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THE TERNARY SYSTEM Gd−Ge−Sn AT 600°C

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The isothermal section at 600°C of the phase diagram of the ternary system Gd−Ge−Sn was constructed in the whole concentration range, based on X-ray powder diffraction and energy-dispersive X-ray spectroscopy. The formation of two continuous solid solutions, $Gd_5Ge_{4-x}Sn_x$ (x=0−4, structure type Sm_5Ge_4, Pearson symbol $oP36$, space group $Pnma$, a=7.8565(12)−8.040(2), b=14.812(2)−15.552(3), c=7.7781(12)−8.201(2) Å) and $Gd_5Ge_{3-x}Sn_x$ (x=0−3, structure type Mn_5Si_3, $hP16$, $P6_3/mcm$, a=8.5702(8)−9.0306(13), c=6.4305(5)−6.5941(10) Å), and limited solid solutions based on the binary compounds $Gd_{11}Ge_{10}$ (6 at.% Sn), $GdSn_3$ (5.5 at.% Ge), Gd_3Sn_7 (2 at.% Ge), $GdSn_2$ (5 at.% Ge), and $Gd_{11}Sn_{10}$ (3.5 at.% Ge) was established. Three following ternary compounds were found in the system at 600°C: $Gd_2Ge_{3.84}Sn_{0.92}$, $GdGe_{0.75-0.85}Sn_{1.25-1.15}$, and $Gd_2Ge_{2.91}Sn_{0.80}$. The detailed crystal structures of two of them were refined on X-ray powder diffraction data: $GdGe_{0.75-0.85}Sn_{1.25-1.15}$, structure type $ScCo_{0.25}Si_{1.75}$, $oS12$, $Cmcm$, a=4.3206(4)−4.3035(4), b=16.4824(15)−16.4433(14), c=4.1270(4)−4.0961(4) Å and $Gd_2Ge_{2.91}Sn_{0.80}$, structure type $Gd_2Ge_{3.38}Bi_{0.42}$, $oS32$, $Cmcm$, a=4.0445(6), b=30.473(5), c=4.1694(6) Å. The third compound, $Gd_2Ge_{3.84}Sn_{0.92}$, adopts the structure type $Nd_2Ge_{3.55}Sn_{1.24}$. The crystal structures are closely related and are built from layers of Gd_6 trigonal prisms centered by Ge atoms (or in part by Sn atoms) and square-mesh nets of Sn atoms (or in part Ge atoms), which alternate along the crystallographic direction [010]. Partial disorder of Ge and Sn atoms is observed.

Keywords: gadolinium, germanium, tin, X-ray powder diffraction, phase diagram, solid solution, ternary compound, crystal structure.

Introduction

The phase diagram of the ternary system Gd−Ge−Sn has previously not been investigated. The existence and crystal structures of two ternary compounds have been reported [1]: $GdGe_{0.83}Sn_{1.17}$ (structure type (ST) $ScCo_{0.25}Si_{1.75}$, Pearson symbol (PS) $oS12$, space group (SG) $Cmcm$, a=4.3005, b=16.441, c=4.0944 Å) [2] and $Gd_2Ge_{2.94}Sn_{0.82}$ (own ST, PS $oS32$, SG $Cmcm$, a=4.2248, b=30.451, c=4.0013 Å) [3]. The structures were determined on single crystals grown by the flux method in molten Sn. Recently, we reported the crystal structure of another ternary compound in the same system, $Gd_2Ge_{3.84}Sn_{0.92}$, with $Nd_2Ge_{3.55}Sn_{1.24}$-type structure (PS $oS40$, SG $Cmcm$, a=4.0434, b=35.284, c=4.1724 Å) [4]. The structures of the three ternary compounds are characterized by partial disorder of Ge and Sn atoms. Despite the presence of sites with mixtures of Ge and Sn atoms, no evidence for the existence of significant homogeneity ranges was reported. Ternary compounds with $ScCo_{0.25}Si_{1.75}$-type structures have also been observed in other ternary R−Ge−Sn systems: R=Y, Tb, Dy, Ho, Er [2]; ternary compounds with $Nd_2Ge_{3.55}Sn_{1.24}$-type structure have been reported with R=Nd and Sm [3], and a compound isotypic to $Gd_2Ge_{2.94}Sn_{0.82}$, $Tb_2Ge_{2.94}Sn_{0.80}$, is known [3].

