Ce$_{11}$Ge$_{3.73(2)}$In$_{6.27}$: Solid-state synthesis, crystal structure and site-preference

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ABSTRACT

A novel intermetallic compound of Ce$_{11}$Ge$_{3.73(2)}$In$_{6.27}$ has been synthesized through the high-tempera-ture solid-state reaction using Nb-ampoules. A batch of well grown block-/short bar-shaped single-crystals has been obtained, and the crystal structure of the title compound has been characterized by single-crystal X-ray diffraction analyses. Ce$_{11}$Ge$_{3.73(2)}$In$_{6.27}$ adopts the Ho$_{11}$Ge$_{10}$-type structure belonging to the tetragonal space group $I4/mmm$ ($Z=4$, Pearson symbol tI84) with nine crystallographically unique atomic positions in the asymmetric unit. The lattice parameters are $a=12.0163(1)$ Å and $c=16.5396(2)$ Å. The overall crystal structure can simply be depicted as an assembly of three different types of co-facial cationic polyhedra centered by anions, which is further enclosed by the three-dimensional (3-D) cage-like anionic framework. The extra amount of In is observed in one of three isolated anionic sites resulting in introducing the Ge/In-mixed site at the $Wyckoff$ 4e site. This unique site-preference of In substitution for Ge at the 4e site has been enlightened via the atomic size-aspect which was fully supported and rationalized by the site- and bond-energies analyses using tight-binding linear muffin-tin orbital (TB-LMTO) calculations. Energy-dispersive X-ray spectroscopy (EDS), density of states (DOS), crystal orbital Hamilton population (COHP), and electron localization function (ELF) analyses for the title compound are also presented. Magnetic susceptibility measurement proves that an antiferromagnetic ordering of Ce atoms at a low temperature with a paramagnetic Curie temperature of -23.2 K.

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1. Introduction

Intermetallic compounds have been an interesting playground for solid-state chemists for decades to explore the relationship between a particular crystal structure and the resultant physical property or vise versa [1–6]. Among a vast number of intermetallic compounds, several series of phases adopting the Ho$_{11}$Ge$_{10}$-type structure [6] and carrying the chemical formula of $RE_{11}Tt_{10-x}$In$_x$ (RE=rare-earth metals; Tt=Si, Ge; $2 \le x \le 6$) [7–12] and $A_{11}Pn_{10-x}Tt_x$ (A=Rb, Cs, Ca, Sr, Ba, Eu, Yb; Pn=Sb, Bi; Tt=Si, Ge, Sn) [13–16] have been thoroughly studied to assess their potential energy-converting or saving capabilities as magnetocaloric or thermoelectric materials.

During our systemic investigation for the $RE_{11}Tt_{10-x}$In$_x$ (RE=rare-earth metals; Tt=tetrels) system to understand the co-re-lationship among crystal structure, electronic structure and phy-sical property, we successfully synthesized two novel isotypic compounds of La$_{11}$Ge$_4$In$_{5.00(1)}$Li$_{1.00}$ and Ce$_{11}$Ge$_{5.96(3)}$In$_{4.04}$ adopting

the Ho$_{11}$Ge$_{10}$-type structure [6] and reported the results of com-prehensive experimental and theoretical investigations in our previous article [11]. In this report, we particularly focused on the site-preference of anionic elements in the three-dimensional (3-D) anionic framework observed during the atomic substitution. More specifically, we firstly performed a series of calculations for several structural models having different anionic arrangements in the 3-D framework to evaluate the total electronic energy of each model. After then, we attempted to provide rationales for the en-ergetically most favorable structural model with a particular atomic site-preference by using the QVAL value criterion [11,17,18].

As a result of our continuous investigation for the $RE_{11}Tt_{10-x}$In$_x$ (RE=rare-earth metals; Tt=tetrels) systems, we have recently synthesized another isotypic compound of Ce$_{11}$Ge$_{3.73(2)}$In$_{6.27}$ in-cluding an excess amount of In substitution for Ge in the parental $RE_{11}Tt_{10-x}$In$_x$ systems [7–12]. As reported in many earlier articles, the available anionic sites for the In substitution were known to be confined within the 3-D framework, which also resulted in limit-ing the maximum In content to six per formula unit (f.u.), e.g., $x \le 6$ for the $RE_{11}Tt_{10-x}$In$_x$ systems [7–12]. However, in the title

compound, the extra amount of In was introduced to one of three "isolated" Ge-sites resulting in producing the Ge/In-mixed anionic site. In addition, the observed site-preference of the extra In among three available isolated Ge-sites can hardly be explained by the QVAL value criterion unlike our previous report [11].

In this article, we report our recent results of experimental and theoretical investigations for the isotypic compound $Ce_{11}Ge_{3.73(2)}In_{6.27}$, which was synthesized by the high-temperature solid-state reaction using Nb-ampoules and characterized by both powder and single-crystal X-ray diffractions analyses. In particular, a series of computational calculations were performed using two structural models with In substitutions at two different sites, and the resultant site- and bond-energies of each model were thoroughly and carefully analyzed to interpret the origin of the site-preference of the extra In atoms toward one of the isolated Ge-sites. Total and partial densities of states (DOS) curves were studied to elucidate orbital contributions of each component to the electronic structure over whole energy window. Crystal orbital Hamilton population (COHP) curves [19] and the electron localization function (ELF) diagram [20–22] were interrogated to understand chemical bonding and paired-electron densities, and magnetic property was also investigated for the title compound.

