Crystal Structure of the New Ternary Antimonide Ho_5GaSb_3

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The crystal structure of the new ternary antimonide Ho_5GaSb_3 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) Å^3, Z = 4, R_F = 0.059, R_w = 0.066 for 9020 reflections. The crystal structure of Ho_5GaSb_3 is a ternary derivative of the Sm_5Ge_4 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 $Pr_{12}Ga_4Sb_{23}$ and the isotypic compounds $RE_{12}Ga_4Sb_{23}$ (*RE* = La, Ce, Sm), $La_{13}Ga_8Sb_{21}$ and *RE*$GaSb_2$ (*RE* = La–Nd, Sm) [1, 2]. The crystal structure of $Pr_{12}Ga_4Sb_{23}$ [1] is related to that of La_6MnSb_{15} [3], in which the position 4*c* is tetrahedrally coordinated by Sb atoms and only partially occupied by Mn atoms. In the structure of $Pr_{12}Ga_4Sb_{23}$, atoms Ga1, Ga2 and Sb1 (positions 4*i*, 4*h*, 8*l*, respectively) are also partially occupied. $La_{13}Ga_8Sb_{21}$ [1] (the precise composition is $La_{12.85}Ga_{7.56}Sb_{21}$) 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 $Pr_{12}Ga_4Sb_{23}$ and $La_{13}Ga_8Sb_{21}$ 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*$GaSb_2$ two structure types have been described. The $SmGaSb_2$ type (space group $C222_1$, also adopted by *RE* = La) represents a stacking variant of the $NdGaSb_2$ type (space group $I4_1/amd$, also adopted by *RE* = Ce–Nd) [2].

Other authors [6] noticed the existence of the ternary compound $SmGaSb_2$, 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 $Yb_{11}GaSb_9$ belongs to the $Ca_{11}InSb_9$ 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 $[GaSb_4]^{9-}$ tetrahedra, $[Sb_2]^{4-}$ dimers and isolated $[Sb]^{3-}$ anions, separated by Yb^{2+} cations: $[Yb^{2+}]_{11}$ $[GaSb_4]^{9-}$ $[Sb_2]^{4-}$ $[Sb^{3-}]_3$. $Eu_7Ga_6Sb_8$ 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 $[Ga_6Sb_8]^{14-}$, arranged together with Eu^{2+} cations to $[(Eu^{2+})_7(Ga_6Sb_8)^{14-}]$ sheets, which are separated by Eu^{2+} cations. A charged-balanced formula is best represented as $[Eu^{2+}]_7$ $[(Ga_4)^{6+}(Ga_2)^{4+}$-$(Sb^{3-})_8]^{14-}$.

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 Ho_5GaSb_3, 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 Ho_5GaSb_3 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 Ho_5GaSb_3 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, λ = 1.54185 Å). Phase analysis was performed using the WINCSD program package [9]. The lattice parameters of Ho_5GaSb_3 were refined by least-squares fitting of the powder data with LaB_6 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 Ho_5GaSb_3 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 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.-%).

Table 1. Crystal data, intensity collection and refinement for Ho_5GaSb_3.

Composition	$Ho_5Ga_xSb_{4-x}$ (x = 0.99(1))
Structure type	ordered superstructure of the Sm_5Ge_4 type
Crystal system	orthorhombic
Space group	*Pnma* (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, λ = 0.71069 Å
Diffractometer	Stoe IPDS II
Linear absorption coefficient, cm^{-1}	534.5
2θ range, deg	2.86 – 64.80
h, k, l	$-9 \le h \le 9$, $-18 \le k \le 18$, $-9 \le l \le 9$
Reflections collected	15222
Independent reflections	9902
R_{int} / R_σ	0.072 / 0.057
Reflections used in refinement [$F_{hkl} \ge 4\sigma(F_{hkl})$]	9020
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.

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 ~$Ho_{55}Ga_{15}Sb_{30}$ 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 Ho_5Ga_3, and the ternary phase $Ho_5(Ga,Sb)_3$ [10]. A single crystal of the new

Table 2. Atomic positional and displacement parameters (B, Å^2) for Ho_5GaSb_3.