The binary systems Gd−Ge, Gd−Sn, and Ge−Sn that delimit the ternary system Gd−Ge−Sn have been studied widely, and the corresponding phase diagrams constructed in the whole concentration range [5]. In total, the formation and crystal structures of 12 binary germanides have been reported in the Gd−

Ge system and 7 binary stannides in the system Gd−Sn [1]. Among them, there are three pairs of isostructural compounds, $Gd_{11}Ge_{10}$ and $Gd_{11}Sn_{10}$ (ST $Ho_{11}Ge_{10}$, PS *tI*84, SG *I4/mmm*), Gd_5Ge_4 and Gd_5Sn_4 (ST Sm_5Ge_4, PS *oP*36, SG *Pnma*), Gd_5Ge_3 and Gd_5Sn_3 (ST Mn_5Si_3, PS *hP*16, SG $P6_3/mcm$), which is a prerequisite for the possible formation of continuous solid solutions in the ternary system Gd−Ge−Sn. No binary compounds are formed in the system Ge−Sn, which is characterized by a eutectic reaction L↔Ge+β-Sn at 231.1^0C and 99.97 at.% Sn. At the temperature of our investigation (600^0C), tin is liquid, *i.e.* a liquid region is present in the Sn-rich corner of the isothermal section of the phase diagram.

In this work, we present the results of an experimental investigation of the phase equilibria in the ternary system Gd−Ge−Sn at 600^0C in the whole concentration range, and crystallographic parameters derived from X-ray powder diffraction for the ternary compounds.

Experimental

72 two- and three-component alloys were synthesized from high-purity metals (Gd≥99.8 wt.%, Ge≥99.99 wt.%, Sn≥99.9 wt.%) by arc melting under argon atmosphere, using a water-cooled copper hearth, a tungsten electrode and Ti sponges as a getter. To achieve homogeneity, the samples were melted twice. After the synthesis, the alloys were wrapped into tantalum foil, sealed in quartz ampoules under vacuum, and annealed at 600^0C for 1 month. Finally, the ampoules with the samples were quenched into cold water. The mass losses, which were controlled at all stages of the synthesis, did not exceed 1% of the total mass, which was approximately 1 g for each alloy.

Phase analysis and structure refinements were performed using X-ray powder diffraction data collected at room temperature on diffractometers DRON-2.0M (FeKa-radiation, angular range $10−20^0≤2θ≤120−140^0$, step 0.05^0) and STOE Stadi P (CuKa$_1$-radiation, angular range $4^0≤2θ≤106^0$, step 0.015^0). The profile and structural parameters were refined by the Rietveld method, using the FullProf Suite program package [6]. Some phase equilibria and the compositions were additionally analyzed by energy-dispersive X-ray spectroscopy (EDX), performed on a scanning electron microscope TESCAN Vega3 LMU equipped with an energy dispersion X-ray analyzer Oxford Instruments Aztec ONE with a detector X-Max^{N}20 or on a raster electron microscope REMMA-102-02 equipped with an energy dispersion X-ray spectrometer EDAR.

Results and discussion

18 two-component alloys were synthesized to confirm the existence, compositions, and crystal structures of the binary compounds in the Gd−Ge and Gd−Sn systems at 600^0C, due to ambiguous literature data on the compositions and polymorphism of some phases. By comparing the experimental X-ray powder diffraction patterns of the synthesized alloys with patterns calculated for the binary compounds, the existence of 13 binaries was confirmed at 600^0C: Gd_3Ge_5 (ST Y_3Ge_5), $GdGe_{1.5}$ (ST AlB_2), Gd_3Ge_4 (ST Gd_3Ge_4), GdGe (ST TlI), $Gd_{11}Ge_{10}$ (ST $Ho_{11}Ge_{10}$), Gd_5Ge_4 (ST Sm_5Ge_4), Gd_5Ge_3 (ST Mn_5Si_3), $GdSn_3$ (ST Cu_3Au), Gd_3Sn_7 (ST Gd_3Sn_7), $GdSn_2$ (ST $ZrSi_2$), $Gd_{11}Sn_{10}$ (ST $Ho_{11}Ge_{10}$), Gd_5Sn_4 (ST Sm_5Ge_4), and Gd_5Sn_3 (ST Mn_5Si_3).

