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The ternary system Sm–Ga–Sn: isothermal section of the phase diagram at 600°C and crystal structures of the compounds

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The isothermal section at 600°C of the phase diagram of the ternary system Sm–Ga–Sn was constructed using X-ray powder diffraction data. Limited solid solutions based on the binary compounds $SmSn_3$ (30 at.% Ga), Sm_5Ga_3 (13.3 at.% Sn), Sm_5Sn_3 (4 at.% Ga), and SmGa (3 at.% Sn) were observed. Three ternary compounds were found at 600°C: $Sm_3Ga_{0.80\text{-}2.48}Sn_{4.20\text{-}2.52}$ (ternary variant of the structure type Pu_3Pd_5, Pearson symbol *oS*32, space group *Cmcm*, *a* = 9.97522(18)-9.89433(18), *b* = 8.02642(16)-7.87246(16), *c* = 10.23304(19)-9.91703(19) Å), $Sm_{11}Ga_{2.30}Sn_{7.70}$ (ternary variant of the structure type $Ho_{11}Ge_{10}$, *tI*84, *I*4/*mmm*, *a* = 11.5876(4), *c* = 17.3089(5) Å), and $Sm_5Ga_{0.76}Sn_{2.24}$ (structure type Nb_5SiSn_2, ternary variant of W_5Si_3, *tI*32, *I*4/*mcm*, *a* = 12.1881(14), *c* = 6.0919(7) Å). The ternary phases are characterized by partial ordering of the Ga and Sn atoms.

Samarium / Gallium / Tin / Phase diagram / X-ray powder diffraction / Crystal structure / Solid solution

Introduction

The ternary systems *R*–Ga–Sn (*R* = rare-earth metal) have not yet been systematically investigated. In the systems with Tb and Dy, several ternary compounds with close-packed structures, forming along the line with 25 at.% *R* in the concentration triangle, have been reported: $TbGa_{2.86}Sn_{0.14}$ (structure type Mg_3In, Person symbol *hR*48, space group *R*-3*m*, *a* = 6.2224, *c* = 27.908 Å) [1], $TbGa_{2.64}Sn_{0.36}$ (own type, *hR*72, *R*3*m*, *a* = 6.2404, *c* = 43.011 Å) [2], $DyGa_{2.74}Sn_{0.26}$ ($TbGa_{2.64}Sn_{0.36}$, *hR*72, *R*3*m*, *a* = 6.18716, *c* = 42.6992 Å) [3], $DyGa_{2.5\text{-}0.8}Sn_{0.5\text{-}2.2}$ (Cu_3Au, *cP*4, *Pm*-3*m*, *a* = 4.3283-4.56990 Å) [4]. The structures of $TbGa_{2.86}Sn_{0.14}$, $TbGa_{2.64}Sn_{0.36}$, and $DyGa_{2.74}Sn_{0.26}$ are characterized by partial ordering of Ga and Sn atoms. Two Cu_3Au-type ternary phases have been reported in the Ho–Ga–Sn system [5]: $HoGa_{2.80\text{-}2.32}Sn_{0.20\text{-}0.68}$ (*a* = 4.259-4.325 Å) and $HoGa_{1.80\text{-}0.88}Sn_{1.20\text{-}2.12}$ (*a* = 4.415-4.564 Å). Equiatomic YPtAs-type (*hP*12, $P6_3/mmc$) ternary compounds have been reported for the systems with Eu and Yb (*a* = 4.5243, *c* = 18.067 Å for EuGaSn [6]; *a* = 4.4352, *c* = 17.291 Å for YbGaSn [7]). In the system Sm–Ga–Sn the crystal structure of a ternary compound of variable composition $Sm_3Ga_{0.80\text{-}2.48}Sn_{4.20\text{-}2.52}$ has been reported [8]. Its structure belongs to an original (own) structure type (*oS*32, *Cmcm*, *a* = 9.97552-9.89433, *b* = 8.02642-7.87246, *c* = 10.23304-9.91703 Å), which is a ternary derivative of the binary structure type Pu_3Pd_5 [9]. The structure remains partially ordered in the whole homogeneity range. Recently, the crystal structure of an isotypic compound with Dy was reported, $Dy_3Ga_{2.54}Sn_{2.46}$ (*a* = 9.7300, *b* = 7.7081, *c* = 9.7985 Å) [10].

The binary systems that delimit the ternary system Sm–Ga–Sn are well studied and the phase diagrams have been constructed in the whole concentration range [[1]1], even if the formation of Sm_2Sn_3 remains unclear. Crystallographic data of the binary compounds reported in the systems Sm–Ga and Sm–Sn are summarized in Table 1. The system Ga–Sn is characterized by a eutectic reaction at 8.4 at.% Sn and 20.5°C. The maximal solubility of Ga in β-Sn at 13°C is 6.4 at.%. At the temperature of investigation (600°C) both Ga and Sn are liquid, *i.e.* a continuous liquid region will be observed on the Ga–Sn side of the isothermal section of the phase diagram of the system Sm–Ga–Sn.

This work presents the results of an experimental investigation of the phase equilibria in the ternary system Sm–Ga–Sn at 600°C and the crystallographic parameters of two new ternary compounds, $Sm_{11}Ga_{2.30}Sn_{7.70}$ and $Sm_5Ga_{0.76}Sn_{2.24}$, derived from X-ray powder diffraction.

Table 1 Crystallographic data for the binary compounds of the systems Sm–Ga and Sm–Sn.

Compound	Structure type	Pearson symbol	Space group	Cell parameters, Å			Reference
				a	*b*	*c*	
Sm_9Ga_4	Sm_9Ga_4	*tI*26	*I*4/*m*	11.940	–	5.081	[12]
Sm_5Ga_3	Cr_5B_3	*tI*32	*I*4/*mcm*	7.796	–	14.280	[13]
Sm_5Ga_3	Ba_5Si_3	*tP*32	*P*4/*ncc*	7.8026	–	14.1880	[14]
Sm_3Ga_2	Gd_3Ga_2	*tI*80	*I*4/*mcm*	11.713	–	15.17	[15]
SmGa	TlI	*oS*8	*Cmcm*	4.385	11.120	4.145	[16]
$SmGa_2$	AlB_2	*hP*3	*P*6/*mmm*	4.235	–	4.183	[17]
$Sm_{0.92}Ga_2$	$Sm_{0.92}Ga_2$	*oS*6	*Cmmm*	4.2484	7.3648	4.1856	[18]
$Sm_{0.86}Ga_{2.41}$	$Sm_{0.86}Ga_{2.41}$	*hP*15	*P*312	7.424	–	4.2176	[19]
$Sm_{1.06}Ga_{2.83}$	$Sm_{1.06}Ga_{2.83}$	*hP*66	*P*-62*c*	12.861	–	8.4402	[19]
$SmGa_{3.64}$	$SmGa_{3.64}$	*oF*140	*Fmmm*	8.493	14.912	17.08	[19]
$SmGa_6$	$PuGa_6$	*tP*14	*P*4/*nbm*	5.963	–	7.608	[20]
Sm_5Sn_3	Mn_5Si_3	*hP*16	*P*6$_3$/*mcm*	9.089	–	6.61	[21]
Sm_4Sn_3	Th_3P_4	*cI*28	*I*-43*d*	9.15	–	–	[22]
Sm_5Sn_4	Sm_5Ge_4	*oP*36	*Pnma*	8.19	15.81	8.19	[22]
$Sm_{11}Sn_{10}$	$Ho_{11}Ge_{10}$	*tI*84	*I*4/*mmm*	11.76	–	17.32	[23]
Sm_2Sn_3	Nd_2Sn_3	*aP*20	*P*-1	6.337 α = 108.38°	8.351 β = 96.51°	10.995 γ = 99.99°	[24]
$SmSn_2$	$ZrGa_2$	*oS*12	*Cmmm*	4.4203	15.8399	4.5054	[25]
Sm_3Sn_7	Tb_3Sn_7	*oS*28	*Cmmm*	4.4468	25.9918	4.5229	[25]
Sm_2Sn_5	Ce_2Sn_5	*oS*28	*Cmmm*	4.5379	34.9123	4.5861	[25]
$SmSn_3$	Cu_3Au	*cP*4	*Pm*-3*m*	4.6866 4.6873(2)	–	–	[26] this work

Experimental

14 two-component and 81 three-component alloys were synthesized from high-purity metals (Sm ≥ 99.9 mass%, Ga ≥ 99.99 mass%, Sn ≥ 99.99 mass%) by arc melting, using a tungsten electrode and a water-cooled copper hearth under a Ti-gettered argon atmosphere. To achieve homogeneity the samples were melted twice. After the synthesis the alloys were wrapped in tantalum foil, sealed in quartz ampoules under vacuum, and annealed at 600°C for 720 h. Finally the ampoules with the samples were quenched into cold water. The weight losses, which were controlled at all stages of the synthesis, did not exceed 1 wt.% of the total mass, which was approximately 1 g for each alloy.

