_{12} ($^2_{\infty}[Ge_{24}^{14-}]$), which are statistically connected. Li₃NaSi₆, also containing two-dimensional polyanions $\binom{2}{\infty}[Si_{6}^{4}]$ has been reported to be a precursor for "allo-Si", which has never been structurally characterized.^[14] However, we have recently found the formation of amorphous Si under the same reaction conditions.^[15] In addition, the formation of amorphous and crystalline germanium from K₄Ge₉ providing high surface areas in form of an inverse opal structure was reported lately.[16]

Alkali metal tetrelides, in which silicon and germanium form solid solutions, may serve as precursors, potentially giving easy access to $Si_{1-x}Ge_x$ materials. However, alkali metal silicide-germanides have been very scarcely investigated. Phases $A_4Si_{4-x}Ge_x$ (A = Na, K, Rb) and $Rb_7NaSi_{8-x}Ge_x$ were characterized crystallographically^[17–20] and cell parameters of the solid solutions $Li_{12}Si_{7-x}Ge_x$ and $Li_7Si_{3-x}Ge_x$ were reported.^[21] The mentioned solid solution systems have in common that both side phases, the pure silicide and the germanide, exist. Although the A-Si and A-Ge phase diagrams are very similar, there are some compounds, which are only known as either silicide or germanide, including Li_3NaSi_6 and Li_7Ge_{12} . Such phases could allow partial substitution of one tetrel element by the other, or any mixing could be impossible.

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For solid solutions in general, the "coloring problem" becomes an issue:^[22] In structures, in which similar elements (Si/Ge or Li/Na) can occupy the same crystallographic positions, the distribution of those elements may or may not be statistical. Various factors such as coordination environment or local charges can influence site preferences.^[22,23] For the mentioned alkali metal silicide-germanides both tetrel atoms statistically mix, sometimes showing specific site preferences. The alkali metals Li and Na however, typically form ordered structures as in the ternary phases Li₃NaSi₆, Li₁₈Na₂Ge₁₇, and Li₃NaGe₂.^[24–26]

Herein we report the synthesis and characterization of solid solutions $Li_{12}Si_{7-x}Ge_x$, $Li_{12-y}Na_ySi_7$, $Na_7LiSi_{8-z}Ge_z$, and $Li_3NaSi_{6-v}Ge_v$ as potential precursors for $Si_{1-x}Ge_x$ materials. They all show site preferences of the statistically mixed atoms.

Results and Discussion

$Li_{12}Si_{7-x}Ge_x$

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Since the binary lithium tetrelides $Li_{12}Si_7$ and $Li_{12}Ge_7$ crystallize isostructurally, it is not surprising that the solid solution $Li_{12}Si_{7-x}Ge_x$ exists. *Nesper* has briefly mentioned it before and also noted "certain site preferences for the different metametal components" in $Li_{12}Si_{7-x}Ge_x$, $[^{21}]$ but no detailed investigation has been published since. We therefore synthesized a series $Li_{12}Si_{7-x}Ge_x$ in the range of $0 \le x \le 7$ by high temperature syntheses from stoichiometric mixtures of the pure elements and characterized them crystallographically.

Analyses of the Si/Ge ratio in the solid solution products with starting mixtures x = 2, 3.5, 5 were performed with singlecrystal X-ray diffraction and energy-dispersive X-ray spectroscopy. In all cases the actual substitution amount x was smaller than expected from the initial stoichiometry (Table S2, Supporting Information). In addition, these products contained increasing amounts of impurities such as $\text{Li}_7\text{Ge}_3^{[27]}$ and elemental Si with increasing Ge contents (Figure 1), indicating that the formation of $\text{Li}_{12}\text{Si}_{7-x}\text{Ge}_x$ becomes less favored. Yet, Si and Ge seem to be fully miscible in $\text{Li}_{12}\text{Si}_{7-x}\text{Ge}_x$.



Figure 1. Experimental powder diffraction patterns of $Li_{12}Si_{7-x}Ge_x$ (starting x = 0, 2, 3.5, 5, 7). Small impurities are marked with * (Si) and † (Li_7Ge_3).

As expected, all phases $Li_{12}Si_{7-x}Ge_x$ crystallize isostructurally in space group $Pnma^{[28,29]}$ and show a proportional increase of cell parameters with increasing Ge content x = 0, 2, 3.5, 5, and 7 according to Vegard's law (Figure 2).^[30]



Figure 2. Vegard plot^[30] illustrating an approximately linear increase of the unit cell volume of $\text{Li}_{12}\text{Si}_{7-x}\text{Ge}_x$ with increasing *x* at 300 and 100 K. The volumes were taken from powder diffraction (300 K) and single crystal (100 K) measurements (Tables S1 and S2). *x* was determined by EDX (300 K, Figures S1–S3) and the single crystal measurements (100 K). Vertical error bars are within the symbols.

The anionic substructure of the $\text{Li}_{12}\text{Si}_{7-x}\text{Ge}_x$ phases contains five-membered rings and Y-shaped stars in a 2:1 ratio (Figure 3). For the following analysis we will employ the most recent model of the anionic clusters as aromatic, cyclopentadienide-like $[T_5]^{6-}$ and carbonate-like $[T_4]^{8-}$ (T = Si, Ge).^[31]



Figure 3. (a) Unit cell (thermal ellipsoids at 90% probability at 100 K) and b) polyanionic tetrel clusters $[T_5]^{6-}$ and $[T_4]^{8-}$ of $\text{Li}_{12}\text{Si}_{7-x}\text{Ge}_x$ [x = 3.08(2)] showing preferential substitution on the mixed Si/Ge positions *T*.