The isothermal section of the phase diagram of the ternary system Gd−Ge−Sn at 600^0C was constructed in the whole concentration range (Fig. 1). It consists of 17 single-phase, 32 two-phase, and 16 three-phase fields. The ternary phase $GdGe_{0.75−0.85}Sn_{1.25−1.15}$ ($GdGe_{1−x}Sn_{1+x}$, x=0.15(4)−0.25(7) at 600^0C) forms the largest number of equilibria (8). At 600^0C, tin is liquid, and the boundary of the liquid phase in the ternary system was extrapolated from its limits in the binary systems: 10 at.% in the system Gd−Sn and 20 at.% in the system Ge−Sn. Three following phases are in equilibrium with the liquid: Ge, the solid solution based on $GdSn_3$, and the ternary compound $GdGe_{0.75−0.85}Sn_{1.25−1.15}$.

Two continuous solid solutions are formed in the system: the first one between the Sm_5Ge_4-type (PS *oP*36, SG *Pnma*) binary compounds Gd_5Ge_4 and Gd_5Sn_4 and the second one between the Mn_5Si_3-type (PS *hP*16, SG $P6_3/mcm$) compounds Gd_5Ge_3 and Gd_5Sn_3. The cell parameters of the continuous solid solutions $Gd_5Ge_{4−x}Sn_x$ (x=0−4) and $Gd_5Ge_{3−x}Sn_x$ (x=0−3) were refined from X-ray powder diffraction data of eight and five samples containing 55.6 and 62.5 at.% Gd, respectively. The composition dependencies of the cell parameters *versus* the Sn content in $Gd_5Ge_{4−x}Sn_x$ (x=0−4) and $Gd_5Ge_{3−x}Sn_x$ (x=0−3) are shown in Fig. 2. Both solid solutions retain the structures of the limiting binary compounds throughout the composition range. The cell parameters increase with increasing Sn content (a=7.8565(12)−8.040(2), b=14.812(2)−15.552(3), c=7.7781(12)−8.201(2) Å for $Gd_5Ge_{4−x}Sn_x$ (x=0−4) and a=8.5702(8)−9.0306(13), c=6.4305(5)−6.5941(10) Å for $Gd_5Ge_{3−x}Sn_x$ (x=0−3)), which is in agreement with the larger atomic radius of Sn, compared to the atomic radius of Ge.

The binary gadolinium germanide $Gd_{11}Ge_{10}$ dissolves 6 at.% Sn, and the binary gadolinium stannides $GdSn_3$, Gd_3Sn_7, $GdSn_2$, and $Gd_{11}Sn_{10}$ can dissolve up to 5.5, 2, 5, and 3.5 at.% Ge, respectively,

at 600⁰C, forming solid solutions characterized by constant Gd concentrations. The other binary compounds do not dissolve noticeable amounts of the third component.
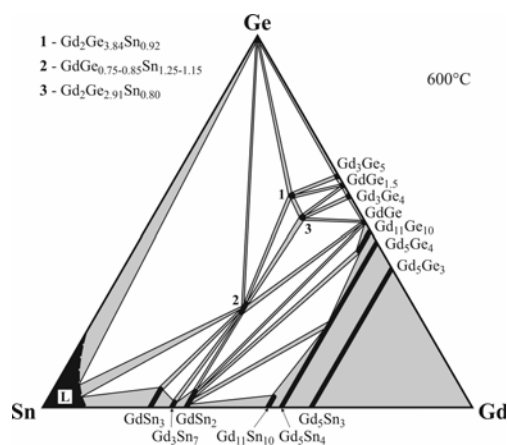

