



Experimental and theoretical investigations for site preference and anisotropic size change of $RE_{11}Ge_4In_{6-x}M_x$ ($RE = La, Ce$; $M = Li, Ge$; $x = 1, 1.96$)



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ABSTRACT

Two polar intermetallic compounds in the $RE_{11}Ge_4In_{6-x}M_x$ ($RE = La, Ce$; $M = Li, Ge$; $x = 1, 1.96$) series have been synthesized by conventional high-temperature reactions and characterized by both single-crystal and powder X-ray diffractions. Both compounds crystallized in the tetragonal crystal system (space group $I4/mmm$, $Z = 4$, Pearson symbol $tI84$) with nine crystallographically independent atomic positions in the asymmetric unit and adopted the $Sm_{11}Ge_4In_6$ -type structure, which can be considered as an ordered version of the $Ho_{11}Ge_{10}$ -type. The lattice parameters are $a = 11.8370(4)$ Å and $c = 17.2308(7)$ Å for $La_{11}Ge_4In_{5.00(1)}Li_{1.00}$; $a = 11.8892(4)$ Å, $c = 16.5736(7)$ Å for $Ce_{11}Ge_{5.96(3)}In_{4.04}$. The overall crystal structures of two isotopic compounds can be described as a combination of the cage-shaped 3-dimensional (3-D) anionic framework and three different types of cationic polyhedra filling the inside of the 3-D frameworks. Anionic elements consisting of the frameworks indicate the particular site preference, which can be understood by QVAL values. Theoretical investigations using tight-binding linear muffin-tin orbital (LMTO) method provide rationales for the anisotropic size change of the unit cell of $La_{11}Ge_4In_{5.00(1)}Li_{1.00}$ using the various crystal orbital Hamilton population (COHP) curves and the possible short-range anionic ordering based on total electronic energy comparisons. Density of states (DOS) curves are also analyzed to explain the orbital interactions among components in the given crystal structure.

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1. Introduction

Polar intermetallic compounds can be considered as an intermediate species between the traditional intermetallic phases including the Hume-Rothery [1,2] and the Laves phase, and the Zintl phase [3–6] adopting the close-shell electronic configuration. This type of compounds consists of the more electropositive components, such as alkali metals, alkaline-earth metals or rare-earth metals, combined with the more electronegative components found near the Zintl border-line in the Periodic Table. In particular, the more electronegative components can form the anionic structural framework that often conform to a simple electron counting rule, such as the Zintl–Klemm formalism [7–9], whereas the electropositive components donate valence electrons to the anionic framework and simply act like cations. Since such polar intermetallic compounds contain both cationic and anionic elements, these

can be good platforms for elemental tuning to obtain particular chemical or physical properties [9–12].

In the recent years, a series of compounds having a chemical formula of $A_{11}M_{10}$ ($Sm_{11}Ge_4In_6$ -type; $A =$ alkaline-earth metals, rare-earth metals, and $M =$ triels, tetrels, pnictogens) [13–18] have been widely investigated given their interesting physical properties. In particular, the series of ternary indide compounds including the $RE_{11}Ge_8In_2$ ($RE = Gd-Tm$) system [19] and the $RE_{11}Tt_4In_6$ ($RE = Y, La, Gd-Er$; $Tt = Si, Ge$) system [20,21] has been known for its interesting magnetocaloric effect. Moreover, a series of isotopic binary or ternary pnictides with some triel or tetrel substitutions including the $A_{11}Pn_{10-x}T_x$ ($A = Rb, Cs, Ca, Sr, Ba, Eu, Yb$; $Pn = Sb, Bi$; and $T = Si, Ge, Sn$) system [18,22–24] has been thoroughly studied given its particular thermoelectric property. However, despite the large amounts of researches on these systems, the majority of studies have been focused on the crystal structures and the physical properties. There exists some reports about the electronic structures of $La_{11}Sn_{10}$ and $La_{11}In_6Ge_4$ [17,20], but those analyses were mostly limited on density of states (DOS) curves. Therefore,

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in order to understand chemical bonding and the overall electronic structure which significantly influence the given crystal structure as well as physical properties, more comprehensive theoretical investigations should be necessary.

In this report, we provide discussions about two isotopic polar intermetallics, $\text{La}_{11}\text{Ge}_4\text{In}_{5.00(1)}\text{Li}_{1.00}$ and $\text{Ce}_{11}\text{Ge}_{5.76(3)}\text{In}_{4.04}$, with respect to synthesis, crystal structure and comprehensive theoretical calculations. In particular, the site preference between Ge and In on the anionic framework of $\text{Ce}_{11}\text{Ge}_{5.76(3)}\text{In}_{4.04}$ was investigated using QVAL values [25]. In addition, the local short-range ordering between anionic elements was suggested by the electronic energy comparison of various structural models which were built based on the “coloring concept” [26–29]. The partial and total DOS as well as crystal orbital Hamilton population (COHP) analyses [30] were also presented to evaluate atomic orbital interactions influencing the local coordination geometry and chemical bonding among components.