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Table 1. Partial occupations of the mixed Si/Ge positions T in $\text{Li}_{12}\text{Si}_{7-x}\text{Ge}_x$ according to single-crystal X-ray diffraction in relation to their respective formal^[31] and Bader charges.^[34]

a) Assuming an electron distribution^[31] of $[T_5]^{6-}$ and $[T_4]^{8-}$. b) As calculated by *Chevrier* et al.^[34]

In this interpretation $\text{Li}_{12}T_7$ cannot be treated as typical Zintl phases due to two additional electrons per unit cell: $(\text{Li}^+)_{12}[T_5]^{6-}([T_4]^{8-})_{0.5}(e^-)_2$. This is in good agreement with the one-dimensional metallicity that has been observed for $\text{Li}_{12}\text{Si}_7$.^[32]

Interestingly, the Si/Ge occupancy ratios on the different tetrel sites in Li₁₂Si_{7-x}Ge_x vary tremendously (Table 1). Atoms *T*2 to *T*4, which form the vertices of the Y-shaped star (Figure 3b; formal charge –2.67), have the highest Ge contents, and atoms *T*5 to *T*9, forming the five-membered ring (formal charge –1.2), are occupied by medium amounts of Ge. In contrast, the central atom of $[T_4]^{8-}$, *T*1 (formal charge 0), contains no significant or very small amounts of Ge in the mixed silicide-germanides. These variations in Ge content correlate strongly with formal charges of the different tetrel sites: the greater the negative charge of a tetrel site, the more Ge, which is more electronegative, prefers the respective sites.^[33] The formal charges derived from our description of the anionic clusters agree qualitatively with Bader charges that have been calculated for Li₁₂Si₇ by *Chevrier* et al.^[34]

$Li_{12-v}Na_vSi_7$

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For all members of the $Li_{12}Si_{7-x}Ge_x$ series we noticed particularly large atomic displacement parameters for Li1 and Li9 (Table S3, Supporting Information).^[35] This could be explained by either partial occupation of these positions or by a larger cavity for Li atoms on these sites.

Partial occupation of Li positions in $Li_{12}T_7$ would lower the number of extra electrons per formula unit, potentially resulting in an electron-precise Zintl phase. Therefore, we first attempted free refinement of the respective site occupancy factors. However, both Li1 and Li9 are fully occupied in all cases. In order to test the hypothesis of a larger cavity for Li1 and Li9 we attempted to substitute these two positions by the larger alkali metal cations Na⁺, K⁺, Rb⁺, and Cs⁺ as well as Ag⁺, which is known to be able to replace Li⁺ in various compounds.^[36] Reactions including K, Rb, Cs, and Ag afforded only pure Li₁₂Si₇ next to known binary and ternary phases. In a reaction aimed at "Li_{10.5}Na_{1.5}Si₇", however, we were able to obtain a solid solution Li_{12-y}Na_ySi₇. This is again clearly indicated in powder diffraction patterns by a shift of all reflections toward smaller angles 2θ and significantly larger cell parameters obtained from indexing (Figure 4).



Figure 4. Powder diffraction patterns of $Li_{12}Si_7$ (grey) and " $Li_{10.5}Na_{1.5}Si_7$ " (black) showing a shift in diffraction angles. Both patterns were referenced with an external Si standard. Cell parameters were determined by indexing the patterns using TREOR^[37] as implemented in WinXPOW.^[38]

Additionally, suitable single crystals were selected from $Li_{12-y}Na_ySi_7$ samples with y = 0 and y = 1.5, which were characterized by X-ray diffraction. The "Li10.5Na1.5Si7" crystal yields a crystallographic composition of Li_{11.56(1)}Na_{0.44}Si₇, whereas Rietveld refinement of the corresponding powder diffraction pattern results in a bulk stoichiometry of Li_{11,39(3)}Na_{0.61}Si₇ (Figure S6, Table S7, Supporting Information). EDX measurements were performed on a single crystal of "Li_{10.5}Na_{1.5}Si₇", further proving that Na is incorporated into the structure (Figure S5). The Na:Si ratio obtained by EDX translates to a sum formula of $Li_{12-v}Na_vSi_7$ with y =0.48(1). The significantly lower Na content than in the starting mixture obtained from three independent methods suggests that Li substitution by Na is very limited. In addition, the powder diffraction pattern (Figure S4) also shows traces of the Nacontaining side phase Na4Si4. We therefore conclude a maximum Na content in $\text{Li}_{12-v}\text{Na}_v\text{Si}_7$ of approximately y < 0.6.

To test for possible substitutions of Li by Na, the site occupancy factors of all Li positions were freely refined in structure determinations from single crystal diffraction and Rietveld refinement. However, only Li1 and Li9 contain significant amounts of Na (Table 2), proving larger cavities for the alkali metal cations there. The partial incorporation of Na on these sites leads to increased Si–A (A = Li/Na) distances with respect to binary Li₁₂Si₇ (Table S4).

Table 2. Partial occupations of Li positions in $\text{Li}_{12-y}\text{Na}_y\text{Si}_7$ with Na (mixed Li/Na positions are abbreviated as *A*) according to single-crystal X-ray diffraction (SCXRD) and Rietveld refinement (RV).

Atom	% Na SCXRD [y = 0.443(8)]	% Na RV [y = 0.61(3)]	Coordination number ^{a)} (Si + Li/A)
A1	15.2(7)	25(2)	3 + 5
Li2	0	0	5 + 5
Li3	0	0	5 + 5
Li4	0	0	5 + 5
Li5	0	0	5 + 5
Li6	0	0	5 + 5
Li7	0	0	5 + 5
Li8	0	0	10 + 5
A9	36.8(5)	48(2)	3 + 4
Li10	0	0	4 + 6
Li11	0	0	5 + 6
Li12	0	0	4 + 6
Li13	0	0	4 + 4

a) All neighboring atoms with interatomic distances of up to 3.1 Å are considered.