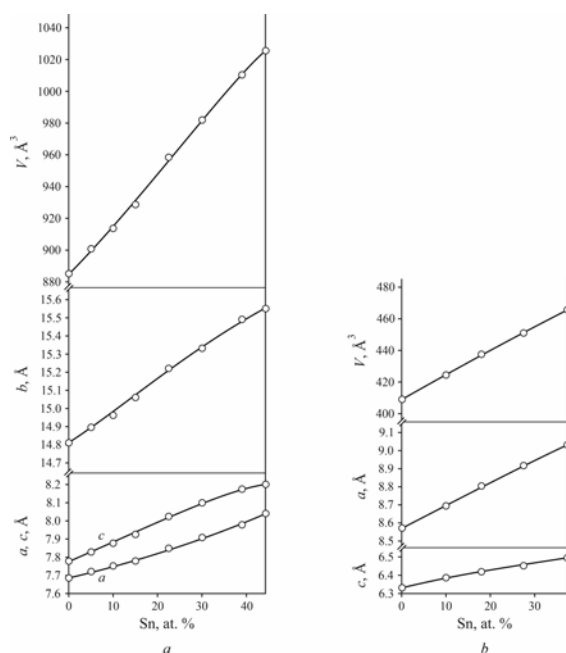Fig. 1. Isothermal section of the phase diagram of the ternary system Gd−Ge−Sn at 600⁰C

Fig. 2. Cell parameters as a function of the Sn content in the continuous solid solutions $Gd_5Ge_{4-x}Sn_x$ ($x=0-4$) (*a*) and $Gd_5Ge_{3-x}Sn_x$ ($x=0-3$) (*b*)

Three ternary compounds exist in the system Gd−Ge−Sn at 600⁰C. Their crystallographic data are summarized in Table 1. Detailed results of the crystal structure determination of the ternary compound $Gd_2Ge_{3.84}Sn_{0.92}$ were reported elsewhere [4]. For the ternary compound with $ScCo_{0.25}Si_{1.75}$-type structure, a certain homogeneity range was found at 600⁰C, $GdGe_{0.75(7)-0.85(4)}Sn_{1.25(7)-1.15(4)}$. The existence of a third ternary compound, $Gd_2Ge_{2.91}Sn_{0.80}$, was confirmed, however the crystal structure refined in this work (ST $Gd_2Ge_{3.38}Bi_{0.42}$) differs from the structure reported for $Gd_2Ge_{2.94}Sn_{0.82}$ in ref. [3].

A detailed structure analysis of alloys along the line with 33.3 at.% Gd showed that substitution of Ge atoms for Sn atoms in $GdSn_2$ (ST $ZrSi_2$, PS $oS12$, SG *Cmcm*, $a=4.4283(5)$, $b=16.412(2)$, $c=4.3221(5)$ Å) leads to the formation of a solid solution $GdGe_{0-0.15}Sn_{2-1.85}$ (0−5 at.% Ge). The incorporation of Ge is accompanied by a decrease in the cell parameters ($a=4.4023(6)$, $b=16.399(3)$ $c=4.2795(6)$ Å for $GdGe_{0.15}Sn_{1.85}$). Further increase of the Ge content leads to the formation of a two-phase field where the solid solution is in equilibrium with a ternary compound $GdGe_{1-x}Sn_{1+x}$ with the structure type $ScCo_{0.25}Si_{1.75}$. According to the X-ray diffraction data, this ternary phase has a homogeneity range $GdGe_{0.75-0.85}Sn_{1.25-1.15}$, assuming partial substitution of Ge atoms for Sn atoms. It should be noted that the structure type $ScCo_{0.25}Si_{1.75}$ is a ternary substitution derivative of $ZrSi_2$, with preferential substitution on one site, and the existence of a broad homogeneity range extending from the binary phase at high temperature cannot be excluded. The crystallographic parameters of the ternary phase were refined by the Rietveld method for the two limiting compositions, using X-ray powder diffraction patterns (diffractometer DRON-2.0M) of the samples $Gd_{33.3}Ge_{28.7}Sn_{38}$ and $Gd_{33.3}Ge_{22}Sn_{44.7}$, respectively (Fig. 3). The sample $Gd_{33.3}Ge_{22}Sn_{44.7}$ contains two phases, one corresponding to the Sn-rich limiting composition of the ternary compound $GdGe_{0.75-0.85}Sn_{1.25-1.15}$ (95(1) wt.%) and the second one the limiting composition of the solid solution $GdGe_{0-0.15}Sn_{2-1.85}$ (5(1) wt.%) based on binary $ZrSn_2$. The sample $Gd_{33.3}Ge_{28.7}Sn_{38}$ contains a single phase,

