Site-Preference among Three Anions in the Quaternary BaAl$_4$-Type Structure: Experimental and Computational Investigations for BaLi$_{1.09(1)}$In$_{0.91}$Ge$_2$

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Zintl phases and polar intermetallics including lithium atoms can offer not only a good opportunity to investigate the correlation among crystal structure, chemical bonding, and physical properties given the unique role of lithium acting as a "*zwitter*" ion,[1-3] but be considered as electrode materials for Li-ion batteries and as thermoelectric materials.[4,5] Since a lithium atom can play a role as either a cation or an anion, various tetrelide phases containing lithium substitution or insertions have been synthesized, and their characteristics have been investigated using both experimental and theoretical approaches.[1-9]

During our recent research activities to investigate the influence of lithium substitution or intercalation for components in the polar intermetallic *AE*/*RE*-In-Ge (*AE* = alkaline-earth metals, *RE* = rare-earth metals) system, we have serendipitously synthesized a quaternary compound BaLi$_{1.09(1)}$In$_{0.91}$Ge$_2$ adopting the BaAl$_4$-type structure.[9,10] The given crystal structure type is one of the most prominent structure types observed among binary *MTr*$_4$ (*M* = alkali-earth metals, rare-earth metals; *Tr* = tetrels) compounds and has already been studied elsewheres.[11,12] Moreover, numerous ternary phases with different substitutions for anionic elements have also been successfully synthesized,[13-21] and the site-preference of anions within the 3-dimensional (3*D*) frameworks has been thoroughly studied in terms of geometric- as well as electronic-perspectives.[11,13,14,21] However, the researches for the quaternary BaAl$_4$-type phases containing an additional anion substitution in the polyanionic frameworks have been limited mostly for transition-metal[22-24] containing compounds due to the allowable range of electron counts between 12-14 to form the BaAl$_4$-type structure. In addition, the site-preference rules established based on numerous ternary compounds have not been applied to the cases of quaternary compounds including a lithium substitution.

In this report, therefore, we focus more on the site-preference of three anions forming the 3*D*-polyanionic frameworks. For this purpose, we start from the parental binary structure BaIn$_4$,[25] then two steps of anion substitutions by Ge and Li will be considered subsequently in terms of geometric- and electronic-factors. Theoretical studies using tight-binding muffin-tin (TB-LMTO) method were also performed. Crystal orbital Hamilton population (COHP) curves as well as density of states (DOS) were interrogated in depth to understand the observed site-preference of anions and chemical bonding.

Experimental

Each element in the stoichiometric ratio of 1:2:2:2 for Ba:Li:In:Ge was loaded in an one end-sealed Nb-tubing inside an argon-filled glove box. The other end of Nb-tubing was sealed by arc-welding under a partial argon atmosphere, then the tubing was subsequently sealed in a fused-silica jacket under vacuum to avoid any contact with oxygen during the reaction at the elevated temperature. The mixture of reactants was initially heated up to 950 °C by 200 °C/h, kept at the temperature for 5 h, then cooled down to 890 °C by 5 °C/h.

After then, the reactants were naturally cooled down to room temperature by turning off the furnace. Block-shaped products with metallic luster were obtained. The products were air- and moisture-stable for at least one month.

Table 1. Crystallographic data and structure refinement parameters for BaLi$_{1.09(1)}$In$_{0.91}$Ge$_2$

Crystal system	Tetragonal
Space group	*I4/mmm*
Unit cell dimensions (Å)	*a* = 4.642(2)
	b = 4.642(2)
	c = 11.012(7)
V (Å^3)	237.3(2)
Z	2
ρ (cald), mg m^{-3}	5.515
μ (Mo Kα), mm^{-1}	24.870
Crystal size (mm^3)	0.08 × 0.06 × 0.06
θ range for data collection (°)	3.70 to 29.12
Index ranges	-6 ≤ *h* ≤ 6, -6 ≤ *k* ≤ 6, -13 ≤ *l* ≤ 14
Reflections collected	1069
Independent reflections	121 [*R*(int) = 0.0681]
Data / restraints / parameters	121 / 0 / 10
Goodness-of-fit on *F*^{2}	1.215
Final *R*^{a} indices [*I* > 2σ$_I$]	R_1 = 0.0257, wR_2 = 0.0528
R^a indices (all data)	R_1 = 0.0302, wR_2 = 0.0551
Min., Max. *p*/e Å^{-3}	0.847 and −1.649