A closer look at the coordination numbers of all Li positions shows why exactly two Li positions are partially substituted by Na (Table 2). Since the structure does not allow clear distinction of the first and second coordination spheres, a maximum interatomic distance of 3.1 Å was arbitrarily chosen for comparison. Pure Li positions have four to ten Si and four to six Li neighbors. In contrast, the mixed positions A1 and A9 are coordinated by only three Si atoms as well as five and four Li atoms, respectively. The resulting coordination spheres are displayed in Figure 5. Clearly, the A1 and A9 atoms are more agile and their thermal ellipsoids are elongated along the direction providing the most space. However, the $Li_{12}Si_7$ structure can apparently not compensate a full occupation of these positions by Na only.

$Na_7 LiSi_{8-z}Ge_z$

During our investigations in the Li-Na-Ge system,^[25,26] the new compound Na₇LiGe₈ was frequently observed as a side phase. The Zintl phase is readily available from a stoichiometric melt of the elements. Rietveld refinement (Table S8, Supporting Information) shows that it is isostructural to the known $A_7A'T_8$ phases, crystallizing in the cubic space group $Pa\bar{3}$.^[17,24,39–41] Na₇LiGe₈ comprises tetrahedral [Ge₄]^{4–} clusters, which are bridged to [Ge₄–Li–Ge₄]^{7–} dimers by η^3 -coordinating Li⁺ cations (Figure 6). Na⁺ cations on two different atomic positions (Na1 on 24*d*, Na2 on 4*a*) balance the charge of the Zintl phase.

For Rb₇NaSi_{8-x}Ge_x, another representative of this structure type, both ternary phases Rb₇NaSi₈ and Rb₇NaGe₈ as well as solid solution phases with x = 1-3 have been characterized previously,^[20,40] and the solid solution was shown to be soluble in liquid ammonia.^[20] In the context of a search for suitable precursors for new Si_{1-x}Ge_x materials, we therefore first attempted to prepare the analogous silicide, Na₇LiSi₈. However,



Figure 5. Coordination spheres of (a) A1 [15.2(7)% Na] and (b) A9 [36.8(5)% Na] in Li_{12-x}Na_xSi₇ [x = 0.443(9); thermal ellipsoids at 90% probability at 123 K]. All neighboring atoms with interatomic distances of up to 3.1 Å are included (Table S4).

it is not available with this synthesis route or from the binary starting materials Na_4Si_4 and $LiSi.^{[42]}$ Nevertheless, solid solution phases $Na_7LiSi_{8-z}Ge_z$ with low Ge contents of as little as z = 1.3(1) were obtained from stoichiometric melts of the elements. The grey powders obtained were characterized by Rietveld analyses (Tables S7 and S9; Figures S7–S11, Supporting Information), and in all samples the side phase $Na_4Si_{4-w}Ge_w$ is also present.

In accordance with Vegard's rule,^[30] the cell volume of the cubic structure decreases linearly with increasing Si content (Figure 7). The site occupancy factors obtained from Rietveld refinement (Table 3) show that the Ge1 position, which is not coordinated by η^3 -capping Li1 (cf. Figure 6b), is preferentially substituted by Si. Yet, partial substitution of Ge2 also occurs.

In order to rationalize the non-existence of Na_7LiSi_8 we analyzed the interatomic distances in $Na_7LiSi_{8-z}Ge_z$ in comparison with those reported for the closely related compound KNa_6LiSi_8 ,^[24] in which Na2 is replaced by K (Figure S12, Supporting Information). Most interatomic distances change inconspicuously and only the large increase of the *T*2–Na1 dis-



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Figure 6. (a) Projection of the unit cell of Na₇LiSi_{8-z}Ge_z (here: z = 8); (b) dimeric $[T_4$ -Li- T_4]⁷⁻ unit. Na atoms are shown in black, Li atoms in white, and mixed Si/Ge positions *T* in blue.



Figure 7. Vegard plot^[30] illustrating the linear reduction of the cubic cell volume in solid solution phases $Na_7LiSi_{8-z}Ge_z$. Vertical error bars are within the symbols, * data for z = 0 from KNa_6LiSi_{8} ,^[24] in which Na2 is replaced by K.

Table 3. Partial occupations of the mixed Si/Ge positions T in Na₇LiSi_{8-z}Ge_z according to Rietveld refinements.

Atom	% Ge in Na $z = 1.3(1)$	$z_7 \text{LiSi}_{8-z} \text{Ge}_z$ z = 2.2(1)	z = 4.5(3)	z = 6.8(3)	<i>z</i> = 8
T1	6(2)	10(2)	30 (4)	68(4)	100
T2	19(1)	34(2)	65(4)	91(4)	100

tance from Na₇LiSi_{6.7(1)}Ge_{1.3} to KNa₆LiSi₈ is somewhat peculiar. Therefore, a reason for the non-existence of Na₇LiSi₈ could be that the resulting *T*2–Na1 contacts (three per *T*2 atom) would be too short in the silicide. In any case, the substitution of Na2 by K in KNa₆LiSi₈ stabilizes the structure compared to Na₇LiSi₈.