Table 1

Crystallographic data for the ternary compounds in the system Gd−Ge−Sn at 600⁰C

Compound	Structure type	Pearson symbol	Space group	Cell parameters, Å		
				a	*b*	*c*
$Gd_2Ge_{3.84}Sn_{0.92}$	$Nd_2Ge_{3.55}Sn_{1.24}$	$oS40$	*Cmcm*	4.0434(6)	35.284(6)	4.1724(6)
$GdGe_{0.75-0.85}Sn_{1.25-1.15}$	$ScCo_{0.25}Si_{1.75}$	$oS12$	*Cmcm*	4.3206(4)- 4.3035(4)	16.4824(15)- 16.4433(14)	4.1270(4)– 4.0961(4)
$Gd_2Ge_{2.91}Sn_{0.80}$	$Gd_2Ge_{3.38}Bi_{0.42}$	$oS32$	*Cmcm*	4.0445(6)	30.473(5)	4.1694(6)

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which corresponds to the established Ge-rich limiting composition of the ternary compound, $GdGe_{0.85}Sn_{1.15}$. Atom coordinates and isotropic displacement parameters for the two compositions of the $GdGe_{0.75-0.85}Sn_{1.25-1.15}$ compound are given in Table 2. The compositions were confirmed by EDX analysis (raster electron microscope REMMA-102-02).
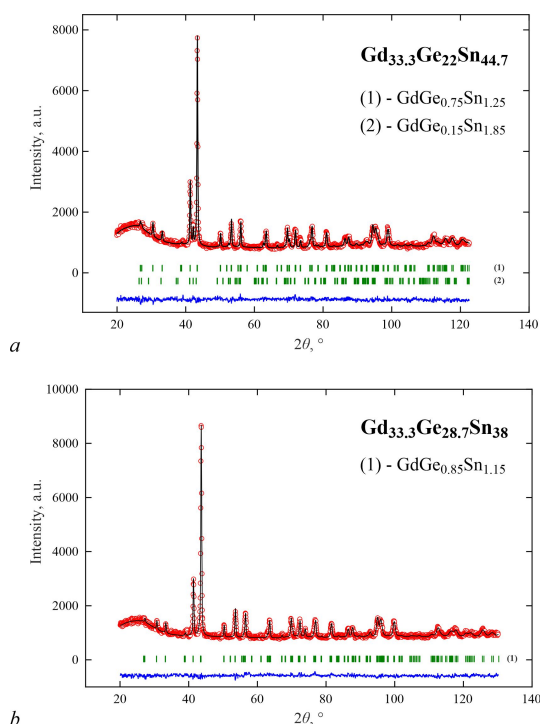

a

b

Fig. 3. Experimental (circles), calculated (continuous line) and difference between experimental and calculated (bottom) X-ray powder diffraction patterns of the samples $Gd_{33.3}Ge_{22}Sn_{44.7}$ (*a*) and $Gd_{33.3}Ge_{28.7}Sn_{38}$ (*b*) (FeKa-radiation); vertical bars indicate the positions of the reflections of the individual phases