[a]$R_1 = \Sigma ||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o{}^2 - F_c{}^2]/\Sigma[w(F_o{}^2)^2]]^{1/2}$, where $w = 1/[\sigma^2 F_o{}^2 + (A - P)^2 + B - P]$, and $P = (F_o{}^2 + 2F_c{}^2)/3$; A and B – weight coefficients.

Single-crystal X-ray diffraction data was collected at room temperature using Bruker SMART APEX2 CCD-based diffractometer equipped with Mo Kα_1 radiation ($\lambda = 0.71073$ Å). The selected crystal was mounted on a glass fiber, and data collection was carried out using the Bruker's *APEX2* software.[26] The structure was solved by direct method and refined to full convergence by full matrix least-squares method on F^2 using *SHELXTL*.[27] During the initial stage of structure refinement, the apical-site (Wyckoff site 4e) was refined as a full occupation of Ge, whereas the basal-site (Wyckoff site 4d) was assigned by In with an electron deficiency of *ca.* 52%. Thus, we eventually allowed a mixed-occupation of Li with In at the 4d-site, and this lead to the final composition of BaLi$_{1.09(1)}$In$_{0.91}$Ge$_2$. In the last stage of refinement, program *STRUCTURE TIDY*[28] was exploited to standardize atomic positions. Important crystallographical data are displayed in Tables 1-3 and deposited with FIZ, Eggenstein-Leopoldshafen, Germany (Deposition No. CSD-426587).

Quantum theoretical calculations were conducted by TB-LMTO method[29] using the LMTO47 program.[30] The program package employs the atomic sphere approximation (ASA) method, in which space is filled with overlapping Wigner-Seitz (WS) atomic spheres.[31] The WS radii are as follows: Ba = 2.378 Å, Li = 1.655 Å, In = 1.655 Å, and Ge = 1.427 Å. The basis sets included 6s, 6p, 5d and 4f orbitals for Ba; 2s, 2p and 3d orbitals for Li; 5s, 5p, 5d and 4f orbitals for In; and 4s, 4p and 4d orbitals for Ge. The Ba 6p, Li 2p and 3d, In 5d and 4f, and Ge 4d orbitals were treated by the Löwdin down-folding technique.[31] The k-space integration was conducted by the tetrahedron method[32] using 262 irreducible k-points in the Brillouin zone.

Results and Discussion

BaLi$_{1.09(1)}$In$_{0.91}$Ge$_2$ crystallized in the BaAl$_4$-type (or the

Table 2. Atomic coordinates, occupancy and equivalent isotropic displacement parameters ($U_{eq}{}^a$) from single-crystal structure refinements for BaLi$_{1.09(1)}$In$_{0.91}$Ge$_2$

Atom	Site	Occupancy	x	y	z	$U_{eq}{}^a$ (Å^2)
Ba	2a	1	0	0	0	0.0100(4)
M^b	4d	0.548(4)/0.452	0	1/2	1/4	0.0111(6)
Ge	4e	1	0	0	0.3843(1)	0.0108(4)

$^a U_{eq}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.
^{b}Refined as a statistical mixture of Li and In.