Atom	Site	*x/a*	*y/b*	*z/c*	B_{eq}	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ho1	8*d*	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	8*d*	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	4*c*	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	8*d*	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]	4*c*	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]	4*c*	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 Ho_5GaSb_3 and Sm_5Ge_4 [11] structures[a].

Chemical composition		Ho_5GaSb_3				Sm_5Ge_4		
Space group		*Pnma*				*Pnma*		
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*
8*d*	Ho1	0.05946	0.11174	0.32580	Sm1	0.1205	0.1157	0.3388
8*d*	Ho2	0.10360	0.62117	0.15847	Sm2	0.0253	0.6004	0.1781
4*c*	Ho3	0.22806	1/4	0.00414	Sm3	0.2880	1/4	0.0024
8*d*	Sb	0.26323	0.54511	0.48180	Ge1	0.2794	0.0449	0.0312
4*c*	M1[b]	0.0947	1/4	0.6256	Ge2	0.1761	1/4	0.6333
4*c*	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 $n = 0, 1, 2, 3,\ldots$) are characteristic for the space groups *Pnma* and $Pna2_1$. 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 Ho_5GaSb_3 revealed that antimony and gallium atoms statistically occupy two crystallographic positions 4*c*: 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 $Ho_5Ga_xSb_{4-x}$ [$x = 0.99(1)$].

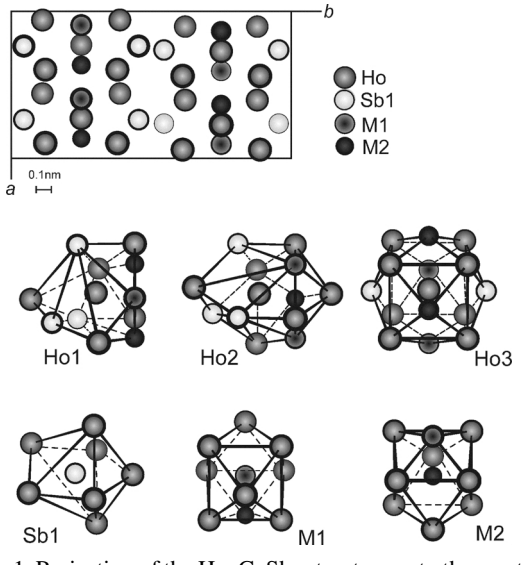

Fig. 1. Projection of the Ho_5GaSb_3 structure onto the crystallographic *ab* plane and coordination polyhedra of the atoms.

A projection of the Ho_5GaSb_3 structure onto the crystallographic *ab* plane and the coordination polyhedra for all atoms are shown in Fig. 1. The structure of Ho_5GaSb_3 is a ternary derivative of the Sm_5Ge_4 type (space group *Pnma*, $a = 7.75$, $b = 14.94$, $c = 7.84$ Å) [11]. In the structure of Sm_5Ge_4, the Ge atoms

Table 4. Interatomic distances (d, Å) for Ho_5GaSb_3.

Atoms	d	Atoms	d	Atoms	d	Atoms	d	Atoms	d	Atoms	d
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)								

