

Crystal Structure of the New Ternary Antimonide Ho₅GaSb₃

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The crystal structure of the new ternary antimonide Ho₅GaSb₃ has been determined from X-ray single-crystal data: space group *Pnma*, $a = 7.9667(8)$, $b = 15.128(2)$, $c = 7.9616(8)$ Å, $V = 959.5(3)$ Å³, $Z = 4$, $R_F = 0.059$, $R_w = 0.066$ for 9020 reflections. The crystal structure of Ho₅GaSb₃ is a ternary derivative of the Sm₅Ge₄ structure type with partially ordered distribution of gallium and antimony atoms.

Key words: Crystal Structure, Ternary Holmium Antimonide

Introduction

The isothermal sections of phase diagrams for the ternary systems *RE*-Ga-Sb (where *RE* = rare-earth metal) have not been reported in literature, but several selected ternary compounds in these systems have been investigated for some time.

Mills and Mar reported on the existence of ternary compounds, such as Pr₁₂Ga₄Sb₂₃ and the isotopic compounds *RE*₁₂Ga₄Sb₂₃ (*RE* = La, Ce, Sm), La₁₃Ga₈Sb₂₁ and *RE*GaSb₂ (*RE* = La–Nd, Sm) [1, 2]. The crystal structure of Pr₁₂Ga₄Sb₂₃ [1] is related to that of La₆MnSb₁₅ [3], in which the position 4*c* is tetrahedrally coordinated by Sb atoms and only partially occupied by Mn atoms. In the structure of Pr₁₂Ga₄Sb₂₃, atoms Ga1, Ga2 and Sb1 (positions 4*i*, 4*h*, 8*l*, respectively) are also partially occupied. La₁₃Ga₈Sb₂₁ [1] (the precise composition is La_{12.85}Ga_{7.56}Sb₂₁) crystallizes with hexagonal symmetry. The peculiarity of the crystal structure of this compound is a partial occupancy of Ga1, Ga2, and La3 (positions 12*n*, 4*h*, 1*a*, respectively). The orthorhombic structures of the compounds Pr₁₂Ga₄Sb₂₃ and La₁₃Ga₈Sb₂₁ are closely related to the hexagonal structures of a large family of metal-rich compounds, generally phosphides and silicides, composed of differently sized triangular arrangements of trigonal prisms [4, 5].

For the layer compounds *RE*GaSb₂ two structure types have been described. The SmGaSb₂ type (space

group *C222*₁, also adopted by *RE* = La) represents a stacking variant of the NdGaSb₂ type (space group *I4*₁/*amd*, also adopted by *RE* = Ce–Nd) [2].

Other authors [6] noticed the existence of the ternary compound SmGaSb₂, which was found during the investigation of the respective ternary system in the section of 50 at.-% of antimony. The X-ray powder pattern of the sample containing 50 % SmSb differs from the powder patterns of other samples also containing binary SmSb. This fact was taken as evidence for the formation of a new ternary compound. Later it was found that this compound belongs to the NaCl structure type (space group *Fm* $\bar{3}$ *m*, $a = 6.0896$ Å) [6].

The ternary compound Yb₁₁GaSb₉ belongs to the Ca₁₁InSb₉ structure type. It is one of the examples of Zintl phases with a high content of rare-earth metal [7]. The structure is built up from Ga-centered [GaSb₄]^{9–} tetrahedra, [Sb₂]^{4–} dimers and isolated [Sb]^{3–} anions, separated by Yb²⁺ cations: [Yb²⁺]₁₁ [GaSb₄]^{9–} [Sb₂]^{4–} [Sb^{3–}]₃. Eu₇Ga₆Sb₈ also belongs to the Zintl phases and crystallizes with its own orthorhombic structure type [8]. In this structure the anionic framework consists of infinite chains [Ga₆Sb₈]^{14–}, arranged together with Eu²⁺ cations to [(Eu²⁺)₇(Ga₆Sb₈)^{14–}] sheets, which are separated by Eu²⁺ cations. A charged-balanced formula is best represented as [Eu²⁺]₇ [(Ga₄)⁶⁺(Ga₂)⁴⁺(Sb^{3–})₈]^{14–}.

The continuation of the crystal structure investigation of the ternary compounds of gallium and antimony with rare-earth metals is worthwhile from a crystal chemistry point of view. The main goal of our work was to determine the crystal structure of the new ternary compound Ho₅GaSb₃, which was identified during the systematic investigation of interactions in the ternary system Ho-Ga-Sb in the region with a high content of holmium.