**Table 3.** Selected interatomic distances (Å) and the iCOHP values for BaLi$_{1.09(1)}$In$_{0.91}$Ge$_2$

| Atomic pair	Distance	iCOHP (eV/cell)
Ba-M^a	3.601(2)	−0.459 (Ba-In)/−0.095 (Ba-Li)
Ba-Ge	3.521(2)	−0.702
In-Li	3.282(2)	−0.119
Ge-M^a	2.752(1)	−2.065 (Ge-In)/−0.455 (Ge-Li)
Ge-Ge	2.547(3)	−2.437

^{a}Refined as a statistical mixture of Li and In.

ternary ThCr$_2$Si$_2$-type) structure adopting the tetragonal space group *I*4/*mmm* with *Z* = 2 (Pearson code *tI*10).[9,10] Detail crystallographic information including lattice parameters, atomic coordinates and selected bond distances are displayed in Tables 1-3. Since the BaAl$_4$-structure type is one of the most prominent structure types observed in the binary *MTr*$_4$ and ternary phases *MT$_x$Tr$_{4-x}$/MT$_x$Pn$_{4-x}$* (*M* = alkali-earth metals or rare-earth metals; *T* = transition metals; *Tr* = triels; and *Pn* = pnictogens) series,[13-15,21] detail discussions of the given crystal structure can be found elsewhere.[11,13] Therefore, we will provide a simple structural description, then pay more attention to the site-preference among three anionic elements within the 3*D* frameworks in this report.

The overall crystal structure of BaLi$_{1.09(1)}$In$_{0.91}$Ge$_2$ is shown in Figure 1(a). There exists three crystallographically independent atomic sites including one cationic and two different anionic sites. In particular, the local coordination environments for two anionic sites are clearly distinctive: 1) the basal-site (Wyckoff site 4d) is coordinated to four identical apical-sites forming a distorted tetrahedron (Figure 1(b)), whereas 2) the apical-site (Wyckoff site 4e) is surrounded by one apical- and four basal-sites forming a distorted square-pyramid (Figure 1(c)). These anionic sites eventually form the 3*D* polyanionic frameworks, which can be considered as stacks of Federov polyhedra[33,34] along all directions in space (Figure 1(d)). Relatively larger Ba atoms are situated at the center of each Fedorov polyhedron having the total coordination number of 18.

Interestingly, in the given structure type, three anionic elements display a distinctive site-preference over two available sites within the anionic frameworks. As can be seen in Figure 1, Ge atoms show an exclusive occupation for the 4e-site, whereas the mixed-occupation of Li and In (*ca.* 55% *vs* 45%) was observed at the 4d-site. This type of site-preference among three anionic elements in the 3*D* frameworks can be described as if two steps of consecutive substitutions,
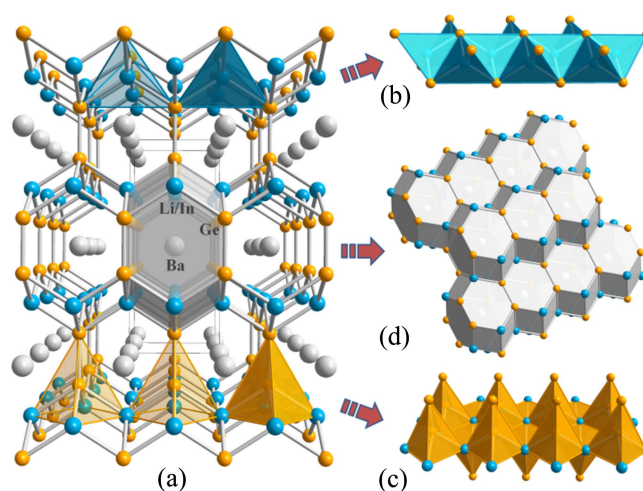
Figure 1. (a) Crystal structure of BaLi$_{1.09(1)}$In$_{0.91}$Ge$_2$ illustrated by a combination of ball-and-stick and polyhedral representations. (b) The local coordination environment around the Li/In mixed-site, (c) the Ge site, and (d) the Ba-site.
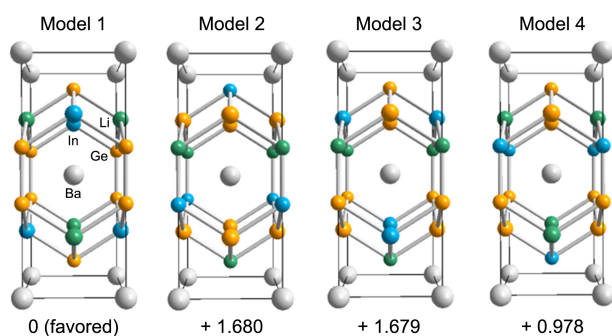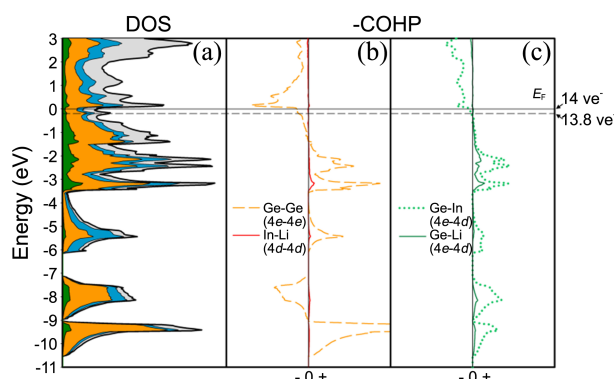
Figure 2. Four structure models of BaLiInGe₂. The relative total electronic energy of each model (eV/cell) compared to the Model 1 is also shown. See text for further detail.