Phase analysis and structure refinements were carried out using X-ray powder diffraction data collected at room temperature on automatic diffractometers (DRON-2.0M, Fe *K*α-radiation; Philips PW1280, Cu *K*α-radiation; STOE Stadi P, Cu *K*α$_1$-radiation; Bruker D8 Advance, Cu *K*α$_1$-radiation). The profile and structural parameters were refined by the Rietveld method, using the program package FullProf Suite [27]. In some cases the profile parameters were refined by a Le Bail fit (profile fit).

Results

The binary systems

By comparing the experimental X-ray powder diffraction patterns of the two-component alloys with patterns calculated for the binary compounds reported in the same system, the existence of 13 binaries at 600°C in the boundary binary systems Sm–Ga and Sm–Sn was confirmed: Sm_9Ga_4, Sm_5Ga_3 (structure type Ba_5Si_3), Sm_3Ga_2, SmGa, $SmGa_2$, Sm_5Sn_3, Sm_4Sn_3, Sm_5Sn_4, Sm_2Sn_3, $SmSn_2$, Sm_3Sn_7, Sm_2Sn_5, and $SmSn_3$. The binary compounds $SmGa_6$ and $Sm_{11}Sn_{10}$, reported in the literature, exist at lower and higher temperatures, respectively. The results obtained here are in good agreement with the phase diagrams of the binary systems evaluated in [11]. The only binary phase displaying a homogeneity range in the phase diagram, $SmGa_{2+x}$ (66.7-80.0 at.% Ga at 600°C), was recently described as a number of separate phases with different structure types: $SmGa_2$, $Sm_{0.92}Ga_2$, $Sm_{0.86}Ga_{2.41}$, $Sm_{1.06}Ga_{2.83}$, and $SmGa_{3.64}$ [19]. These structures form by gradual substitution of Ga atoms for Sm atoms in the parent AlB_2-type structure, which exists at the stoichiometric composition $SmGa_2$. The similarity of their X-ray powder diffraction patterns makes it difficult to distinguish them, and the group of phases will be referred to as $SmGa_{2+x}$ below.

Isothermal section of the phase diagram of the system Sm–Ga–Sn at 600°C

The isothermal section of the phase diagram of the ternary system Sm–Ga–Sn at 600°C was constructed (Fig. 1). It consists of 18 single-phase, 36 two-phase and 19 three-phase fields. The binary phase $SmGa_{2+x}$ forms the largest number of equilibria (7). At 600°C, the alloys of the binary system Ga–Sn are liquid. The boundary of the liquid phase in the ternary system was interpolated from its limits in the binary systems: 4.5 at.% in the system Sm–Ga and 3.7 at.% in the system Sm–Sn. Two phases, $SmGa_{2+x}$ and the solid solution based on $SmSn_3$, are in equilibrium with the liquid phase. Due to the high instability of the samples in the concentration range 40-55 at.% Sm, 0-10 at.% Ga, 35-60 at.% Sn in air, it was complicated to obtain X-ray powder diffraction patterns suitable for phase analysis. Therefore, the phase equilibria are drawn by dashed lines in this part of the isothermal section.

Two of the binary compounds, $SmSn_3$ (structure type Cu_3Au) and Sm_5Ga_3 (Ba_5Si_3), dissolve significant amounts of the third component, forming extended (up to 30 at.% Ga and 13.3 at.% Sn, respectively) solid solutions with constant Sm contents. The solubility of the third component in the other binary compounds of the systems Sm–Ga and Sm–Sn does not exceed 4 at.%. Three ternary compounds were found in the system Sm–Ga–Sn at 600°C. The compound $Sm_3Ga_{0.80\text{-}2.48}Sn_{4.20\text{-}2.52}$ has a homogeneity range of 21 at.% Ga (Sn) at a constant Sm content of 37.5 at.%, whereas the compound $Sm_5Ga_{0.76}Sn_{2.24}$ has a point composition. The homogeneity range of the phase $Sm_{11}Ga_{2.30}Sn_{7.70}$ was not determined.

Solid solutions based on the binary compounds

The binary compound $SmSn_3$ dissolves 30 at.% of Ga, forming a substitutional solid solution $SmGa_{0\text{-}1.2}Sn_{3\text{-}1.8}$. The cell parameters, derived from the Le Bail fit of the X-ray powder diffraction patterns from eight samples collected on a Bruker D8 diffractometer, are listed in Table 2. With increasing Ga content, the cell parameter of the cubic Cu_3Au phase decreases linearly within the solid solution.

The binary gallides Sm_5Ga_3 and SmGa dissolve 13.3 and 3 at.% Sn, respectively, and the stannide Sm_5Sn_3 4 at.% Ga. The boundary compositions of the solid solutions were determined by Rietveld refinements carried out on diffraction patterns collected with DRON-2.0M and Philips PW1280 diffractometers on multicomponent samples (Table 3).

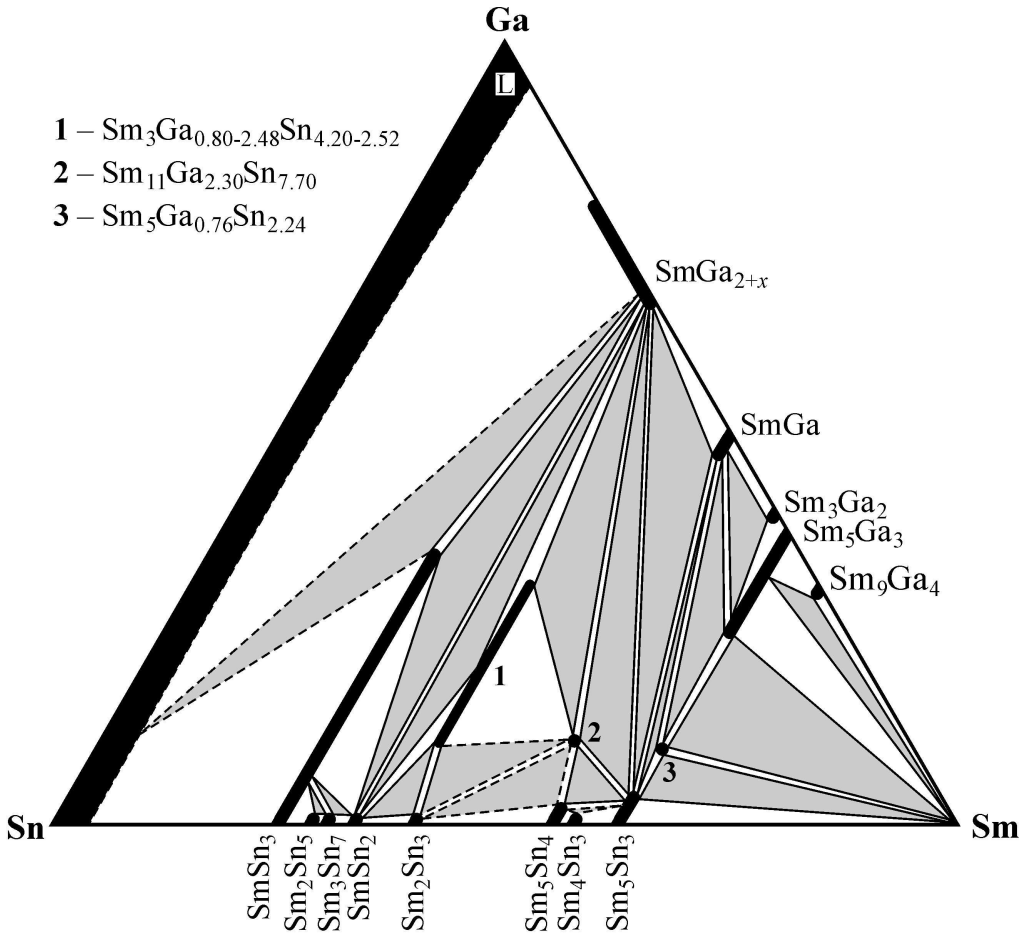

Fig. 1 Isothermal section of the phase diagram of the ternary system Sm–Ga–Sn at 600°C.