Experimental Section

Synthesis

The sample for the crystal structure investigation of the new ternary compound Ho₅GaSb₃ was prepared from pieces of holmium, gallium and antimony (all with minimum purities > 99.5 %). A stoichiometric mixture of these pieces (total amount 1 g) was melted several times in an arc furnace on a water-cooled copper bottom under purified argon atmosphere to improve homogeneity. Weight losses were found to be within 1 % of the original mass. The sample was subsequently wrapped in tantalum foil and annealed in a silica tube under an argon atmosphere for 1000 h at 500 °C, followed by quenching in cold water without breaking the vacuum ampoule. The sample is stable in air over months in powdered as well as in polycrystalline form. Single crystals of Ho₅GaSb₃ were isolated from the crushed sample after the thermal treatment.

X-Ray powder diffraction

All samples were characterized by X-ray powder diffraction performed with a DRON-3M diffractometer (CuK α radiation, $\lambda = 1.54185$ Å). Phase analysis was performed using the WINCSD program package [9]. The lattice parameters of Ho₅GaSb₃ were refined by least-squares fitting of the powder data with LaB₆ as an internal standard ($a = 7.966(2)$, $b = 15.089(4)$, $c = 7.954(3)$ Å).

Single-crystal X-ray diffraction

Single-crystal intensity data of Ho₅GaSb₃ were collected at r.t. on a Stoe IPDS II image plate diffractometer with monochromatized MoK α radiation by oscillation of the crystal around the ω axis. Crystallographic data and information on data collection and evaluation are listed in Table 1. All structure calculations were performed using the WINCSD software package [9].

Energy-dispersive X-ray spectroscopy analysis

Energy-dispersive X-ray spectroscopy analysis (EDXS) of the polished sample and the single crystal by a scanning electron microscope (TESCAN 5130MM with Oxford

Table 1. Crystal data, intensity collection and refinement for Ho₅GaSb₃.

Composition	Ho ₅ Ga _x Sb _{4-x} ($x = 0.99(1)$)
Structure type	ordered superstructure of the Sm ₅ Ge ₄ type
Crystal system	orthorhombic
Space group	<i>Pnma</i> (no. 62)
Pearson symbol	oP36
a , Å	7.9667(8)
b , Å	15.128(2)
c , Å	7.9616(8)
V , Å ³	959.5(3)
Number of formula units per cell, Z	4
Calculated density, g cm ⁻³	8.72
Radiation and wavelength	MoK α , $\lambda = 0.71069$ Å
Diffractometer	Stoe IPDS II
Linear absorption coefficient, cm ⁻¹	534.5
2θ range, deg	2.86–64.80
h, k, l	$-9 \leq h \leq 9$, $-18 \leq k \leq 18$, $-9 \leq l \leq 9$
Reflections collected	15222
Independent reflections	9902
$R_{\text{int}} / R_{\sigma}$	0.072 / 0.057
Reflections used in refinement	9020
$[F_{\text{hkl}} \geq 4\sigma(F_{\text{hkl}})]$	
Number of variable parameters	48
Mode of refinement	F_{hkl}
R_F	0.058
R_w	0.065
Goodness of fit	1.09
Largest diff. peak / hole ^a , e Å ⁻³	5.4 / -2.5

^a Largest residual electron density found close (< 1.0 Å) to Ho3.

Si-detector) confirmed the presence of only holmium, gallium and antimony. The nominal composition in atomic percentages measured by EDXS on several crystals was found to be Ho : Ga : Sb = 52.5 : 9.9 : 37.6 (standard deviations estimated to be about 1.5 at.-%).

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-420712.

Results and Discussion

During the systematic investigation of the system Ho-Ga-Sb at 500 °C a new ternary phase with the approximate composition $\sim\text{Ho}_{55}\text{Ga}_{15}\text{Sb}_{30}$ was found. The X-ray and EDXS analysis of the samples of different compositions revealed the existence of this ternary compound in the phase equilibrium with the binary compounds HoGa, HoSb and Ho₅Ga₃, and the ternary phase Ho₅(Ga,Sb)₃ [10]. A single crystal of the new

Table 2. Atomic positional and displacement parameters (B , Å²) for Ho₅GaSb₃.