2. Experimental

2.1. Synthesis

All sample preparation processes were conducted inside an argon-filled glove-box with O_2 and H_2O amounts below 0.1 ppm or under vacuum condition. Three reactants purchased from Alfa (99.99%) were loaded in the one end-sealed Nb-ampoule (diameter=1 cm, length=4 cm) inside the glove-box with the stoichiometric ratio of Ce/Ge/In=11:3:7. The other end of the Nb-ampoule was sealed by arc-welding under argon atmosphere after all reactants were loaded, and then the ampoule was sealed again inside a fused-silica jacket to avoid oxidation during the high-temperature reaction process. The Nb-ampoule with reactants was heated up to 950 °C by 80 °C/h, held there for 2 h, and then cooled down to 700 °C by 10 °C/h. After then, the reactants were annealed at 700 °C for two weeks, and the furnace was turned-off to allow products be cooled down naturally to room temperature. This reaction produced batches of aggregated small but very nicely grown block/short-bar shaped single-crystals with metallic lustrous, which were stable under ambient condition at least for one month. The complete sealing of the Nb-ampoule and the prolonged annealing process provided an appropriate reaction condition to grow single-crystals of the title compound.

2.2. Single crystal X-ray diffraction

Single crystal X-ray diffraction data were collected at room temperature using Bruker SMART APEX2 CCD-based diffractometer equipped with Mo Kα radiation ($\lambda=0.71073$ Å). Several block/short-bar shaped crystals were initially selected from a crushed product, and they were briefly quality-checked by a rapid scan. The best crystal was chosen for the further data collection, and a full data collection was processed by the Bruker's *APEX2* software [23] at room temperature. Data reduction, integration and unit cell refinements were conducted using *SAINT* program [24]. *SADABS* program [25] was used to perform semi-empirical absorption correction based on equivalents. The entire sets of reflections of the title compound were well matched with the tetragonal crystal system, and the space group *I4/mmm* was finally chosen. The crystal structure was solved by the direct methods and refined to convergence by full matrix least-squares methods

Table 1
Single-crystal crystallographic data and structure refinement result for $Ce_{11}Ge_{3.73(2)}In_{6.27}$.

Formula weight, $Z=4$	2531.90
Space group	*I4/mmm*
Temperature (K)	296
Unit cell dimensions (Å)	$a=12.0163(1)$
	$c=16.5396(2)$
Volume (Å³)	2388.18(5)
Density (calculated, g cm⁻³)	7.042
Absorption coefficient (cm⁻¹)	3.0974
Final R^a indices [$I>2\sigma_I$]	$R_1=0.0202$, $wR_2=0.0363$
R^a indices (all data)	$R_1=0.0223$, $wR_2=0.0368$
Goodness-of-fit on F^2	1.282

[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 $w=1/[\sigma^2F_o^2+(A\cdot P)^2+B\cdot P]$, and $P=(F_o^2+2F_c^2)/3$; A and B are weight coefficients.

on F^2. Refined parameters include the scale factors, the atomic positions with anisotropic displacement parameters, extinction coefficients, and occupancy factors for the Ge/In-mixed site. In the last stage of the refinement cycle, atomic positions were standardized using *STRUCTURE TIDY* program [26]. Important crystallographic data are provided in Tables 1–3. CIF is deposited with Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: +49 7247 808 666; e-mail: crysdata@fiz.karlsruhe.de) with depository numbers: CSD-429813 for $Ce_{11}Ge_{3.73(2)}In_{6.27}$.

2.3. Electronic structure calculations

Theoretical investigations were performed to understand the overall electronic structure including the site-preference of In atoms in the title compound using two hypothetical structural models with an idealized composition of $Ce_{11}Ge_3In_7$. A series of TB-LMTO calculations with the atomic sphere approximation (ASA) were conducted with the Stuttgart LMTO47 program [27], and the local density approximation (LDA) [28] was used to treat exchange and correlation. All relativistic effects except spin–orbit coupling were taken into account by using a scalar relativistic approximation. In the ASA method, space is filled with overlapping Wigner–Seitz (WS) atomic spheres [27]. The symmetry of the potential is considered spherical inside each WS sphere, and a combined correction is used to take into account the overlapping part [28]. The radii of WS spheres were obtained by requiring that the overlapping potential be the best possible approximation to the full potential, and were determined by an automatic procedure [28]. 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. No empty spheres were used. The used WS radii were as follow: Ce=1.88−2.32 Å, In=1.80−1.88 Å, and Ge=1.61−1.71 Å. The basis sets included 6*s*, 6*p*, 5*d* and 4*f* orbitals for Ce; 4*s*, 4*p* and 4*d* orbitals for Ge; and 5*s*, 5*p*, 5*d* and 4*f* orbitals for In. The Ce 6*p*, In 5*d*, 5*f* and Ge 4*d* orbitals were treated by the Löwdin downfolding technique [29]. The 4*f* orbitals of Ce were treated as core functions. The *k*-space integration was performed by the tetrahedron method [30], and the self-consistent charge density was obtained using 224 irreducible *k*-points in the Brillouin zone.

2.4. Energy-dispersive X-ray spectroscopy (EDS)

Elemental analysis by using EDS was taken by a ULTRA Plus field-emission scanning electron microscope (SEM) system with an acceleration voltage of 30 kV. Several block/short-bar shaped single-crystals were selected from a batch of the product and were carefully mounted on circumference of an aluminum puck with double-side conducting carbon tapes. The resultant chemical