The structure of the ternary compound $GdGe_{0.75-0.85}Sn_{1.25-1.15}$ is characterized by partial disorder of the *p*-element atoms Ge and Sn and by three crystallographically independent sites in Wyckoff position 4*c*: one site is occupied by Gd atoms, one site by Sn atoms, and one site by a statistical mixture of Ge and Sn atoms. The content of the unit cell and the coordination polyhedra in the structure of $GdGe_{0.85}Sn_{1.15}$ are shown in Fig. 4. The Gd atoms center 16-vertex polyhedra $\underline{Gd}M_6Sn_4Gd_6$, which may be seen as a square antiprism M_4Sn_4 with eight additional atoms, six Gd and two *M* atoms. Site *M*, occupied by a statistical mixture of Ge and Sn atoms in the ratio 0.85:0.15, is surrounded by a 2-capped trigonal prism $\underline{M}Gd_6M_2$. The closest coordination environment of the Sn atoms consists of 4 Gd and 4 Sn atoms, which form an 8-vertex polyhedron $\underline{Sn}Gd_4Sn_4$ called a *gyrobifastigium*, built by joining two mutually perpendicular trigonal prisms through a square face. The shortest interatomic distance between the *M* and Sn sites is 3.893(9) Å and 3.749(6) Å for $GdGe_{0.75}Sn_{1.25}$ and $GdGe_{0.85}Sn_{1.15}$, respectively.

With the aim of confirming its existence at 600⁰C and refining the crystal structure of the ternary compound $Gd_2Ge_{2.94}Sn_{0.82}$ reported earlier [3], a sample of composition $Gd_{34.5}Ge_{51.5}Sn_{14}$ was synthesized. The EDX analysis (scanning electron microscope TESCAN Vega3 LMU) indicated the formation of a ternary compound of composition $Gd_2Ge_{2.89(2)}Sn_{0.80(2)}$ $(Gd_{35.2(4)}Ge_{50.8(4)}Sn_{14.0(3)})$. The X-ray powder diffraction pattern (STOE Stadi P diffractometer) was successfully fitted with the space group *Cmcm* and the cell parameters $a=4.04449(2)$, $b=30.4731(2)$, $c=4.16938(2)$ Å, using the Le Bail-fit procedure implemented in the FullProf Suite program package.

Table 2

Atomic coordinates, site occupancies and isotropic displacement parameters for $GdGe_{0.75-0.85}Sn_{1.25-1.15}$ (structure type $ScCo_{0.25}Si_{1.75}$, Pearson symbol *oS*12, space group *Cmcm*)

Site	Wyckoff position	x	y	z	B_{iso}, Å^2
$GdGe_{0.75(7)}Sn_{1.25(7)}$: $a=4.3206(4)$, $b=16.4824(15)$, $c=4.1270(4)$ Å; $R_B=0.0860$, $R_F=0.0992$, $R_p=0.0393$, $R_{wp}=0.0527$, $\chi^2=1.98$; phase composition from EDX: $GdGe_{0.77(5)}Sn_{1.23(5)}$					
Gd	4*c*	0	0.4078(4)	1/4	0.36(16)
M (0.75(7)Ge+0.25(7)Sn)	4*c*	0	0.0506(5)	1/4	1.2(4)
Sn	4*c*	0	0.7491(4)	1/4	1.13(18)
$GdGe_{0.85(4)}Sn_{1.15(4)}$: $a=4.3035(4)$, $b=16.4433(14)$, $c=4.0961(4)$ Å; $R_B=0.0641$, $R_F=0.0684$, $R_p=0.0346$, $R_{wp}=0.0444$, $\chi^2=1.06$; phase composition from EDX: $GdGe_{0.86(5)}Sn_{1.14(5)}$					
Gd	4*c*	0	0.4033(3)	1/4	0.51(5)
M (0.85(4)Ge+0.15(4)Sn)	4*c*	0	0.0546(3)	1/4	1.11(6)
Sn	4*c*	0	0.7544(3)	1/4	1.03(11)