Atom	Site	x/a	y/b	z/c	B_{eq}	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ho1	8d	0.05946(5)	0.11174(3)	0.32580(6)	0.921(9)	1.15(2)	0.75(1)	0.86(2)	0.140(5)	0.171(5)	0.033(5)
Ho2	8d	0.10360(5)	0.62117(3)	0.15847(6)	0.794(8)	1.06(2)	0.51(1)	0.81(2)	−0.000(5)	−0.181(5)	0.039(5)
Ho3	4c	0.22806(6)	1/4	0.00414(6)	0.49(1)	0.66(2)	0.42(2)	0.39(2)	0	−0.025(7)	0
Sb1	8d	0.26323(6)	0.54511(4)	0.48180(7)	0.74(1)	0.78(2)	0.54(2)	0.91(2)	−0.016(6)	−0.117(7)	0.042(7)
M1 ^a	4c	0.0947(1)	1/4	0.6256(1)	0.78(2)	0.89(3)	0.70(3)	0.74(4)	0	−0.02(1)	0
M2 ^a	4c	0.3649(1)	1/4	0.3583(2)	0.77(2)	0.93(3)	0.54(3)	0.83(2)	0	−0.08(1)	0

^a Occupation: M1 = 30.7(2) % Ga + 69.3(2) % Sb; M2 = 68.8(1) % Ga + 31.2(1) % Sb.

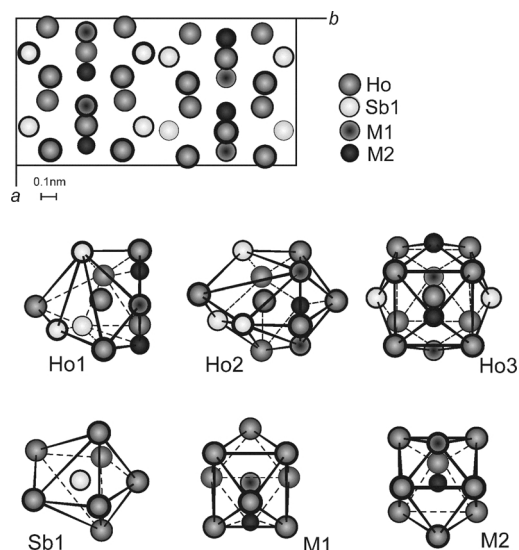
Table 3. Comparison of the Ho₅GaSb₃ and Sm₅Ge₄ [11] structures^a.

Chemical composition		Ho ₅ GaSb ₃				Sm ₅ Ge ₄			
Space group		<i>Pnma</i>				<i>Pnma</i>			
a , Å		7.9667				7.75			
b , Å		15.128				14.94			
c , Å		7.9616				7.84			
Wyckoff positions	Atom	x	y	z	Atom	x	y	z	
8d	Ho1	0.05946	0.11174	0.32580	Sm1	0.1205	0.1157	0.3388	
8d	Ho2	0.10360	0.62117	0.15847	Sm2	0.0253	0.6004	0.1781	
4c	Ho3	0.22806	1/4	0.00414	Sm3	0.2880	1/4	0.0024	
8d	Sb	0.26323	0.54511	0.48180	Ge1	0.2794	0.0449	0.0312	
4c	M1 ^b	0.0947	1/4	0.6256	Ge2	0.1761	1/4	0.6333	
4c	M2 ^b	0.3649	1/4	0.3583	Ge3	0.41320	1/4	0.3885	

^a Atomic coordinates were standardized using the program STRUCTURE TIDY [25]; ^b M1 and M2 are statistical mixtures of Ga and Sb atoms.

ternary antimonide was isolated from a heat-treated sample in which the unknown ternary phase was the main phase. Pre-screening of the single crystal revealed orthorhombic symmetry with the lattice parameters listed in Table 1. The systematic extinctions ($0kl$, $k+l = 2n+1$; $hk0$, $h = 2n+1$, where $n = 0, 1, 2, 3, \dots$) are characteristic for the space groups *Pnma* and *Pna2₁*. The solution by Direct Methods was successful in the centrosymmetric space group *Pnma*. The model was refined by full-matrix least-squares methods on F . The final values of the atomic coordinates and anisotropic displacement parameters for all atoms are listed in Table 2. During data reduction and refinement the crystal was supposed to be pseudomerohedrally twinned. The relation of two twin domains can be expressed by the matrix $\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$. The refined twin volume ratio is 0.829(1):0.171(1).

The crystal structure refinement of Ho₅GaSb₃ revealed that antimony and gallium atoms statistically occupy two crystallographic positions 4c: M1 = 30.7(2) % Ga + 69.3(2) % Sb and M2 = 68.8(1) % Ga + 31.2(1) % Sb. All other sites are fully occupied by either holmium or antimony atoms (Table 2). The final composition of the new compound can be described as Ho₅Ga _{x} Sb_{4− x} [$x = 0.99(1)$].