2. Experimental

2.1. Synthesis

All procedures for sample preparation were conducted inside an argon-filled glove-box or under vacuum. Two title compounds, $\text{La}_{11}\text{Ge}_4\text{Li}_{1.00(1)}\text{In}_{5.00}$ and $\text{Ce}_{11}\text{Ge}_{5.96(3)}\text{In}_{4.04}$, have been synthesized using pure elements as obtained from Alfa or Aldrich: La (ingot, 99.9%), Ce (ingot, 99.999%), Li (wire, 99.8%), In (shot, 99.99%), and Ge (pieces, 99.999%). Since the originally targeted compounds were quaternary derivatives of the $RE_5\text{Tt}_4$ (RE = rare-earth metals, Tt = tetrels) system [31], the originally loaded compositions were $\text{La}_4\text{Li}_{0.35}\text{In}_{0.65}\text{Ge}_4$ and $\text{Ce}_4\text{LiInGe}_3$, respectively. Each reactant mixture was loaded into a Nb-tube (diameter = 1 cm, length = 4 cm), and both ends of the tube were sealed by arc-welding under an argon atmosphere. Tanned or oxidized surfaces of rare-earth metals and Li-wire were peeled-off using a scalpel in a glove-box just before loaded in the reaction container. Then, the Nb-tube was sealed inside a fused-silica jacket acting as a secondary container under vacuum to prevent the tube from being oxidized at the maximum reaction temperature. Both reactions were initially heated up to 1080 °C at the rate of 200 °C/h, kept there for 5 h, then cooled down to 750 °C at the rate of 10 °C/h, and finally annealed at 750 °C for 2 days. After the annealing process, a furnace was tuned-off allowing the reactants were cooled down to room temperature naturally. Two reactions produced each title compound mixed with some La_4LiGe_4 , La_2InGe_2 and Ce_4LiGe_4 [11,32], respectively, according to powder X-ray diffraction patterns. Both compounds became visibly moisture- and air-sensitive after one day. Once both title compounds were characterized, we repeated those reactions using the refined chemical compositions with the identical temperature profile, and two title compounds were eventually obtained as major phases.

2.2. Crystal structure determination

Both $\text{La}_{11}\text{Ge}_4\text{Li}_{1.00(1)}\text{In}_{5.00}$ and $\text{Ce}_{11}\text{Ge}_{5.96(3)}\text{In}_{4.04}$ have been characterized by powder and single crystal X-ray diffraction analyses. Powder X-ray diffraction patterns were collected using Bruker D8 diffractometer with monochromatic Cu K α 1

Table 1
Single crystal data and structure refinement results for $\text{La}_{11}\text{Ge}_4\text{In}_{5.00(1)}\text{Li}_{1.00}$ and $\text{Ce}_{11}\text{Ge}_{5.96(3)}\text{In}_{4.04}$.

	$\text{La}_{11}\text{Ge}_4\text{In}_{5.00(1)}\text{Li}_{1.00}$	$\text{Ce}_{11}\text{Ge}_{5.96(3)}\text{In}_{4.04}$
Formula weight (g/mol)	2399.41	2412.72
Space group; Z	$I4/mmm$ (No. 139); 4	
Lattice parameters (Å)	$a = 11.8370(4)$ $c = 17.2308(7)$	$a = 11.8892(4)$ $c = 16.5736(7)$
Volume (Å ³)	2414.3(2)	2342.7(2)
d_{calcd} (g/cm ³)	6.601	6.841
θ range for data collection	2.36°–28.30°	2.11°–26.72°
Independent reflections	901 [$R_{\text{int}} = 0.0424$]	751 [$R_{\text{int}} = 0.0580$]
Data/restraints/parameters	901/0/40	751/0/40
R^2 indices ($I > 2\sigma_1$)	$R_1 = 0.0226$ $wR_2 = 0.0404$	$R_1 = 0.0238$ $wR_2 = 0.0471$
R^2 indices (all data)	$R_1 = 0.0274$ $wR_2 = 0.0417$	$R_1 = 0.0300$ $wR_2 = 0.0491$
GOF on F^2	1.119	1.125
Largest diff. peak and hole (e/Å ³)	1.202 and –2.011	1.279 and –1.608

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum (w(F_o^2 - F_c^2))^2] / \sum (w(F_o^2))^2]^{1/2}$, 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.