Li₃NaSi_{6-v}Ge_v

Syntheses of $Li_3NaSi_{6-\nu}Ge_{\nu}$ with varying ν were attempted using two different approaches (a) and (b), which were proven to be successful synthesis routes for Li_3NaSi_6 :^[15]

(a) $\text{Li}_{12}\text{Si}_{7-x}\text{Ge}_x + \text{Na}_4\text{Si}_{4-w}\text{Ge}_w + 13\text{Si} \rightarrow 4\text{Li}_3\text{Na}\text{Si}_{6-v}\text{Ge}_v$ (b) $3\text{LiH} + \text{NaH} + (6-v)\text{Si} + v\text{Ge} \rightarrow \text{Li}_3\text{Na}\text{Si}_{6-v}\text{Ge}_v + 2\text{H}_2$

Route (a) employs silicide-germanides $Li_{12}Si_{7-x}Ge_x$ $(0 \le x \le 7)$ and Na₄Si_{4-w}Ge_w $(0 \le w \le 4)$, which are both readily available with different Si/Ge ratios.[18,21] These reactants were characterized by X-ray diffraction (XRD), Rietveld refinements, energy-dispersive X-ray spectroscopy or singlecrystal X-ray diffraction. We chose this synthesis approach because Si/Ge mixing on an atomic level in the precursor compounds could facilitate the formation of a solid solution of Si and Ge in the diffusion-controlled solid state reaction. XRD powder patterns of route (a) syntheses show that "Li₃NaSi_{5.5}Ge_{0.5}" (reactants Li₁₂Si₇, Na₄Si₂Ge₂, α-Si) contains only minor impurities (Figure S14, Supporting Information). All reflections for "Li3NaSi5.5Ge0.5" are shifted towards smaller diffraction angles 2θ with respect to Li₃NaSi₆, indicating a successful incorporation of Ge into the anionic Si substructure (Figure 8). A comparison of cell parameters from indexing powder diffraction patterns confirms this.



Figure 8. Powder diffraction patterns of Li_3NaSi_6 (grey) and "Li₃NaSi_{5.5}Ge_{0.5}" (black) from synthesis (a) showing a slight shift in diffraction angles. Both patterns were referenced with an external Si standard. Cell parameters were determined by indexing the patterns using DICVOL04^[43] as implemented in WinXPOW.^[38]

All materials synthesized with route (a) are microcrystalline and do not yield single crystals suitable for X-ray diffraction studies. Instead, from route (b) employing the alkali metal hydrides LiH and NaH, needle-shaped single crystals were obtained, allowing the structure determination of $Li_3NaSi_{5.56(1)}Ge_{0.44(1)}$. However, products from this route contain larger amounts of side products.

Li₃NaSi_{6-v}Ge_v syntheses were attempted with varying overall Ge contents ($0 \le v \le 3$; cf. Table 6). Product analyses by



Route	% Si	% Ge	Sum formula	Method of analysis
(a)	92.5(2)	7.5(2)	$\begin{array}{c} Li_{3}NaSi_{5.55(1)}Ge_{0.45}\\ Li_{3}NaSi_{5.56(1)}Ge_{0.44}\\ Li_{3}NaSi_{5.53(3)}Ge_{0.47}\end{array}$	Rietveld refinement
(b)	92.7(2)	7.3(2)		single-crystal XRD
(b)	92.1(4)	7.9(4)		EDX

indexing of XRD powder patterns show that the greatest possible incorporation of Ge into the anionic substructure is reached for $v \approx 0.5$ in both synthesis routes. Greater overall Ge contents of reactants only lead to greater amounts of more Ge-rich side products such as $Li_{12}Si_{7-x}Ge_x$, $Na_7LiGe_{8-z}Si_z$ and Li₁₈Na₂Ge₁₇.^[25] Therefore, the purest samples of $Li_3NaSi_{6-\nu}Ge_{\nu}$ with a maximum ν were obtained with overall Ge contents of v = 0.5. The resulting products were analyzed for their Si/Ge ratios with Rietveld refinement [route (a) product, Figure S16, Table S13, Supporting Information], singlecrystal X-ray diffraction [route (b) product, Tables S10-S12, Supporting Information], and EDX of a single crystal [route (b) product, Figure S13, Supporting Information]. The results for all methods are summarized in Table 4 and agree well, indicating a maximum Ge content of $0.4 \le v \le 0.5$ or 6.7 to 8.3 % in the anionic substructure of Li₃NaSi_{6-v}Ge_v.

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Li₃NaSi_{5.56(1)}Ge_{0.44} crystallizes isostructurally with Li₃NaSi₆^[14] in space group *Pnma* with a = 17.949(2) Å, b = 3.8085(3) Å, c = 10.2947(8) Å and Z = 8 (Table S11). It contains two-dimensional sheets of $c_{\infty}^2[T_6]^{4-}$ (T = Si, Ge) which are separated by Li and Na cations (Figure 9a). The tetrel sheets are constructed from four-valent *T*1, *T*5, and *T*6, three-valent *T*3 and *T*4, as well as two-valent *T*2, resulting in the alternative



Figure 9. (a) Projection of the unit cell of Li₃NaSi_{5.56(1)}Ge_{0.44} onto the *ac* plane (thermal ellipsoids at 90% probability at 100 K), mixed Si/Ge positions are abbreviated as *T*; (b) subunit of the $\frac{2}{\infty}[T_6]^{4-}$ polyanion showing preferential substitution of the *T*2, *T*3, and *T*4 positions by Ge.

formulation ${}^2_{\infty}[(4b-T^0)_3(3b-T^-)_2(2b-T^{2-})]$ for the polyanion (Figure 9b).

As in Li₁₂Si_{7-x}Ge_x, the Si/Ge occupancy ratios on the different tetrel sites in Li₃NaSi_{5.56(1)}Ge_{0.44(1)} vary tremendously (Table 5). The formally neutral, four-valent sites 4b- T^0 contain no significant amount of Ge, whereas 3b- T^- sites have Ge contents of 6.8(6) and 8.9(5)%, and 2b- T^{2-} shows a Ge occupancy of 24.3(7)% in the single crystal measurements. Rietveld refinement gives similar results. Again, these variations in Ge content correlate with formal charges of the different tetrel sites, and the greater the negative charge of a tetrel site, the more Ge, which is more electronegative, prefers the respective sites.^[33]

Table 5. Partial occupations of the mixed Si/Ge positions T in Li₃NaSi_{6-v}Ge_v according to single-crystal X-ray diffraction (SCXRD) and Rietveld refinement (RV) and their respective formal charges.