Fig. 1. Projection of the Ho₅GaSb₃ structure onto the crystallographic ab plane and coordination polyhedra of the atoms.

A projection of the Ho₅GaSb₃ structure onto the crystallographic ab plane and the coordination polyhedra for all atoms are shown in Fig. 1. The structure of Ho₅GaSb₃ is a ternary derivative of the Sm₅Ge₄ type (space group *Pnma*, $a = 7.75$, $b = 14.94$, $c = 7.84$ Å) [11]. In the structure of Sm₅Ge₄, the Ge atoms

Table 4. Interatomic distances (*d*, Å) for Ho₅GaSb₃.

Atoms	<i>d</i>	Atoms	<i>d</i>	Atoms	<i>d</i>	Atoms	<i>d</i>	Atoms	<i>d</i>	Atoms	<i>d</i>
Ho1–M2	2.9877(9)	Ho2–M1	3.0414(8)	Ho3–M2	3.023(1)	Sb1–Ho2	3.0710(7)	M1–M2	3.027(2)	M2–2Ho1	2.9877(9)
Sb1	3.1317(7)	Sb1	3.0710(7)	M2	3.094(1)	Ho2	3.0932(7)	2Ho2	3.0414(8)	Ho3	3.023(1)
Sb1	3.1578(7)	Sb1	3.0932(7)	M1	3.098(1)	Ho3	3.1055(5)	Ho3	3.098(1)	M1	3.027(2)
M1	3.1862(9)	M2	3.094(1)	2Sb1	3.1055(5)	Ho1	3.1317(7)	2Ho2	3.1053(8)	Ho3	3.094(1)
M2	3.2191(9)	M1	3.1053(8)	M1	3.195(1)	Ho2	3.1502(7)	2Ho1	3.1862(9)	2Ho2	3.094(1)
Sb1	3.2423(7)	Sb1	3.1502(7)	2Ho2	3.5293(6)	Ho1	3.1578(7)	Ho3	3.195(1)	2Ho1	3.2191(9)
Ho3	3.5689(6)	Ho3	3.5293(6)	2Ho1	3.5689(6)	Ho1	3.2423(7)				
Ho3	3.6302(6)	Ho3	3.6292(6)	2Ho2	3.6292(6)						
Ho2	3.7737(6)	Ho1	3.7737(6)	2Ho1	3.6302(6)						
Ho2	3.7832(6)	Ho1	3.7832(6)								
Ho2	4.0709(7)	Ho2	3.8980(5)								
		Ho1	4.0709(7)								