Table 2 Cell parameters of the solid solution $SmGa_xSn_{3-x}$ (x = 0-1.2, Cu_3Au, *cP*4, *Pm*-3*m*).

Alloy	Phase	*a*, Å	*V*, Å^3	R_p, χ^2
$Sm_{25}Sn_{75}$	$SmSn_3$	4.6873(2)	102.982(8)	0.0460, 1.53
$Sm_{25}Ga_5Sn_{70}$	$SmGa_{0.2}Sn_{2.8}$	4.66555(14)	101.557(5)	0.0468, 1.57
$Sm_{25}Ga_{10}Sn_{65}$	$SmGa_{0.4}Sn_{2.6}$	4.64007(10)	99.902(4)	0.0449, 1.78
$Sm_{25}Ga_{15}Sn_{60}$	$SmGa_{0.6}Sn_{2.4}$	4.61892(9)	98.542(3)	0.0446, 1.91
$Sm_{25}Ga_{20}Sn_{55}$	$SmGa_{0.8}Sn_{2.2}$	4.59327(10)	96.909(4)	0.0409, 1.84
$Sm_{25}Ga_{25}Sn_{50}$	$SmGaSn_2$	4.57841(13)	95.972(5)	0.0460, 2.27
$Sm_{25}Ga_{30}Sn_{45}$	$SmGa_{1.2}Sn_{1.8}$	4.55239(17)	94.345(6)	0.0509, 2.93
$Sm_{25}Ga_{35}Sn_{40}$ [a]	$SmGa_{1.2}Sn_{1.8}$	4.55251(12)	94.352(4)	0.0421, 2.35

[a] Two-phase sample.

Table 3 Atomic coordinates, site occupancies and isotropic displacement parameters at the boundary compositions of the solid solutions $Sm_5Ga_{3-x}Sn_x$ (x = 0-1.15), $SmGa_{1-x}Sn_x$ (x = 0-0.06), and $Sm_5Ga_xSn_{3-x}$ (x = 0-0.33).

Site	Wyckoff position	*x*	*y*	*z*	B_{iso}, Å^2
$Sm_5Ga_{1.85(4)}Sn_{1.15(4)}$ (Ba_5Si_3, *tP*32, *P*4/*ncc*, *a* = 8.0194(7), *c* = 13.9435(18) Å, R_B = 0.0671, R_F = 0.0731)					
Sm1	16*g*	0.0872(15)	0.5838(15)	0.1032(2)	0.53(5)
Sm2	4*c*	¼	¼	0.2403(11)	0.46(13)
*M*1 (0.90(2)Ga+0.10(2)Sn)	8*f*	0.3761(8)	0.6239(8)	¼	0.94(13)
*M*2 (0.13(4)Ga+0.87(4)Sn)	4*c*	¼	¼	0.0022(16)	0.34(14)
$SmGa_{0.94(2)}Sn_{0.06(2)}$ (TlI, *oS*8, *Cmcm*, *a* = 4.4411(14), *b* = 11.223(2), *c* = 4.1687(14) Å, R_B = 0.0846, R_F = 0.0784)					
Sm	4*c*	0	0.3597(7)	¼	0.69(6)
M (0.94(2)Ga+0.06(2)Sn)	4*c*	0	0.0747(9)	¼	1.12(15)
$Sm_5Ga_{0.33(6)}Sn_{2.67(6)}$ (Mn_5Si_3, *hP*16, *P*6$_3$/*mcm*, *a* = 9.0713(6), *c* = 6.6083(5) Å, R_B = 0.0739, R_F = 0.0661)					
Sm1	6*g*	0.2384(5)	0	¼	0.58(4)
Sm2	4*d*	⅓	⅔	0	0.49(6)
M (0.11(2)Ga+0.89(2)Sn)	6*g*	0.6068(6)	0	¼	0.88(12)

Rietveld refinements of the profile and structure parameters for the Sm_9Ga_4-, Gd_3Ga_2-, AlB_2-, Nd_2Sn_3-, $ZrGa_2$-, Tb_3Sn_7-, and Ce_2Sn_5-type phases in the three-component multiphase samples indicated no significant solubility of the third component in the binary compounds Sm_9Ga_4, Sm_3Ga_2, $SmGa_{2+x}$, Sm_2Sn_3, $SmSn_2$, Sm_3Sn_7, and Sm_2Sn_5.

The ternary phase $Sm_3Ga_{0.80-2.48}Sn_{4.20-2.52}$

The crystal structure of the ternary phase $Sm_3Ga_{0.80-2.48}Sn_{4.20-2.52}$ was solved from X-ray diffraction on a single crystal of composition $Sm_3Ga_{1.89}Sn_{3.11}$ and reported in [8]. It represents an original structure type (*oS*32, *Cmcm*, *a* = 9.9680(13), *b* = 7.9720(17), *c* = 10.056(2) Å), which is a ternary variant of the structure type Pu_3Pd_5. The structure is characterized by partial ordering of Ga and Sn atoms on three crystallographic sites: the site in Wyckoff position 8*g* is mainly occupied by Sn atoms, while the sites in 8*f* and 4*c* are occupied by statistical mixtures of Ga and Sn atoms. The evolution of the site occupancies within the homogeneity range of the compound was studied by Rietveld refinement on X-ray powder diffraction data obtained for eight samples. Within the homogeneity range $Sm_3Ga_{0.80-2.48}Sn_{4.20-2.52}$, substitution of Ga atoms for Sn atoms leads to a decrease of the cell parameters (*a* = 9.97522(18)-9.89433(18), *b* = 8.02642(16)-7.87246(16), *c* = 10.23304(19)-9.91703(19) Å) and to an increase of the amount of Ga atoms in only two (8*f* and 4*c*) of the three sites occupied by Ga and Sn atoms. The third site (8*g*) is occupied almost exclusively by Sn atoms in the whole concentration range.