Position	% Ge SCXRD [v = 0.44(1)]	% Ge RV [$v = 0.45(2)$]	Formal charge
<i>T</i> 1	1.6(5)	0	0
T2	24.3(7)	28.3(3)	-2
T3	8.9(5)	9.1(3)	-1
<i>T</i> 4	6.8(6)	7.4(4)	-1
T5	1.2(5)	0	0
<i>T</i> 6	1.3(5)	0	0

Conclusions

We have shown that both constituents of the Zintl-like phase Li₁₂Si₇ can be substituted by the related elements Na and Ge, respectively. Since Li12Si7 and Li12Ge7 exist isostructurally, the full solid solution series $Li_{12}Si_{7-x}Ge_x$ is accessible. The distribution of Si and Ge in Li₁₂Si_{7-x}Ge_x onto the various positions in cyclopentadienide-like $[T_5]^{6-}$ and carbonate-like $[T_4]^{8-}$ clusters varies greatly. These preferences can be explained by the respective electronegativities, with more electronegative Ge atoms preferring the more negatively charged positions. This statistical mixing behavior is typical for the two neighboring tetrel elements. The alkali metals Li and Na typically form ordered structures with clearly separated Li and Na positions. Remarkably, a solid solution Li_{12-v}Na_vSi₇ with a maximum Na content of y < 0.6 was obtained, explaining the large isotropic displacement parameters for the two partially substitutable Li positions in all $Li_{12}Si_{7-x}Ge_x$ phases.

In addition, Na₇LiGe₈ and its solid solution Na₇LiSi_{8-z}Ge_z are readily available from stoichiometric melts of the constituting elements. Although we observe a large solution range $(1.3 \le z \le 8)$, ternary Na₇LiSi₈ cannot be obtained under these conditions. When attempting to prepare Li₃NaSi_{6-v}Ge_v we discovered that the synthesis of this solid solution is limited to a

maximum Ge content of $v \approx 0.5$. The distribution of Si and Ge atoms onto the different crystallographic positions in the twodimensional polyanions can also be explained by the more electronegative Ge preferring the formally more negatively charged atomic positions.

Overall, we have shown that it is possible to synthesize various mixed alkali metal silicide-germanides that may serve as precursors for novel $Si_{1-x}Ge_x$ materials. However, the miscibility of Si and Ge strongly differs between the different compounds. Thus, there remains a lot to be learned about the mixing behavior of similar elements in Zintl and Zintl-like phases. Further investigations on such systems could give more insight on the existence and extent of substitution in different solid solutions.

Experimental Section

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General Remarks: All steps of synthesis and sample preparation were carried out in an argon-filled glove box (MBraun, H₂O level <0.6 ppm, O₂ level <1.2 ppm). >99% Li rods (Rockwood-Lithium) and >99% Na rods (Chempur) were freed from oxidic layers before use, whereas 99.9% Si powder (Wacker), 99.999% Ge pieces (Chempur), 98% LiH powder (Alfa Aesar) and 95% NaH powder (Sigma Aldrich) were utilized without further purification.

Synthesis of LiSi: LiSi was synthesized by mechanical alloying.^[44] A stoichiometric mixture of the pure elements (total mass 2.0 g) and three WC grinding balls (diameter 15 mm) were placed inside a 50 mL WC milling jar which was then sealed airtight. Using a planetary ball mill (Retsch, PM 100) the jar was rotated for 12 h at 300 rpm with 2 min breaks and inversion of the rotation direction after each 30 min interval.

Synthesis of Li₁₂Si_{7-x}Ge_x: Compounds Li₁₂Si_{7-x}Ge_x (x = 0, 2, 3.5, 5, 7) were synthesized from the pure elements in Ta ampules. Sealed ampules containing stoichiometric reaction mixtures with a total mass of 0.5 g, respectively, were placed inside a silica reaction container, which was evacuated and heated to 750 °C for 1 h. The resulting melt was cooled down at a rate of 0.5 K·min⁻¹ to 400 °C, at which temperature annealing of the product was allowed for 6 h.

Synthesis of Li_{12-y}Na_ySi₇: Compounds Li_{12-y}Na_ySi₇ (y = 0, 1.5) were synthesized from of LiSi, Li (and Na) in Ta ampules. Sealed ampules containing a stoichiometric reaction mixture with a total mass of 0.4 g, respectively, were placed inside a silica reaction container which was evacuated and heated to 750 °C for 1 h. The resulting melt was cooled down at a rate of 0.5 K·min⁻¹ to 400 °C, at which temperature annealing of the product was allowed for 6 h.

Synthesis of Na₇LiSi_{8-z}Ge_z: Na₇LiGe_{8-z}Si_z was synthesized from stoichiometric amounts (z = 1, 2, 4, 6, 8) of the elements with a total mass of 1 g in tantalum ampules which were treated as described above. The reaction mixture was heated to 750 °C at 5 K min⁻¹ and after 1 h of dwelling cooled to 300 °C at 0.5 K·min⁻¹. Subsequent dwelling for 3 h afforded the desired products.

Synthesis of Na₄Si_{4-w}Ge_w: Compounds Na₄Si_{4-w}Ge_w (w = 0, 2, 3, 4) were synthesized in 1 g batches from the pure elements in Ta ampules. Sealed ampules containing stoichiometric reaction mixtures were placed inside a silica reaction container which was then evacuated and preheated to 500 °C for 1 h. The reaction mixture was brought to a reaction at 600 °C for 30 h.