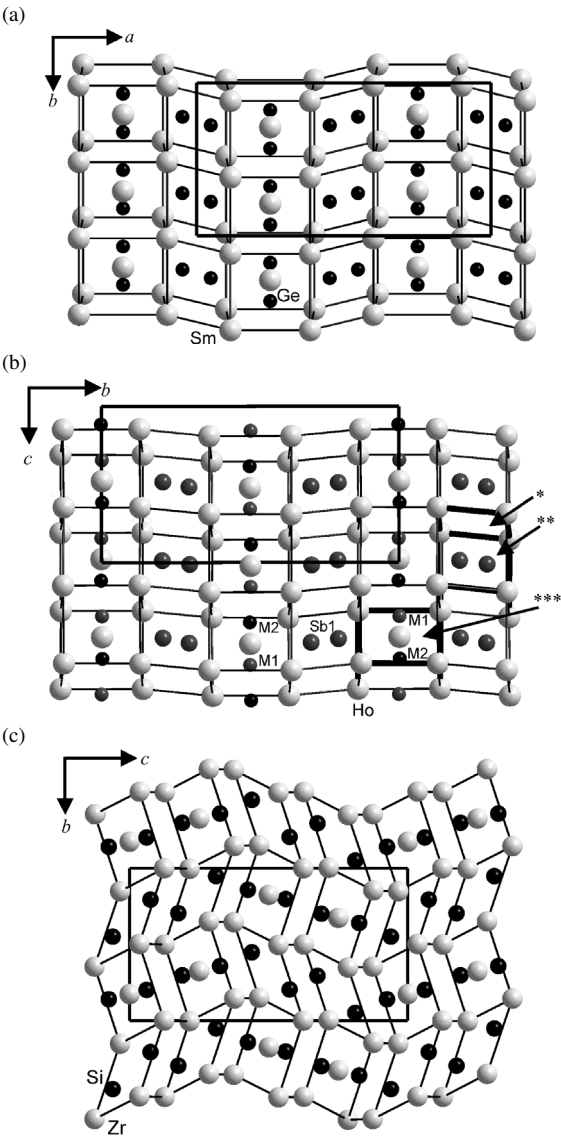


Fig. 2. Fragments of the structures of Sm₅Ge₄ (a), Ho₅GaSb₃ (b), Zr₅Si₄ (c), and Tm₅Sb₂Si₂ (d). The α-Po*, CuAl₂**, and U₃Si₂*** type slabs are emphasized.

occupy two 4*c* and one 8*d* sites. In the Ho₅GaSb₃ structure, the 8*d* site is occupied by Sb only, and two 4*c* positions are statistically occupied by Ga and Sb atoms. A comparative analysis of these structures is given in Table 3. Replacement of germanium positions by antimony and gallium atoms does not change the coordination numbers and coordination polyhedra of the atoms (Fig. 1). In the Ho₅GaSb₃ structure, the Ho1 and Ho2 atoms are coordinated by polyhedra with 11 and 12 vertices, respectively, whereas the Ho3 atoms center slightly distorted hexa-capped cubes [coordination number 14 (8 + 6)]. The Sb atoms are situated in the centers of polyhedra with 7-vertices. The coordination polyhedra around the positions of the statistical mixtures of Sb and Ga atoms are tricapped trigonal prisms (Fig. 1).

Interatomic distances between the atoms in Ho₅GaSb₃ are listed in Table 4. The distances are in good agreement with the respective sums of atomic radii of the components (*r*_{Ho} = 1.74 Å, *r*_{Ga} = 1.35 Å, *r*_{Sb} = 1.41 Å [12]). The shortest distances in this structure are between Ho1 and M2 (2.9877(9) Å) and Ho3 and M2 (3.023(1) Å). Deviations of these

interatomic distances from the sum of their atomic radii are smaller than 5 %.

The Sm₅Ge₄ structure type [11] is adopted by many rare-earth silicides and germanides (RE₅Si₄ for RE = Y, Sm, Gd–Er; RE₅Ge₄ for RE = all rare-earth metals, except Pm, Eu) [13–16]. Exceptions are RE₅Si₄ for RE = La–Nd, which crystallize in the tetragonal Zr₅Si₄ structure type [17], and RE = Lu, which crystallizes in its own monoclinic structure [13]. For these parent types several superstructures are known, which can be derived by splitting or combining the Wyckoff sites.

According to ref. [18] the structure of Tm₅Sb₂Si₂ is a ternary version of the binary structure type Eu₅As₄ [19] with a fully ordered distribution of antimony and silicon atoms on the crystallographic positions 8*d* and 8*f*. For the Zr₅Si₄ type only one ternary superstructure has been described, namely Sc₂Re₃Si₄ [20]. For the Sm₅Ge₄ type two ternary superstructures are known: Ce₂Sc₃Si₄ [21] and LiTm₄Ge₄ [22]. The relations between these structure variants are close, but they can be addressed neither as isotypical nor as isostructural.

Besides the Ho₅GaSb₃ structure with partially ordered gallium and antimony atomic positions, the structure of Sm₅SiGe₃ with the Sm₅Ge₄ type was ob-

served also with disordered non-metal atomic positions [23]. In the investigation of the pseudo-binary system Gd₅Si₄–Gd₅Ge₄ the appearance of an intermediate ternary phase Gd₅(Si₂Ge₂) with a monoclinic crystal structure was observed [24]. The formation of this intermediate phase is probably due to the large difference in bonding characteristics of Si and Ge in the compounds Gd₅Si₄ and Gd₅Ge₄ which crystallize in the orthorhombic Sm₅Ge₄ type. Fig. 2 shows these related structures and also the relations between the new ternary compound Ho₅GaSb₃ and Sm₅Ge₄. All these related structures contain slabs of the CuAl₂, U₃Si₂ and α-Po types, as emphasized in Fig. 2.

Conclusion

During the systematic investigations of the holmium-rich part of the ternary system Ho–Ga–Sb a new ternary antimonide Ho₅GaSb₃ has been synthesized at 500 °C, and its crystal structure was studied using single crystal X-ray data. Ho₅GaSb₃ is a ternary derivative of the Sm₅Ge₄ structure type with a partially ordered distribution of gallium and antimony atoms.

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