Figure 3. DOS and COHP curves of Model **1**. (a) Total DOS - solid line; partial DOS of Ba, In, Ge, and Li – gray, blue, orange, and green area, respectively. E_F (solid line) is the energy reference at 0 eV, and the DOS value corresponding the refined composition is also marked with a dashed line. Four COHP curves representing various interatomic interactions are also shown in (b) and (c). The region with the "+" sign represents bonding interactions, whereas the region with the "–" sign represents antibonding interactions.

respectively, by Ge and Li occur for its parental binary phase BaIn₄.[25] Firstly, as Ge atoms having the larger electronegativity and the smaller size than In atoms (Pauling scale: Ge = 2.01 *vs* In = 1.63; and r_{Ge} = 1.23 Å *vs* r_{In} = 1.63 Å)[35,36] are introduced to the anionic frameworks in BaIn₄, the site occupation between Ge an In seems to follow the site-preference rules reported by Miller and Häussermann *et al*.: the more electronegative atom should prefer to occupy the 4*e*-site over the 4*d*-site.[11,13]

There have been numerous reported examples supporting this argument: EuMg$_x$Ga$_{4-x}$ (0 ≤ x ≤ 1.95),[11] AEMg$_{1.7(1)}$Ga$_{2.3}$ (AE = Sr, Ba),[13] BaAuIn₃,[18] AEMg$_x$In$_{4-x}$ (AE = Sr, 0.85 ≤ x ≤ 1.53; AE = Ba, 0 ≤ x ≤ 1.79)[14] and REZn$_x$Al$_{4-x}$ (RE = Yb, x = 1.65; RE = Nd, x = 2.3).[17] In addition, Corbett *et al*. also proved that in the case like SrZnIn₃, where only a small electronegativity difference existed between anionic elements, the geometric factor would play a major role to decide the preferred anionic sites.[14]

Based on these criteria, the site-occupation of Ge in the title compound is fully understandable. Secondly, if we apply the same criteria for the site-occupation of Li, it seems to be rational that Li atoms having the smallest electronegativity among three anions and the larger size than Ge but similar size to In (Pauling scale: Li = 0.98, r_{Li} = 1.52 Å)[35,36] should prefer to occupy the 4*d*-site resulting in a mixed-occupation with In. Therefore, we can conclude that the site-preference among three anions reasonably follows the site-preference rules with respect to the electronic- and geometric-factors. Further analysis for electronic structures and chemical bonding within the polyanionic frameworks will be discussed in the subsequent section.