Synthesis of Li₃NaSi_{6-v}Ge_v: Synthesis attempts of compounds Li₃NaSi_{6-v}Ge_v ($0 \le v \le 3$) were performed in 0.5 g batches using two different synthesis routes (Table 6). To obtain single phase product, Li₃NaSi_{6-v}Ge_v was synthesized using stoichiometric amounts of Li₁₂Si_{7-x}Ge_x (x = 0, 3.5), Na₄Si_{4-w}Ge_w (w = 0, 2, 3, 4) and α -Si, which were mixed thoroughly by grinding in an agate mortar. The reaction mixtures were pressed to pellets and sealed in Ta ampules. For single crystals of Li₃NaSi_{6-v}Ge_v, stoichiometric amounts of LiH, NaH, α -Si, and α -Ge were mixed thoroughly in an agate mortar and sealed in Ta ampules. All ampules were placed inside silica reaction containers which were evacuated and heated to 550 °C for 24–72 h. The reaction mixtures were cooled down very slowly at a rate of 0.075 K·min⁻¹.

Structure Determination: Crystals of, Li₁₂Si_{7-x}Ge_x, Li_{12-v}Na_vSi₇, and Li₃NaSi_{6-v}Ge_v were selected in an argon-filled glove box and sealed in 0.3 mm glass capillaries. For the best specimens intensity data were collected at 100 K with a Bruker AXS X-ray diffractometer equipped with a CCD detector (APEX II, ĸ-CCD), a MONTEL optic monochromator. A fine-focused sealed tube $(Li_{12}Si_{7-x}Ge_x \text{ and } Li_{12-y}Na_ySi_7)$ and a rotating anode FR591 (Li₃NaSi_{6-v}Ge_v) with Mo- K_{α} radiation (λ = 0.71073 Å), respectively, were used as X-ray sources. Data collection was controlled with the Bruker APEX Software package.[45] Integration, data reduction and absorption correction were performed with the SAINT^[46] and SADABS^[47] packages. The structures were solved with direct methods (SHELXS-2014/7) and refined with full-matrix leastsquares on F^2 (SHELXL-2014/7).^[48] For the refinement of mixed occupancies, the respective sites were split. Atom coordinates and atomic displacement parameters were constrained to be identical for both atom types. Free refinement of site occupation factors resulted in similar results as after constraining to a total occupancy of one.

Further details of the crystal structures investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request for deposited data.html) on quoting the depository numbers CSD-430491

Table 6. Product mixtures from various synthesis attempts of $Li_3NaSi_{6-\nu}Ge_{\nu}$. Main products are marked in bold.

Reactants	x	Products
Li ₁₂ Si ₇ , Na ₄ Si ₄ , Si	0	Li_3NaSi_{6} , $Li_{12}Si_{7-x}Ge_x$, Si
LiH, NaH, Si	0	Li ₃ NaSi ₆
Li ₁₂ Si ₇ , Na ₄ Si ₂ Ge ₂ , Si	0.5	$Li_3NaSi_{6-\nu}Ge_{\nu}$, Si
LiH, NaH, Si, Ge	0.5	$Li_3NaSi_{6-\nu}Ge_{\nu}$, $Li_{12}Si_{7-x}Ge_x$, Si
Li ₁₂ Si ₇ , Na ₄ SiGe ₃ , Si	0.75	$Li_3NaSi_{6-\nu}Ge_{\nu}$, $Li_{12}Si_{7-\nu}Ge_{\nu}$, Si, Na ₇ LiGe ₈₋₂ Si ₂
Li ₁₂ Si _{3.5} Ge _{3.5} , Na ₄ Si ₄ , Si	0.875	$Li_3NaSi_{6-\nu}Ge_{\nu}, Li_{12}Si_{7-x}Ge_x$, Si, Na ₇ LiGe _{8-z} Si _z
Li ₁₂ Si ₇ , Na ₄ Ge ₄ , Si	1.0	$Li_3NaSi_{6-\nu}Ge_{\nu}$, $Li_{12}Si_{7-x}Ge_x$, Si, Na ₇ LiGe _{8-z} Si _z
Li ₁₂ Si _{3.5} Ge _{3.5} , Na ₄ Si ₂ Ge ₂ , Si	1.375	$Li_{12}Si_{7-x}Ge_x$, Si, Na ₇ LiGe _{8-z} Si _z
Li ₁₂ Si _{3.5} Ge _{3.5} , Na ₄ Si ₂ Ge ₂ , Si, Ge	3.0	$Li_{12}Si_{7-x}Ge_x$, Si, $Si_{1-w}Ge_w$, Na ₇ LiGe _{8-z} Si _z , $Li_{18}Na_2Ge_{17}$
LiH, NaH, Si, Ge	3.0	$Li_{12}Si_{7-x}Ge_x$, Si, Na ₇ LiGe _{8-z} Si _z , Li ₁₈ Na ₂ Ge ₁₇

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Powder X-ray Diffraction (PXRD): PXRD patterns of $\text{Li}_{12}\text{Si}_{7-x}\text{Ge}_x$ (x = 0, 2, 3.5, 5, 7), $\text{Li}_{12-y}\text{Na}_y\text{Si}_7$ (y = 1.5), $\text{Na}_7\text{LiSi}_{8-z}\text{Ge}_z$ (z = 1, 2, 4, 6, 8), and $\text{Li}_3\text{NaSi}_{6-\nu}\text{Ge}_v$ (v = 0, 0.5; from binary compounds and hydride routes) were recorded with a Stoe STADI P diffractometer equipped with a Ge(111) monochromator for Cu- K_α radiation ($\lambda = 1.54056$ Å) and a Dectris MYTHEN DCS 1 K solid state detector. Crystalline samples of these synthesis products were ground in an agate mortar and filled into 0.3 mm glass capillaries, which were then sealed. The samples were measured within a 2θ range of 5–89° (PSD steps: 0.075°; time/step: 45 s). For indexing, selected PXRD patterns were angle-corrected with external α -silicon^[49] standards.