radiation ($\lambda = 1.54059$ Å). The collected step size was set at 0.05°, and the total exposure time was ca. 1 h. Phase purity and lattice parameters of unit cells were initially examined by program *Rietica* [33]. For single crystal X-ray diffraction experiments, several silvery lustrous crystals were selectively picked-up from each batch of crushed products, and those crystals were briefly checked for their qualities by a rapid scan using Bruker SMART APEX2 CCD-based diffractometer equipped with Mo K α 1 radiation ($\lambda = 0.71073$ Å). After then, the best crystals were selected for the full data collection at room temperature using Bruker's APEX2 software [34]. Data reduction, integration, and unit cell refinement were conducted by using *SAINT* program [35]. The program *SADABS* was exploited for semi-empirical absorption correction [36]. The entire sets of reflections of both compounds were well matched with the tetragonal crystal system, and the space group $I4/mmm$ was chosen for crystal structures with four formula units per unit cell. Two crystal structures were solved by direct method and eventually refined on F^2 by full-matrix least-squares method using *SHELXTL* software package [37]. Refined parameters included the scale factor, atomic positions with anisotropic displacement parameters and extinction coefficients. In the last stage of a refinement cycle, atomic positions of two compounds were standardized using *STRUCTURE TIDY* [38]. Important crystallographic data are provided in Tables 1–3. CIFs are deposited with Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: (49) 7247-808-666; e-mail: crysdata@fiz.karlsruhe.de) with depository numbers: CSD-428066 for $\text{La}_{11}\text{Ge}_4\text{Li}_{1.00(1)}\text{In}_{5.00}$, and CSD-428067 for $\text{Ce}_{11}\text{Ge}_{5.96(3)}\text{In}_{4.04}$.

2.3. Computational details

Tight-binding, linear muffin-tin orbital (TB-LMTO) calculations [39] were carried out in the atomic sphere approximation (ASA) using the Stuttgart program [39]. Exchange and correlation were treated by the local density approximation (LDA) [40]. All relativistic effects except spin-orbit coupling were taken into account by using a scalar relativistic approximation. In the ASA method, the space in a unit cell is filled with overlapping Wigner-Seitz (WS) atomic spheres [39]. A combined correction is used to take into account the overlapping part [40]. The radii of WS spheres were determined by an automatic procedure [40] and by requiring that the overlapping potential be the best possible approximation to the full potential. This overlap should not be too large because the error in kinetic energy introduced by the combined correction is proportional to the fourth power of the relative sphere overlap. The used WS radii are as follows: La = 1.906–2.416 Å, Ge = 1.601–1.835 Å, In 1.647–1.754 Å, and Li = 1.660–1.749 Å for $\text{La}_{11}\text{Ge}_4\text{LiIn}_5$; and Ce = 1.877–2.308 Å, Ge = 1.529–1.804 Å, and In = 1.764–1.822 Å for $\text{Ce}_{11}\text{Ge}_6\text{In}_4$. The basis sets included 6s, 6p and 5d orbitals for La, 6s, 6p and 5d orbitals for Ce, 4s, 4p and 4d orbitals for Ge, 5s, 5p and 5d orbitals for In, and 2s, 2p and 3d orbitals for Li. The La 6p, Ce 6p, Ge 4d, In 5d, and Li 2p and 3d orbitals were treated by the Löwdin downfolding technique [41], and the La and Ce 4f wave functions were treated as core functions. DOS and various COHP curves as well as QVAL values [25] were thoroughly evaluated to understand the relative influences of different interatomic orbital interactions and the site preference between components. The k -space integrations were performed by the tetrahedron method [42], and the self-consistent charge density was obtained using 272 irreducible k -points in the Brillouin zone for both compounds.

3. Results and discussion

3.1. Crystal structure and structural comparison

Both $\text{La}_{11}\text{Ge}_4\text{In}_{5.00(1)}\text{Li}_{1.00}$ and $\text{Ce}_{11}\text{Ge}_{5.96(3)}\text{In}_{4.04}$ have crystallized in the tetragonal crystal system with a space group $I4/mmm$ ($Z = 4$, Pearson code $tI84$) and adopted the $\text{Sm}_{11}\text{Ge}_4\text{In}_6$ -type structure [14], which can be considered as an ordered version of the $\text{Ho}_{11}\text{Ge}_{10}$ -type [13]. Total nine crystallographically independent atomic sites in the asymmetric unit were observed in each unit cell of two compounds. Those included four cationic sites occupied by either La or Ce and five anionic sites occupied by one mixture of elements at Wyckoff 16m, one In atom at Wyckoff 8h and three Ge atoms at Wyckoff 8j, 4e, and 4d, respectively. In particular, the local geometries of these five anionic sites can be described as a “dumbbell-shaped” mixed-site for the 16m, a “square-shaped” In-site for the 8h and three “isolated” Ge-sites for 8j, 4e and 4d. Therefore, the isotopic crystal structure of both compounds can generally be described as an assembly of three different types of co-facial cationic polyhedra centered by three isolated Ge-sites (Fig. 1(a) and (b)), which are situated within a large “cage-like” 3-dimensional (3-D) anionic framework (Fig. 1(d)). This anionic framework is built by cross-linking of the dumbbell-sites (Wyckoff 16m) and the square-sites (Wyckoff 8h) as shown in Fig. 1(c). In particular, the dumbbell-site displays the mixed-occupation of In

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