The ternary compound $Sm_{11}Ga_{2.30}Sn_{7.70}$

The crystal structure of the ternary phase $Sm_{11}Ga_{2.30(6)}Sn_{7.70(6)}$ was refined by the Rietveld method using X-ray powder diffraction data for a two-phase sample of composition $Sm_{50}Ga_{20}Sn_{30}$ collected on a diffractometer Bruker D8 Advance (Cu $K\alpha_1$-radiation) in the angular range 2θ = 16-110° with a step size of 0.0144° and scanning time of 6 s per step. According to the phase analysis the sample contained two phases: a main phase with a $Ho_{11}Ge_{10}$-type related structure and the AlB_2-type binary gallide $SmGa_2$. Atomic coordinates for the structure type $Ho_{11}Ge_{10}$ [28], to which the structure of the binary compound $Sm_{11}Sn_{10}$ belongs [23], were chosen as starting model for the refinement of the structural parameters of the

main phase. In the beginning it was assumed that all the five sites available for the *p*-element atoms were occupied by statistical mixtures of Ga and Sn atoms. However, the refinement of the occupancy parameters suggested partial ordering: statistical mixtures of Ga and Sn atoms occupy only two of the sites (Wyckoff positions 8*j* and 8*h*), whereas the three other sites (16*m*, 4*e* and 4*d*) are exclusively occupied by Sn atoms. In the final refinement cycles two overall isotropic displacement parameters were refined: one for the Sm atoms and another one for the *p*-element atoms. In total, 30 parameters were refined for the two phases: sample shift, 2 scale factors, 4 cell parameters, 6 profile parameters (pseudo-Voigt profile function), 11 atom positional, 2 displacement, 2 occupancies and 2 texture parameters. The background was defined using a Fourier filtering technique. Experimental and calculated X-ray powder diffraction patterns and the difference between them for the sample of nominal composition $Sm_{50}Ga_{20}Sn_{30}$ are shown in Fig. 2. Experimental details and crystallographic data for the individual phases are listed in Table 4, atomic coordinates, site occupancies and isotropic displacement parameters for the structure of $Sm_{11}Ga_{2.30(6)}Sn_{7.70(6)}$ in Table 5, interatomic distances and coordination numbers in Table 6.

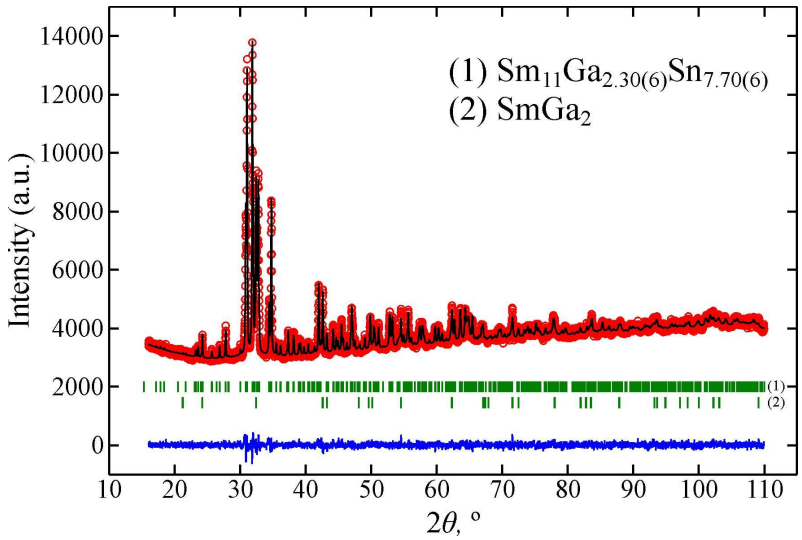

Fig. 2 Experimental (circles), calculated (continuous line) and difference between experimental and calculated (bottom) X-ray powder diffraction patterns of the sample $Sm_{50}Ga_{20}Sn_{30}$ (Cu $K\alpha_1$-radiation). Vertical bars indicate the positions of the reflections of $Sm_{11}Ga_{2.30(6)}Sn_{7.70(6)}$ and $SmGa_2$.

Table 4 Experimental details and crystallographic data for the individual phases in the samples $Sm_{50}Ga_{20}Sn_{30}$ and $Sm_{62.5}Ga_{11}Sn_{26.5}$.

Sample		$Sm_{50}Ga_{20}Sn_{30}$		$Sm_{62.5}Ga_{11}Sn_{26.5}$
Phase		$Sm_{11}Ga_{2.30(6)}Sn_{7.70(6)}$	$SmGa_2$	$Sm_5Ga_{0.76(3)}Sn_{2.24(3)}$
Content, mass%		84.8(6)	15.2(1)	100
Structure type		$Ho_{11}Ge_{10}$	AlB_2	Nb_5SiSn_2
Pearson symbol		*tI*84	*hP*3	*tI*32
Space group		*I*4/*mmm*	*P*6/*mmm*	*I*4/*mcm*
Cell parameters:	*a*, Å	11.5876(4)	4.24014(15)	12.1881(14)
	c, Å	17.3089(5)	4.1822(2)	6.0919(7)
Cell volume *V*, Å^3		2324.11(12)	65.117(5)	904.96(18)
Formula units per cell *Z*		4	1	4
Density D_X, g cm^{-3}		7.801	7.391	7.859
Preferred orientation: value / [direction]		0.967(2) / [001]	0.935(11) / [110]	0.775(5)
Reliability factors:	R_B	0.0519	0.0510	0.0416
	R_F	0.0452	0.0446	0.0527
Profile parameters	*U*	0.071(9)		0.077(16)
	V	0.011(8)		0.011(14)
	W	0.0129(16)		0.019(3)
Shape parameter		0.715(11)		0.800(10)
Asymmetry parameters		-0.048(12), 0.0211(13)		0.098(7), 0.0250(13)
Reliability factors:	R_p	0.0146		0.0199
	R_{wp}	0.0187		0.0253
	χ^2	1.33		1.10

Table 5 Atomic coordinates, site occupancies and isotropic displacement parameters for $Sm_{11}Ga_{2.30(6)}Sn_{7.70(6)}$ (*tI*84, *I*4/*mmm*, *a* = 11.5876(4), *c* = 17.3089(5) Å).

Site	Wyckoff position	*x*	*y*	*z*	B_{iso}, Å^2
Sm1	16*n*	0	0.2512(2)	0.31094(18)	0.65(4)
Sm2	16*n*	0	0.3244(3)	0.09931(19)	
Sm3	8*h*	0.3174(3)	0.3174(3)	0	
Sm4	4*e*	0	0	0.1598(3)	
*M*1 (0.42(2)Ga+0.58(2)Sn)	8*j*	0.1380(5)	½	0	
*M*2 (0.73(2)Ga+0.27(2)Sn)	8*h*	0.1202(5)	0.1202(5)	0	
Sn1	16*m*	0.2076(2)	0.2076(2)	0.1759(2)	0.66(6)
Sn2	4*e*	0	0	0.3940(5)	
Sn3	4*d*	0	½	¼	

Table 6 Interatomic distances (δ) and coordination numbers (CN) in the structure of $Sm_{11}Ga_{2.30(6)}Sn_{7.70(6)}$ (*tI*84, *I*4/*mmm*, *a* = 11.5876(4), *c* = 17.3089(5) Å).

Atoms		δ, Å	CN
Sm1	– 1 Sn3	3.070(2)	15
	– 1 Sn2	3.246(5)	
	– 2 Sn1	3.393(4)	
	– 2 Sn1	3.429(2)	
	– 1 *M*1	3.515(3)	
	– 1 Sm2	3.760(5)	
	– 2 Sm2	3.856(4)	
	– 1 Sm4	3.914(4)	
	– 2 Sm3	3.978(4)	
	– 2 Sm1	4.116(2)	
Sm2	– 2 Sn1	3.061(3)	15
	– 2 *M*1	3.107(4)	
	– 2 *M*2	3.239(6)	
	– 1 Sn3	3.308(3)	
	– 1 Sm2	3.438(5)	
	– 1 Sm1	3.760(5)	
	– 2 Sm1	3.856(4)	
	– 1 Sm4	3.902(4)	
	– 2 Sm3	4.060(3)	
	– 1 Sm2	4.070(5)	
Sm3	– 2 *M*1	2.966(5)	17
	– 1 *M*2	3.230(7)	
	– 2 Sn2	3.511(5)	
	– 2 Sn1	3.534(4)	
	– 4 Sm1	3.978(4)	
	– 4 Sm2	4.060(3)	
	– 2 Sm3	4.234(5)	
Sm4	– 4 *M*2	3.396(5)	17
	– 4 Sn1	3.413(2)	
	– 4 Sm2	3.902(4)	
	– 4 Sm1	3.914(4)	
	– 1 Sn2	4.054(10)	