Rietveld Refinement: Rietveld refinements were performed using Jana2006.^[50] 15th order Chebychev functions were used to fit the background and the zero point error was refined freely. Reflections were fitted with the Pseudo Voigt function and the Berar Baldinozzi model with four refined parameters for peak asymmetry. Crystal structures of $\text{Li}_{12}\text{Si}_{7}$,^[29] K₇LiSi₈,^[41] and Li_3NaSi_6 ,^[14] respectively, were used as initial structural models. All cell parameters and atom positions as well as site occupancies for mixed positions were refined. Displacement parameters were refined when possible. Detailed results of Rietveld refinements are given in the Supporting Information.

Energy-Dispersive X-ray Spectroscopy (EDX): EDX spectra of crystalline materials were obtained with a JSM 7500F scanning electron microscope (JEOL) and an Oxford X-Max EDX analyzer with internal Mn standard. Single crystals were mounted onto an Al stub using graphite tape. Ratios of Na, Si and Ge in the single crystals were determined from several EDX measurements (elements with an atomic number <4 cannot be detected by this method).

Supporting Information (see footnote on the first page of this article): Detailed single crystal and powder X-ray diffraction data, Rietveld refinement results and EDX data of the investigated solid solutions $Li_{12}Si_{7-x}Ge_x$, $Li_{12-v}Na_vSi_7$, $Na_7LiSi_{8-z}Ge_z$, and $Li_3NaSi_{6-v}Ge_v$.

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References

- [1] International Energy Agency, *World Energy Outlook*, OECD, Paris, **2014**.
- [2] S. Chu, A. Majumdar, Nature 2012, 488, 294–303.
- [3] S. Delbos, EPJ Photovolt. 2012, 3, 35004.
- [4] S. D. Stranks, P. K. Nayak, W. Zhang, T. Stergiopoulos, H. J. Snaith, Angew. Chem. 2015, 127, 3288–3297; Angew. Chem. Int. Ed. 2015, 54, 3240–3248.
- [5] a) C. Eisele, M. Berger, M. Nerding, H. P. Strunk, C. E. Nebel, M. Stutzmann, *Thin Solid Films* **2003**, 427, 176–180; b) R. Lechner, M. Buschbeck, M. Gjukic, M. Stutzmann, *Phys. Status Solidi C* **2004**, *1*, 1131–1143.
- [6] J. S. Kline, F. H. Pollack, M. Cardona, *Helv. Phys. Acta* 1968, 41, 968–977.

- [7] B. Böhme, A. M. Guloy, Z. Tang, W. Schnelle, U. Burkhardt, M. Baitinger, Y. Grin, J. Am. Chem. Soc. 2007, 129, 5348–5349.
- [8] A. Ammar, C. Cros, M. Pouchard, N. Jaussaud, J.-M. Bassat, G. Villeneuve, M. Duttine, M. Ménétrier, E. Reny, *Solid State Sci.* 2004, *6*, 393–400.
- [9] A. M. Guloy, R. Ramlau, Z. Tang, W. Schnelle, M. Baitinger, Y. Grin, *Nature* **2006**, *443*, 320–323.
- [10] a) R. A. Bley, S. M. Kauzlarich, J. Am. Chem. Soc. 1996, 118, 12461–12462; b) D. Neiner, H. W. Chiu, S. M. Kauzlarich, J. Am. Chem. Soc. 2006, 128, 11016–11017; c) B. R. Taylor, S. M. Kauzlarich, H. W. H. Lee, G. R. Delgado, Chem. Mater. 1998, 10, 22–24; d) B. M. Nolan, T. Henneberger, M. Waibel, T. F. Fässler, S. M. Kauzlarich, Inorg. Chem. 2015, 54, 396–401.
- [11] a) G. S. Armatas, M. G. Kanatzidis, *Science* 2006, *313*, 817–820;
 b) G. S. Armatas, M. G. Kanatzidis, *Adv. Mater.* 2008, *20*, 546–550;
 c) D. Sun, A. E. Riley, A. J. Cadby, E. K. Richman, S. D. Korlann, S. H. Tolbert, *Nature* 2006, *441*, 1126–1130.
- [12] A. Grüttner, R. Nesper, H. G. von Schnering, Angew. Chem. 1982, 94, 933; Angew. Chem. Int. Ed. Engl. 1982, 21, 912–913.
- [13] F. Kiefer, A. J. Karttunen, M. Döblinger, T. F. Fässler, *Chem. Mater.* 2011, 23, 4578–4586.
- [14] H. G. von Schnering, M. Schwarz, R. Nesper, J. Less-Common Met. 1988, 137, 297–310.
- [15] M. Zeilinger, L.-A. Jantke, L. M. Scherf, F. J. Kiefer, G. Neubüser, L. Kienle, A. J. Karttunen, S. Konar, U. Häussermann, T. F. Fässler, *Chem. Mater.* 2014, 26, 6603–6612.
- [16] M. M. Bentlohner, M. Waibel, P. Zeller, K. Sarkar, P. Müller-Buschbaum, D. Fattakhova-Rohlfing, T. F. Fässler, *Angew. Chem. Int. Ed.* 2016, 55, 2441–2445.
- [17] J. Llanos, Dissertation, Universität Stuttgart, Germany 1984.
- [18] H. Morito, K. Momma, H. Yamane, J. Alloys Compd. 2015, 623, 473–479.
- [19] M. Waibel, G. Raudaschl-Sieber, T. F. Fässler, *Chem. Eur. J.* 2011, 17, 13391–13394.
- [20] M. Waibel, O. Pecher, B. Mausolf, F. Haarmann, T. F. Fässler, *Eur. J. Inorg. Chem.* 2013, 2013, 5541–5546.
- [21] R. Nesper, Prog. Solid State Chem. 1990, 20, 1–45.
- [22] G. J. Miller, Eur. J. Inorg. Chem. 1998, 1998, 523-536.
- [23] M. Jehle, I. Dürr, S. Fink, B. Lang, M. Langenmaier, J. Steckhan, C. Röhr, J. Solid State Chem. 2015, 221, 351–363.
- [24] M. Schwarz, Dissertation, Universität Stuttgart, Germany 1987.
- [25] L. M. Scherf, M. Zeilinger, T. F. Fässler, *Inorg. Chem.* 2014, 53, 2096–2101.
- [26] L. M. Scherf, A. J. Karttunen, O. Pecher, P. C. M. M. Magusin, C. P. Grey, T. F. Fässler, *Angew. Chem.* **2016**, *128*, 1087–1091; *Angew. Chem. Int. Ed.* **2016**, *55*, 1075–1079.
- [27] a) A. Grüttner, R. Nesper, H. G. v. Schnering, Acta Crystallogr, Sect. A 1981, 37, C161; b) A. Grüttner, Dissertation, Universität Stuttgart 1982.
- [28] H. G. von Schnering, R. Nesper, J. Curda, K.-F. Tebbe, Angew. Chem. 1980, 92, 1070; Angew. Chem. Int. Ed. Engl. 1980, 19, 1033–1034.
- [29] R. Nesper, H. G. von Schnering, J. Curda, *Chem. Ber.* 1986, 119, 3576–3590.
- [30] L. Vegard, Z. Phys. 1921, 5, 17-26.
- [31] a) A. Kuhn, P. Sreeraj, R. Pöttgen, H.-D. Wiemhöfer, M. Wilkening, P. Heitjans, *Angew. Chem.* 2011, *123*, 12305–12308; *Angew. Chem. Int. Ed.* 2011, *50*, 12099–12102; b) R. Nesper, S. Wengert, F. Zürcher, A. Currao, *Chem. Eur. J.* 1999, *5*, 3382–3389.
- [32] S. Wengert, Dissertation, ETH Zürich , Switzerland 1997.
- [33] Electronegativities: 2.02 (Ge) and 1.74 (Si). A. L. Allred, E. G. Rochow, J. Inorg. Nucl. Chem. 1958, 5, 264–268.
- [34] V. L. Chevrier, J. W. Zwanziger, J. R. Dahn, J. Alloys Compd. 2010, 496, 25–36.
- [35] von Schnering et al. also mentioned this in Ref. [29].
- [36] a) H.-J. Deiseroth, S.-T. Kong, H. Eckert, J. Vannahme, C. Reiner, T. Zaiß, M. Schlosser, *Angew. Chem.* 2008, *120*, 767–770; *Angew. Chem. Int. Ed.* 2008, *47*, 755–758; b) A. Henze, T. F. Fässler, *Inorg. Chem.* 2016, *55*, 822–827.