The refined cell parameters differ from those reported in ref. [3] (a=4.2248, b=30.451, c=4.0013 Å, c/a<1), whereas the composition is the same. Attempts to refine the crystallographic parameters using the structural model reported in ref. [3] were not successful. Therefore, the structure of the ternary compound was solved by global optimization in direct space by simulated annealing (in parallel tempering mode) using the program FOX [7] and then refined by the Rietveld method using the FullProf Suite program package. In addition to the ternary compound, the sample $Gd_{34.5}Ge_{51.5}Sn_{14}$ contained traces of elementary Sn. For the main phase, the following parameters were refined: scale factor, three cell parameters, 2θ-shift parameter, six profile parameters (pseudo-Voigt profile), eight positional, five displacement, three occupational parameters, and one texture parameter. The admixture phase $Sn_{1-x}(Ge,Gd)_x$ (4.1(2) wt.%), was modeled with individual scale factor and two cell parameters, while the profile parameters were constrained to be the same for both phases. In total 31 parameters were included in the final cycles of the refinement. The background was defined using the polynomial function and Fourier filtering technique. Experimental, calculated and difference X-ray powder diffraction patterns are presented in Fig. 5; experimental details and crystallographic data for the individual phases in the sample $Gd_{34.5}Ge_{51.5}Sn_{14}$ are listed in Table 3.
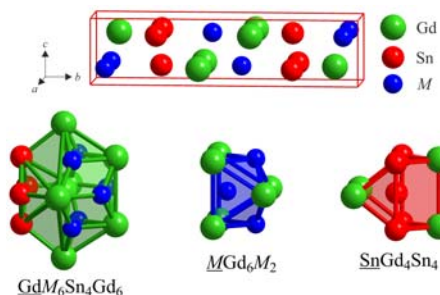

Fig. 4. Cell content and coordination polyhedra in the structure of $GdGe_{0.85}Sn_{1.15}$

The crystal structure of the ternary compound corresponds to the structural model firstly reported for the ternary compound $Gd_2Ge_{3.38}Bi_{0.42}$ (PS $oS32$, SG *Cmcm*, a=4.0404, b=30.444, c=4.1629 Å) [8]. Atom coordinates, isotropic displacement parameters, and site occupancies for $Gd_2Ge_{2.91(4)}Sn_{0.80(2)}$ are given in Table 4. The structure is characterized by two sites in Wyckoff position $4c$ occupied by Gd atoms, four sites occupied exclusively by Ge atoms, and one site occupied by a statistical mixture of Ge and Sn atoms in the ratio of 0.20:0.80. The main features of the refined structure are almost complete ordering of the Ge and Sn atoms, and positional disorder of Ge atoms. The best agreement was observed when the

third Ge site in Wyckoff position $4c$ (site Ge3B, occupied on 41%) was in part split into a site in Wyckoff position $8f$ (site Ge3A, occupied on 15%). The refined separation within the split site Ge3A is 0.908(1) E and the distance between sites Ge3A and Ge3B is 0.734(9) Å. As a consequence, the occupancy of site Ge3A cannot exceed 50% and the total occupancy of sites Ge3A and Ge3B cannot exceed the sum 2×occ.(Ge3A)+1×occ.(Ge3B)=1, i.e. neighboring positions of these sites cannot be occupied simultaneously. Full occupation of site Ge3B, or 50% occupation of site Ge3A, would correspond to the formula $Gd_2(Sn,Ge)Ge_3$. The occurrence of ~30% Ge vacancies distributed over Ge3B and Ge3A gives the actual composition $Gd_2(Sn_{0.80(2)}Ge_{0.20(2)})Ge_{2.71(5)}$ and is assumed to explain the partial displacement of Ge atoms towards neighboring unoccupied positions. The cell content of the ternary compound $Gd_2Ge_{2.91}Sn_{0.80}$ is shown in Fig. 6.
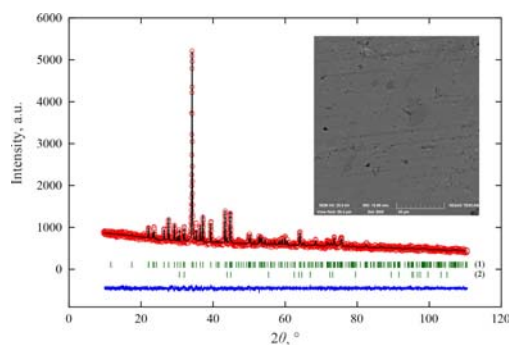