Atoms		δ, Å	CN
*M*1	– 2 Sm3	2.966(5)	9
	– 4 Sm2	3.107(4)	
	– 1 *M*1	3.198(8)	
	– 2 Sm1	3.515(3)	
*M*2	– 2 *M*2	2.786(8)	12
	– 1 Sm3	3.230(7)	
	– 4 Sm2	3.239(6)	
	– 2 Sn1	3.363(4)	
	– 2 Sm4	3.396(5)	
	– 1 *M*2	3.940(8)	
Sn1	– 1 Sn1	2.920(5)	10
	– 2 Sm2	3.061(3)	
	– 1 *M*2	3.363(4)	
	– 2 Sm1	3.393(4)	
	– 1 Sm4	3.413(2)	
	– 2 Sm1	3.429(2)	
	– 1 Sm3	3.534(4)	
Sn2	– 4 Sm1	3.246(5)	10
	– 4 Sm3	3.511(5)	
	– 1 Sn2	3.669(12)	
	– 1 Sm4	4.054(10)	
Sn3	– 4 Sm1	3.070(2)	8
	– 4 Sm2	3.308(3)	

The crystal structure of $Sm_{11}Ga_{2.30(6)}Sn_{7.70(6)}$ belongs to the structure type $Ho_{11}Ge_{10}$ (*tI*84, *I*4/*mmm*) and is a Ga-stabilized form of the binary compound $Sm_{11}Sn_{10}$, which exists at higher temperatures (1170-1240°C). The cell parameters of the ternary phase are smaller than those of the corresponding binary compound, thereby confirming partial replacement of Sn atoms by Ga atoms. The unit cell content and the coordination polyhedra of the atoms in the structure of $Sm_{11}Ga_{2.30(6)}Sn_{7.70(6)}$ are shown in Fig. 3. The polyhedra are similar to those observed in the parent structure type $Ho_{11}Ge_{10}$. The Sm atoms center 15- or

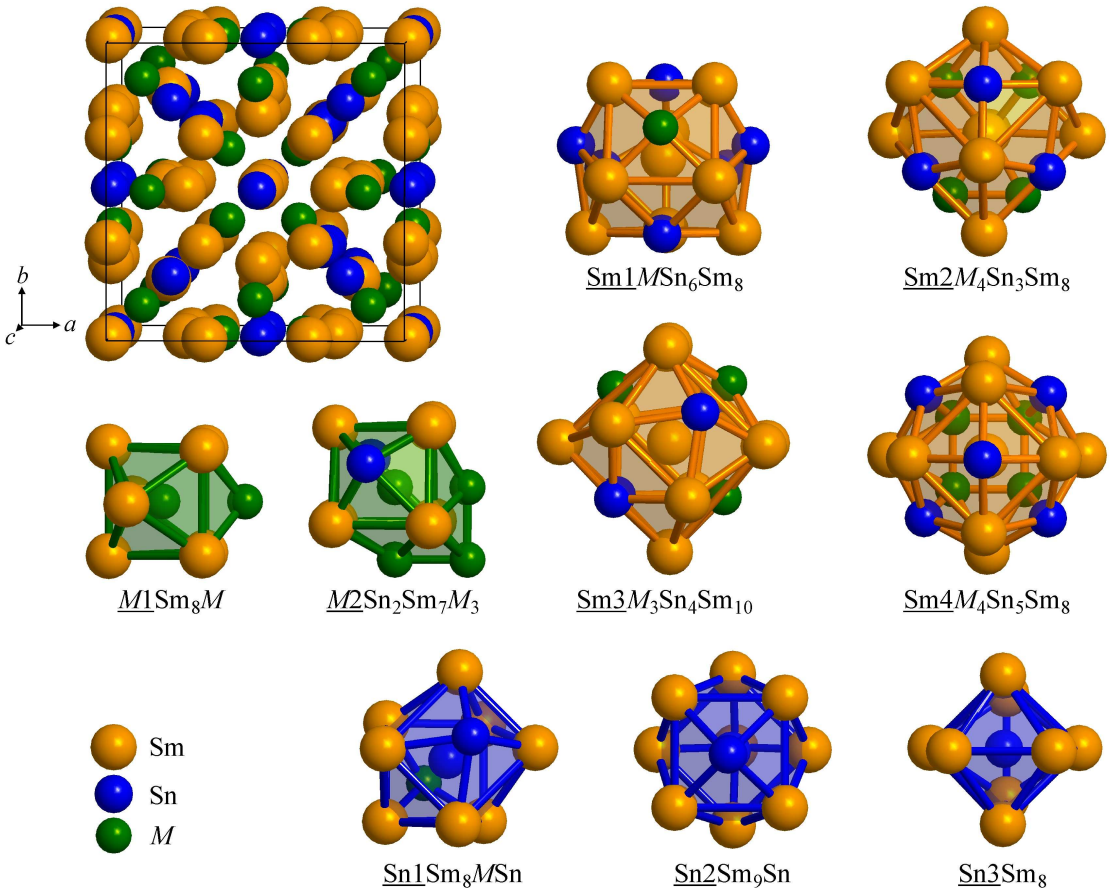

Fig. 3 Unit cell content and coordination polyhedra of the atoms in the structure of $Sm_{11}Ga_{2.30(6)}Sn_{7.70(6)}$.

17-vertex polyhedra: 5-capped pentagonal prisms Sm1*M*Sn$_6$Sm$_8$, 15-vertex Frank-Kasper polyhedra Sm2M_4Sn$_3$Sm$_8$, and 7-capped pentagonal prisms Sm3M_3Sn$_4$Sm$_{10}$ or Sm4M_4Sn$_5$Sm$_8$. The sites *M*1 and *M*2, occupied by statistical mixtures of Ga and Sn atoms, are surrounded by tricapped trigonal prisms, *M*1Sm$_8$*M*, and icosahedra, *M*2Sn$_2$Sm$_7M_3$, respectively. The Sn atoms are characterized by square-antiprismatic coordination: square antiprisms with the square faces capped by additional atoms: Sn1Sm$_8$*M*Sn and Sn2Sm$_9$Sn, and square antiprisms Sn3Sm$_8$.

The ternary compound $Sm_5Ga_{0.76}Sn_{2.24}$

A new ternary compound with the point composition $Sm_5Ga_{0.76(3)}Sn_{2.24(3)}$ was found in the quasi-binary system Sm_5Ga_3–Sm_5Sn_3. Its crystal structure was determined by means of X-ray powder diffraction. An experimental pattern was collected at room temperature on a single-phase sample of composition $Sm_{62.5}Ga_{9.5}Sn_{28}$ on a diffractometer STOE Stadi P (Cu $K\alpha_1$-radiation) in the angular range 2θ = 15-110.625° with a step size of 0.015°. Profile and structure parameters were refined by the Rietveld method using the FullProf Suite software package (Fig. 4). In total, 19 parameters were refined: sample shift, scale factor, 2 cell parameters, 6 profile parameters (pseudo-Voigt profile function), 3 positional parameters, 4 displacement parameters, 1 occupancy and 1 texture parameter. The background was defined using a Fourier filtering technique. Experimental details and crystallographic data for $Sm_5Ga_{0.76(3)}Sn_{2.24(3)}$ are listed in Table 4, atomic coordinates, site occupancies and isotropic displacement parameters in Table 7, interatomic distances and coordination numbers of the atoms in Table 8.

The crystal structure of the ternary compound $Sm_5Ga_{0.76(3)}Sn_{2.24(3)}$ belongs to the structure type Nb_5SiSn_2, which is an ordered ternary derivative of the structure type W_5Si_3. The content of the unit cell and the coordination polyhedra of the atoms $Sm_5Ga_{0.76(3)}Sn_{2.24(3)}$ are shown in Fig. 5. The Sm atoms are coordinated by 15 and 14 atoms forming Frank-Kasper polyhedra of composition Sm1M_2Sn$_4$Sm$_9$ and Sm2Sn$_4$Sm$_{10}$, respectively. The polyhedron of the site *M*, occupied by a statistical mixture of Ga and Sn atoms, is a bicapped square antiprism *M*Sm$_8M_2$. The Sn atoms are surrounded by ten Sm atoms forming SnSm$_{10}$ polyhedra, which can be considered as trigonal prisms with four additional atoms in the equatorial plane. The only homoatomic contacts between *p*-element atoms are Ga-Ga distances (3.0459(3) Å).