- [37] P.-E. Werner, L. Eriksson, M. Westdahl, J. Appl. Crystallogr. 1985, 18, 367–370.
- [38] WinXPOW, STOE & Cie GmbH, Darmstadt, Germany, 2003.

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- [39] a) L. M. Scherf, O. Pecher, K. J. Griffith, F. Haarmann, C. P. Grey, T. F. Fässler, *Eur. J. Inorg. Chem.* 2016, published online, DOI:10.1002/ejic.201600735; b) O. Pecher, M. Esters, A. Görne, B. Mausolf, A. Ormeci, F. Haarmann, *Z. Anorg. Allg. Chem.* 2014, 640, 2169–2176.
- [40] a) T. Goebel, Y. Prots, A. Ormeci, O. Pecher, F. Haarmann, Z. Anorg. Allg. Chem. 2011, 637, 1982–1991; b) J. Llanos, R. Nesper, H. G. von Schnering, Angew. Chem. 1983, 95, 1026–1027; Angew. Chem. Int. Ed. Engl. 1983, 22, 998.
- [41] H. G. von Schnering, M. Schwarz, R. Nesper, Angew. Chem. 1986, 98, 558–559; Angew. Chem. Int. Ed. Engl. 1986, 25, 566– 567.

- [42] The isostructural phase K_7LiSi_8 can only be synthesized from binary precursors (Ref. [39a]). Stoichiometric mixtures of the elements yield a product mix of K_3NaSi_4 and K_4Si_4 .
- [43] A. Boultif, D. Louer, J. Appl. Crystallogr. 2004, 37, 724–731.
- [44] W. S. Tang, J.-N. Chotard, R. Janot, J. Electrochem. Soc. 2013, 160, A1232–A1240.
- [45] APEX Suite of Crystallographic Software, Bruker AXS Inc., Madison, WI, USA, 2008.
- [46] SAINT, Bruker AXS Inc., Madison, WI, USA, 2001.
- [47] SADABS, Bruker AXS Inc., Madison, WI, USA, 2001.
- [48] G. M. Sheldrick, Acta Crystallogr., Sect. A 2008, 64, 112-122.
- [49] C. R. Hubbard, H. E. Swanson, F. A. Mauer, J. Appl. Crystallogr. 1975, 8, 45–48.
- [50] V. Petříček, M. Dušek, L. Palatinus, Z. Kristallogr. Cryst. Mater. 2014, 229, 345.

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Site-Specific Substitution Preferences in the Solid Solutions $Li_{12}Si_{7-x}Ge_x$, $Li_{12-y}Na_ySi_7$, $Na_7LiSi_{8-z}Ge_z$, and $Li_3NaSi_{6-\nu}Ge_{\nu}$