A series of quantum theoretical calculations have been conducted 1) to understand the observed site-preference among anionic elements from the electronic perspective, and 2) to investigate an overall electronic structure of the title compound. Initially, four structure models with various anionic arrangements were designed and exploited for calculations - Model 1: refined crystal structure, and Model 2, 3, 4: hypothetical model structures (Figure 2). After then, total electronic energy of each model was compared in order to find out energetically the most favorable structure, and the model with the lowest energy was further analyzed to

interrogate its electronic structure based on DOS and COHP plots. TB-LMTO-ASA method[29-31] was the method of our calculation choice. The ideal composition of BaLiInGe₂ was adopted for the practical reason. In addition, to apply the given stoichiometric composition, a space group was lowered from *I*4/*mmm* (no. 139) to *Imm*2 (no. 44). Model 1 showed an atomic arrangement resembling that of the refined structure, in which the 4*e*-site was exclusively occupied by Ge, whereas the 4*d*-site was alternatively occupied by Li and In. On the other hand, Model 2 located Ge at the 4*d*-site exclusively, while the mixture of Li and In was situated at the 4*e*-site. Model 3 and 4 were designed based on the hypothesis what if Li was mixed with Ge either at the 4*e*-site or at the 4*d*-site, respectively.

After a series of calculations, the total electronic energy comparison proved that Model 1 based on the refined crystal structure was energetically the most favorable structure (Figure 2). Thus, the quantum theoretical approach provided a consistent result to the experimental observation.

Total and partial DOS plots shown in Figure 3(a) were obtained using Model 1. Throughout the whole range of energy, a strong orbital mixing of components was observed. In particular, the valence region implying interatomic interactions among four elements can be divided into three sections. The region between −10.5 and −7 eV is mostly contributed by In 5*s* and Ge 4*s* orbitals with a small amounts of Li 2*s* orbital participation. In particular, the lower peak corresponds to the σ bonding, whereas the upper peak is related to σ* anti-bonding interactions among three components. The next region between −6 and −3.5 eV contains the major contributions from Ge 4*p$_z$* and In 5*p$_z$* orbitals. The last region from −3.5 eV up to the Fermi level (E_F) also includes the largest contributions from Ge and In, but those are descended from 4*p$_x$* and 4*p$_y$*, and 5*p$_x$* and 5*p$_y$* orbitals, respectively, as well as some contributions from Li orbital. E_F for the ideal composition BaLiInGe₂ (corresponding to 14 ve⁻) and for

the refined composition $BaLi_{1.09(1)}In_{0.91}Ge_2$ (corresponding to 13.82 ve⁻) were found near the local DOS minimum (also known as pseudogap) indicating that the title compound having a given chemical composition is energetically stable with the $BaAl_4$-type structure. Interestingly, the significantly sharp DOS peaks are observed just above E_F, and these are closely related to the anti-bonding characters found in COHP curves.

Total four COHP curves representing interatomic interactions within the polyanionic frameworks are shown in Figure 3(b) and (c). Two COHP curves representing strong interactions around the 4*e*-site (Ge-Ge (4*e*-4*e*) and Ge-In (4*e*-4*d*)) show relatively larger integrated COHP (iCOHP) values with shorter bond distances (Table 3). Some antibonding characters of Ge-Ge COHP curve near E_F were compensated by Ba-Ge and Ba-In/Li bonding characters (Supporting Information Figure S1). Two other COHP curves representing In-Li (4*d*-4*d*) and Ge-Li (4*e*-4*d*) interactions display relatively weaker bonding characters with smaller iCOHP values (Table 3). However, both curves are well optimized at E_F indicating energetically stable interactions. Thus, total DOS and various COHP curves clearly indicate that the title compound is energetically stable with a given chemical composition $BaLi_{1.09(1)}In_{0.91}Ge_2$ and the $BaAl_4$-type crystal structure.

Supporting Information. Crystallographic data can be obtained free of charge from FIZ, D-76344, Eggenstein-Leopoldshafen, Germany, E-mail: crysdata@fiz-karlsruhe.de. Three COHP curves for Ba-Ge, Ba-In and Ba-Li interactions are provided.

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