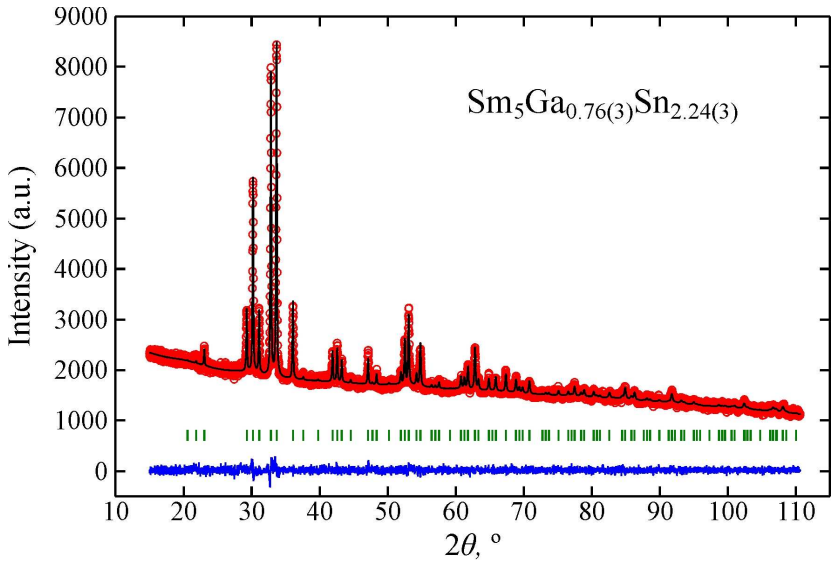

Fig. 4 Experimental (circles), calculated (continuous line) and difference between experimental and calculated (bottom) X-ray powder diffraction patterns of the sample $Sm_{62.5}Ga_{11}Sn_{26.5}$ (Cu $K\alpha_1$-radiation). Vertical bars indicate the positions of the reflections of $Sm_5Ga_{0.76(3)}Sn_{2.24(3)}$.

Table 7 Atomic coordinates, site occupancies and isotropic displacement parameters for $Sm_5Ga_{0.76(3)}Sn_{2.24(3)}$ (*tI*32, *I*4/*mcm*, *a* = 12.1881(14), *c* = 6.0919(7) Å).

Site	Wyckoff position	*x*	*y*	*z*	B_{iso}, Å^2
Sm1	16*k*	0.0806(2)	0.2142(2)	0	1.27(7)
Sm2	4*b*	0	½	¼	0.88(11)
M (0.76(3)Ga+0.24(3)Sn)	4*a*	0	0	¼	0.76(17)
Sn	8*h*	0.16222(17)	0.66222(17)	0	1.31(11)

Table 8 Interatomic distances (δ) and coordination numbers (CN) in the structure of $Sm_5Ga_{0.76(3)}Sn_{2.24(3)}$ (*tI*32, *I*4/*mcm*, *a* = 12.1881(14), *c* = 6.0919(7) Å).

Atoms	δ, Å	CN
Sm1 – 2 *M*	3.178(2)	15
– 1 Sn	3.198(3)	
– 1 Sn	3.321(3)	
– 1 Sm1	3.537(3)	
– 2 Sn	3.5406(17)	
– 2 Sm1	3.6246(19)	
– 2 Sm1	3.818(2)	
– 2 Sm2	3.927(2)	
– 2 Sm1	3.945(3)	
Sm2 – 2 Sm2	3.0459(3)	14
– 4 Sn	3.1840(19)	
– 8 Sm1	3.927(2)	

Atoms	δ, Å	CN
M – 2 *M*	3.0459(3)	10
– 8 Sm1	3.178(2)	
Sn – 2 Sm2	3.1840(19)	10
– 2 Sm1	3.198(3)	
– 2 Sm1	3.321(3)	
– 4 Sm1	3.5406(17)	

Discussion

The ternary system Sm–Ga–Sn is the first *R*–Ga–Sn system for which an isothermal section of the phase diagram has been constructed. The presence of two *p*-elements in the system leads to the formation of three ternary compounds. The non existence of isotypic binary compounds in the systems Sm–Ga and Sm–Sn prevents the formation of continuous solid solutions. However, limited solid solutions form based on some of the binary compounds. On the line with a Sm content of 25 at.%, an extended solid solution $SmGa_xSn_{3-x}$ (x = 0-1.2) with cubic Cu_3Au-type structure, was found. The formation of compounds

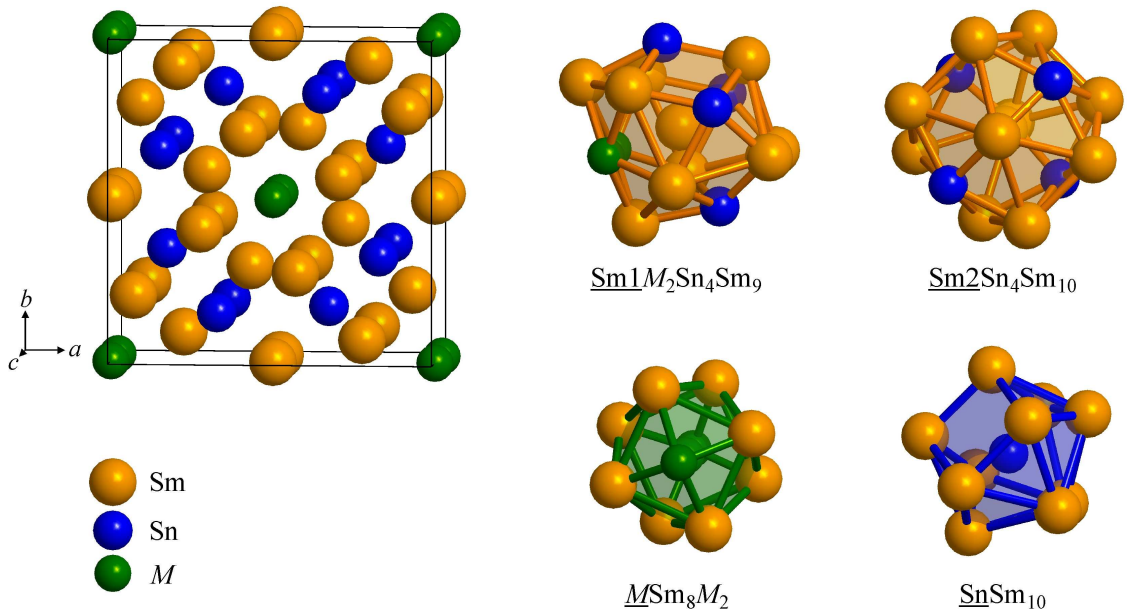

Fig. 5 Unit cell content and coordination polyhedra of the atoms in the structure of $Sm_5Ga_{0.76(3)}Sn_{2.24(3)}$.

with close-packed structures has also been observed in other *R*–Ga–Sn systems. For example, the existence of a few polymorphic modifications of the binary gallides $TbGa_3$ and $DyGa_3$ leads to the formation of ternary phases with close-packed structures in the systems {Tb,Dy}–Ga–Sn at 600°C [1-4]. Addition of Sn to the binary trigallides stabilizes the low-temperature modifications, and other structures, which belong to the structural family of close-packed structures with the general composition AB_3, are also formed.

In the structures of the three ternary compounds found in the system Sm–Ga–Sn at 600°C, a tendency towards ordering of the Ga and Sn atoms is observed. The crystal structures belong to ternary derivatives of binary structure types, which are not represented in the boundary binary systems at 600°C. With decreasing overall content of Ga and Sn, the tendency towards isolated *p*-element atoms in the structures increases. Obviously, the size of the *p*-element atoms (size-factor) has a great influence on the character of the interaction.