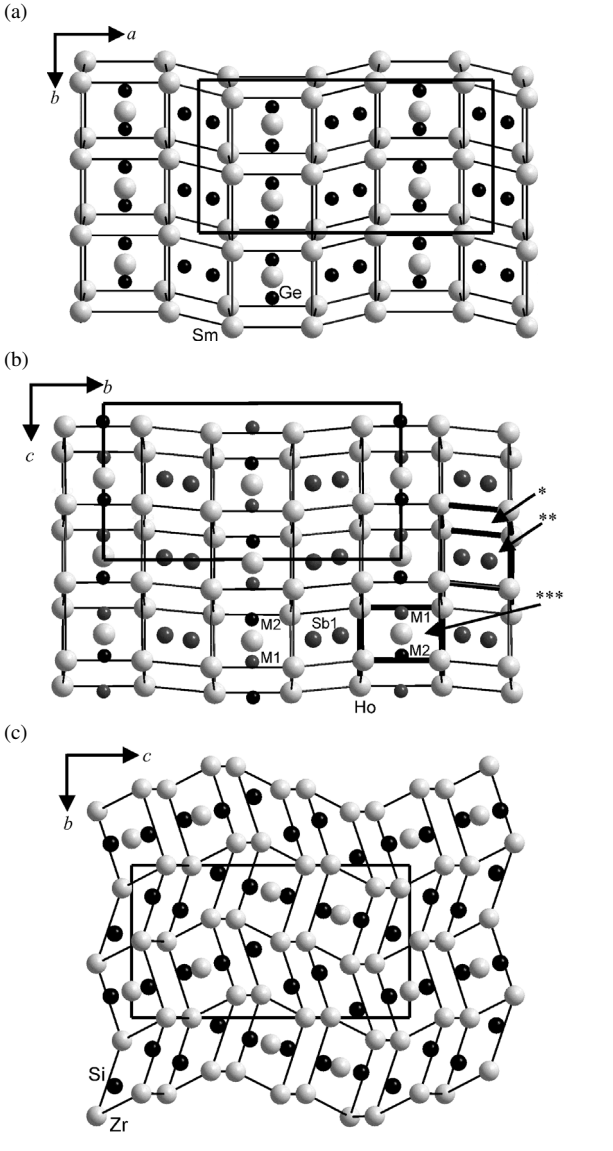

Fig. 2. Fragments of the structures of Sm_5Ge_4 (a), Ho_5GaSb_3 (b), Zr_5Si_4 (c), and $Tm_5Sb_2Si_2$ (d). The α-Po*, $CuAl_2$**, and U_3Si_2*** type slabs are emphasized.

occupy two 4*c* and one 8*d* sites. In the Ho_5GaSb_3 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 Ho_5GaSb_3 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 Ho_5GaSb_3 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 Sm_5Ge_4 structure type [11] is adopted by many rare-earth silicides and germanides (RE_5Si_4 for RE = Y, Sm, Gd–Er; RE_5Ge_4 for RE = all rare-earth metals, except Pm, Eu) [13 – 16]. Exceptions are RE_5Si_4 for RE = La–Nd, which crystallize in the tetragonal Zr_5Si_4 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 $Tm_5Sb_2Si_2$ is a ternary version of the binary structure type Eu_5As_4 [19] with a fully ordered distribution of antimony and silicon atoms on the crystallographic positions 8*d* and 8*f*. For the Zr_5Si_4 type only one ternary superstructure has been described, namely $Sc_2Re_3Si_4$ [20]. For the Sm_5Ge_4 type two ternary superstructures are known: $Ce_2Sc_3Si_4$ [21] and $LiTm_4Ge_4$ [22]. The relations between these structure variants are close, but they can be addressed neither as isotypical nor as isostructural.

Besides the Ho_5GaSb_3 structure with partially ordered gallium and antimony atomic positions, the structure of Sm_5SiGe_3 with the Sm_5Ge_4 type was observed also with disordered non-metal atomic positions [23]. In the investigation of the pseudo-binary system Gd_5Si_4-Gd_5Ge_4 the appearance of an intermediate ternary phase $Gd_5(Si_2Ge_2)$ 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 Gd_5Si_4 and Gd_5Ge_4 which crystallize in the orthorhombic Sm_5Ge_4 type. Fig. 2 shows these related structures and also the relations between the new ternary compound $Ho_5GaSb_3$and Sm_5Ge_4. All these related structures contain slabs of the $CuAl_2$, U_3Si_2 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 Ho_5GaSb_3 has been synthesized at 500 °C, and its crystal structure was studied using single crystal X-ray data. Ho_5GaSb_3 is a ternary derivative of the Sm_5Ge_4 structure type with a partially ordered distribution of gallium and antimony atoms.

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