Two ternary compounds with partially ordered Pu_3Pd_5-type structure, $Sm_3Ga_{0.80-2.48}Sn_{4.20-2.52}$ [8] and $Dy_3Ga_{2.54}Sn_{2.46}$ [10], have been found in the systems *R*–Ga–Sn up to now. Both phases are characterized by homogeneity ranges along the lines with 37.5 at.% *R*. The homogeneity range of the Sm-containing phase is wider (21 at.% Ga/Sn) than that of the Dy-containing phase (6 at.% Ga/Sn) at 600°C. Moreover, the composition of the ternary compound in the system Dy–Ga–Sn is shifted to a higher Ga content (26-32 at.%), as compared to the Sm-containing compound (10-31 at.%).

The ternary compound $Sm_{11}Ga_{2.30}Sn_{7.70}$ at 600°C can be regarded as a partially ordered, Ga-stabilized derivative of the high-temperature binary stannide $Sm_{11}Sn_{10}$ (structure type $Ho_{11}Ge_{10}$), which exists in the temperature range 1170-1240°C [[1]1]. Ga atoms substitute for Sn atoms on two of the five sites leading to the formation of a partially ordered ternary structure that derives from the structure type $Ho_{11}Ge_{10}$ (*tI*84, *I*4/*mmm*) [28]. Three ordered ternary variants of the structure type $Ho_{11}Ge_{10}$ having the same symmetry and Wyckoff sequence ($n^2mjh^2e^2d$) have been reported till now: $Sc_{11}Al_2Ge_8$ (a = 10.419, c = 14.974 Å) [29], $Sm_{11}In_6Ge_4$ (a = 11.540, c = 16.325 Å) [30], and $Sc_7Cr_4(Cr_{0.4}Si_{0.6})_2Si_8$ (a = 9.757, c = 13.884 Å) [31]. These structures differ by the distribution of the atoms over the different sites in space group *I*4/*mmm* (Table 9). The distribution of the atoms in the structure of $Sm_{11}Ga_{2.30}Sn_{7.70}$ is different from all the above mentioned structures, allowing us to state that it represents a new ternary ordered derivative of the structure type $Ho_{11}Ge_{10}$.

The structure type $Ho_{11}Ge_{10}$ is typical for binary compounds of rare-earth metals with *p*-elements of group IV (Ge, Sn, Pb) [32]. Replacement of 1/5 of the atoms of group IV (Ge) by atoms of group III (Al) leads to the formation of the structure type $Sc_{11}Al_2Ge_8$, in which the Al atoms populate one of the sites in Wyckoff position 8*h*. In the structure of $Sm_{11}Ga_{2.30}Sn_{7.70}$, the Ga atoms (*p*-element of group III) partially substitute for Sn atoms (*p*-element of group IV) on two sites (Wyckoff position 8*j* and 8*h*). Replacement of 3/5 of the atoms of group IV (Ge) by In atoms (group III) leads to the formation of the structure type $Sm_{11}In_6Ge_4$ in which the In atoms

Table 9 Distribution of the chemical elements on the different sites (space group *I*4/*mmm*) in the isopointal structure types $Ho_{11}Ge_{10}$, $Sc_{11}Al_2Ge_8$, $Sm_{11}Ga_{2.30}Sn_{7.70}$, $Sm_{11}In_6Ge_4$, and $Sc_7Cr_4(Cr_{0.4}Si_{0.6})_2Si_8$.

Wyckoff position	Structure type				
	$Ho_{11}Ge_{10}$	$Sc_{11}Al_2Ge_8$	$Sm_{11}Ga_{2.30}Sn_{7.70}$	$Sm_{11}In_6Ge_4$	$Sc_7Cr_4(Cr_{0.4}Si_{0.6})_2Si_8$
16*n* (0 *y z*)	**Ho** *y* = 0.2518 *z* = 0.3103	**Sc** *y* = 0.2507 *z* = 0.3102	**Sm** *y* = 0.2512 *z* = 0.3109	**Sm** *y* = 0.2516 *z* = 0.3110	**Sc** *y* = 0.2536 *z* = 0.3117
16*n* (0 *y z*)	**Ho** *y* = 0.3241 *z* = 0.1025	**Sc** *y* = 0.3356 *z* = 0.1024	**Sm** *y* = 0.3244 *z* = 0.0993	**Sm** *y* = 0.3418 *z* = 0.1003	**Cr** *y* = 0.3231 *z* = 0.1005
16*m* (*x x z*)	**Ge** *x* = 0.2097 *z* = 0.1814	**Ge** *x* = 0.2047 *z* = 0.1711	**Sn** *x* = 0.2076 *z* = 0.1795	**In** *x* = 0.2071 *z* = 0.1708	**Si** *x* = 0.2062 *z* = 0.1672
8*j* (*x* ½0)	**Ge** *x* = 0.1370	**Ge** *x* = 0.1470	**0.42Ga + 0.58Sn** *x* = 0.1380	**Ge** *x* = 0.1519	**Si** *x* = 0.1214
8*h* (*x x* 0)	**Ge** *x* = 0.1197	**Al** *x* = 0.1270	**0.73Ga + 0.27Sn** *x* = 0.1202	**In** *x* = 0.1272	**0.6Si + 0.4Cr** *x* = 0.1221
8*h* (*x x* 0)	**Ho** *x* = 0.3214	**Sc** *x* = 0.3272	**Sm** *x* = 0.3174	**Sm** *x* = 0.3305	**Sc** *x* = 0.3212
4*e* (0 0 *z*)	**Ho** *z* = 0.1606	**Sc** *z* = 0.1688	**Sm** *z* = 0.1598	**Sm** *z* = 0.1643	**Sc** *z* = 0.1625
4*e* (0 0 *z*)	**Ge** *z* = 0.3871	**Ge** *z* = 0.3815	**Ge** *z* = 0.3940	**Ge** *z* = 0.3797	**Si** *z* = 0.3920
4*d* (0 ½ ¼)	**Ge**	**Ge**	**Ge**	**Ge**	**Ge**

populate two sites (16*m* and 8*h*). The rare-earth metal atoms (Sc and Sm) in the structure types $Sc_{11}Al_2Ge_8$, $Sm_{11}Ga_{2.30}Sn_{7.70}$, and $Sm_{11}In_6Ge_4$ populate the same positions as the Ho atoms in the parent structure type $Ho_{11}Ge_{10}$. In the structure type $Sc_7Cr_4(Cr_{0.4}Si_{0.6})_2Si_8$, atoms of the *d*-element Cr substitute for atoms of the rare-earth element Sc (Wyckoff position 16*n*), and for atoms of the *p*-element Si (statistical mixture 0.6Si + 0.4Cr on the site in Wyckoff position 8*h*). In the structure types $Sc_{11}Al_2Ge_8$, $Sm_{11}Ga_{2.30}Sn_{7.70}$, and $Sm_{11}In_6Ge_4$, the atoms of the *p*-elements of group III (Al, Ga, In) preferentially occupy the site in 8*h*, forming M_4 squares around the origin of the tetragonal body-centered unit cell: $\delta_{Al\text{-}Al}$ = 2.647 Å in $Sc_{11}Al_2Ge_8$, $\delta_{M2\text{-}M2}$ = 2.786 Å in $Sm_{11}Ga_{2.30}Sn_{7.70}$, $\delta_{In\text{-}In}$ = 2.936 Å in $Sm_{11}In_6Ge_4$. The atoms occupying the site in 16*m* form dumb-bells: $\delta_{Ge\text{-}Ge}$ = 2.714 Å in $Sc_{11}Al_2Ge_8$, $\delta_{Sn1\text{-}Sn1}$ = 2.920 Å in $Sm_{11}Ga_{2.30}Sn_{7.70}$, $\delta_{In\text{-}In}$ = 2.941 Å in $Sm_{11}In_6Ge_4$. The other *p*-element atoms are isolated in the three structures.

The existence of the ternary compound $Sm_5Ga_{0.76}Sn_{2.24}$ with Nb_5SiSn_2-type structure along the line Sm_5Ga_3–Sm_5Sn_3 makes the system Sm–Ga–Sn similar to related systems containing heavy *d*-metals instead of rare-earth metals. Isotypic phases were recently found in the systems {Zr,Hf}–Ga–{Sn,Sb} [33-35] and Ta–Ga–Sn [36]. The compositions of the Nb_5SiSn_2-type ternary compounds usually contain higher contents of the *p*-element that is heavier and has larger atom size.

Decrease of the overall content of the *p*-elements in the ternary compounds of the system Sm–Ga–Sn is accompanied by a tendency to avoid contacts between *p*-element atoms. In the structure of $Sm_3Ga_{0.80\text{-}2.48}Sn_{4.20\text{-}2.52}$, the Ga and Sn atoms form empty square-pyramidal clusters of ideal composition Ga_3Sn_2 (considering local atom ordering). In the structure of $Sm_{11}Ga_{2.30}Sn_{7.70}$ they form isolated squares M_4 (mostly Ga atoms) and dumb-bells Sn_2, whereas in the structure of $Sm_5Ga_{0.76}Sn_{2.24}$ only linear *M*-*M* chains (mostly Ga atoms) along the crystallographic direction [001] are observed.

Conclusions

The ternary system Sm–Ga–Sn at 600°C is characterized by the existence of limited solid solutions based on the binary compounds $SmSn_3$ (30 at.% Ga), Sm_5Ga_3 (13.3 at.% Sn), Sm_5Sn_3 (~4 at.% Sn), and SmGa (3 at.% Sn), and three ternary compounds, $Sm_3Ga_{0.80\text{-}2.48}Sn_{4.20\text{-}2.52}$ (ternary variant of the structure type Pu_3Pd_5), $Sm_{11}Ga_{2.30(6)}Sn_{7.70}$ (ternary variant of the structure type $Ho_{11}Ge_{10}$), and $Sm_5Ga_{0.76}Sn_{2.24}$ (ternary variant of the structure type W_5Si_3). The ternary phases show partial ordering of Ga and Sn atoms.

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References

[1] V. Fedyna, A. Fedorchuk, Ya. Tokaychuk, R. Gladyshevskii, *Coll. Abstr. 9th Sci. Conf. "Lviv Chemical Readings 2011"*, Lviv, Ukraine, 2011, H80 (in Ukrainian).

[2] Ya. Tokaychuk, A. Fedorchuk, *J. Alloys Compd.* 541 (2012) 23-28.

[3] V. Fedyna, A. Fedorchuk, Ya. Tokaychuk, R. Gladyshevskii, *Book Abstr. XVIII Int. Sem. Phys. Chem. Solids*, Lviv, Ukraine, 2012, p. 37.

[4] V. Fedyna, I. Mokra, A. Fedorchuk, Ya. Tokaychuk, *Visn. Lviv. Univ. Ser. Khim.* 50 (2009) 113-117 (in Ukrainian).

[5] A.V. Maevskii, *Coll. Abstr. VI Meet. Cryst. Chem. Inorg. Coord. Compd.*, Lviv, Ukraine, 1992, p. 196.

[6] T.S. You, Y. Grin, G.J. Miller, *Inorg. Chem.* 46 (2007) 8801-8811.

[7] J.R. Salvador, F. Guo, T.P. Hogan, M.G. Kanatzidis, *Nature* 425 (2003) 702-705.

[8] Ya.O. Tokaychuk, Ya.O. Filinchuk, A.O. Fedorchuk, O.I. Bodak, *Acta Crystallogr. C* 59 (2003) i125-i127.

[9] D.T. Cromer, *Acta Crystallogr. B* 32 (1976) 1930-1932.

[10] V. Fedyna, Ya. Tokaychuk, R. Gladyshevskii, *Chem. Met. Alloys* 5 (2012) 160-165.

[11] T.B. Massalski, H. Okamoto, P.R. Subramanian, L. Kacprzak (Eds.), *Binary Alloy Phase Diagrams*, ASM International, Materials Park (OH), USA, 1990.

[12] S.P. Yatsenko, Y. Grin, O.M. Sitschewitsch, K.A. Tschuntonow, Y.P. Yarmolyuk, *J. Less-Common Met.* 106 (1985) 35-40.

[13] A. Palenzona, E.A. Franceschi, *J. Less-Common Met.* 14 (1968) 47-53.

[14] G.H. Feng, L. Lacroix Orio, M. Tillard, C. Belin, *Acta Crystallogr. C* 61 (2005) i71-i72.

[15] S.P. Yatsenko, R.E. Gladyshevskii, O.M. Sitschewitsch, V.K. Belskii, A.A. Semyannikov, Y. Grin, Y.P. Yarmolyuk, *J. Less-Common Met.* 115 (1986) 17-22.

[16] W. Rieger, E. Parthé, *Monatsh. Chem.* 98 (1967) 1935-1940.

[17] S.P. Yatsenko, A.A. Semyannikov, B.G. Semenov, K.A. Chuntonov, *J. Less-Common Met.* 64 (1979) 185-199.

[18] Yu. Grin, A.O. Fedorchuk, *Russ. Metall.* (5) (1992) 197-200.

[19] M. Tillard, D. Zitoun, C. Belin, *Inorg. Chem.* 48 (2009) 2399-2406.

[20] J. Pelleg, G. Kimmel, D. Dayan, *J. Less-Common Met.* 81(1981) 33-44.

[21] A. Palenzona, F. Merlo, G.B. Bonino, *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend.* 40 (1966) 617-622.

[22] A. Percheron Guégan, *Colloq. Int. C. N. R. S.* 180 (1970) 165-172.

[23] M.L. Fornasini, F. Merlo, G.B. Bonino, *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend.* 50 (1971) 186-196.

[24] M.L. Fornasini, P. Manfrinetti, A. Palenzona, S.K. Dhar, *Z. Naturforsch. B* 58 (2003) 521-527.

[25] F. Weitzer, K. Hiebl, P. Rogl, *J. Solid State Chem.* 98 (1992) 291-300.

[26] I.R. Harris, G.V. Raynor, *J. Less-Common Met.* 9 (1965) 7-19.

[27] J. Rodriguez-Carvajal, *Commission on Powder Diffraction (IUCr), Newsletter* 26 (2001) 12-19.

[28] G.S. Smith, Q.C. Johnson, A.G. Tharp, *Acta Crystallogr.* 23 (1967) 640-644.

[29] J.T. Zhao, E. Parthé, *Acta Crystallogr. C* 47 (1991) 4-6.

[30] Yu.B. Tyvanchuk, K.Yu. Miliyanchuk, V.I. Zaremba, J. Stepien Damm, Ya.M. Kalychak, *Ukr. Khim. Zh.* 67(11) (2001) 15-18 (in Ukrainian).

[31] B.Ya. Kotur, O.I. Bodak, V.E. Zavodnik, *Sov. Phys. Crystallogr.* 30 (1985) 521-523.

[32] P. Villars, K. Cenzual (Eds.), *Pearson's Crystal Data – Crystal Structure Database for Inorganic Compounds*, ASM International, Materials Park (OH), USA, Release 2014/15.

[33] I. Voznyak, Ya. Tokaychuk, R. Gladyshevskii, *Coll. Abstr. XI Int. Conf. Cryst. Chem. Intermet. Compd.*, Lviv, Ukraine, 2010, p. 135.

[34] I. Voznyak, Ya. Tokaychuk, R. Gladyshevskii, *Chem. Met. Alloys* 4 (2011) 175-187.

[35] I. Tokaychuk, Ya. Tokaychuk, R. Gladyshevskii, *Chem. Met. Alloys* 6 (2013) 75-80.

[36] I. Tokaychuk, Ya. Tokaychuk, R. Gladyshevskii, *Visn. Lviv. Univ., Ser. Khim.* 54 (2013) 110-115 (in Ukrainian).