Fig. 5. Experimental (circles), calculated (continuous line) and difference between experimental and calculated (bottom) X-ray powder diffraction patterns of the sample $Gd_{34.5}Ge_{51.5}Sn_{14}$ ($CuKa_1$-radiation). Vertical bars indicate the positions of reflections for $Gd_2Ge_{2.91}Sn_{0.80}$ (1) and Sn (2). The inset shows a microphotograph of the polished surface of the sample in a beam of secondary electrons (TESCAN Vega3 LMU)

Interatomic distances, coordination numbers and coordination polyhedra of the atoms in the structure of $Gd_2Ge_{2.91}Sn_{0.80}$ are presented in Table 5. The atoms in site Gd1 center 20-vertex polyhedra of composition $\underline{Gd1}Ge_{12}Gd_8$, represented by pentagonal prisms Ge_{10} capped by two Ge and eight Gd atoms. The Gd2 atoms center square antiprisms Ge_4M_4 with eight additional atoms, six Gd and two Ge, forming 16-vertex polyhedra $\underline{Gd2}Ge_6M_4Gd_6$. The coordination polyhedra of the Ge atoms are trigonal prisms Gd_6 with two (Ge2) or three (Ge1, Ge3A, and Ge3B) additional Ge atoms capping the rectangular faces of the prisms. The closest coordination environment of site M, hosting all the Sn and part of the Ge atoms, consists of four Gd and four M atoms, forming a *gyrobifastigium* $\underline{M}Gd_4M_4$, similar to the ones described

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above, by joining two trigonal prisms M_4Gd_2 through the square faces M_4. The polyhedra around sites Gd1, Ge1, Ge3A, and Ge3B are variable due to the positional disorder of the Ge atoms. The shortest distances in the structure are Ge−Ge contacts, indicating strong interaction between the Ge atoms. The shortest Ge−M distance is 3.757(11) Å, but Ge−Sn contacts should occur for Ge atoms (M−M distance) replacing Sn on the M site.

The structure of the ternary compound $Gd_2Ge_{2.91}Sn_{0.80}$ determined in this work is closely related to the structure of $Gd_2Ge_{2.94}Sn_{0.82}$ reported in ref. [3]. Both structures belong to the family of linear intergrowth structures composed by AlB_2- and CaF_2-type slabs and contain triple layers of trigonal prisms, separated by double slabs of «half octahedral» [9]. The members of this family are mainly orthorhombic structures with two short cell parameters (~4 Å, here a and c) and a much larger third parameter (stacking direction, here b). The structures type $Gd_2Ge_{3.38}Bi_{0.42}$, and $Gd_2Ge_{2.94}Sn_{0.82}$ reported in ref. [3], shown together in Fig. 7, both contain triple AlB_2-type slabs alternating with double CaF_2-type slabs. However, they differ in the way consecutive AlB_2-type layers within the triple slab are stacked. In $Gd_2Ge_{3.38}Bi_{0.42}$, the layers are stacked so that all prism axes are parallel, as in the parent structure AlB_2, whereas in $Gd_2Ge_{2.94}Sn_{0.82}$ the prism axes in consecutive layers are mutually perpendicular, as in α-$ThSi_2$. The binary structure type $DyGe_{1.85}$ also contains AlB_2-type slabs with parallel prism axes, alternating with double CaF_2-type layers, but was refined in space group $Cmc2_1$ (PS $oS24$). In addition, vacancies were detected in the central layer in this structure. Another structure type defined on a binary germanide is also built from AlB_2- and CaF_2-slabs in the ratio 3:2, $TbGe_2$ (PS $oS24$, SG $Cmmm$). In this structure, consecutive AlB_2-type slabs are stacked as in α-$ThSi_2$, but an important difference occurs in the CaF_2-type slabs. In $TbGe_2$, the two neighboring CaF_2-type layers are merged so that a mirror plane appears at the interface, whereas in all the other structures there is a glide plane at the interface.

Both structural models proposed for $Gd_2Ge_{2.91}Sn_{0.80}$ ($Gd_2Ge_{2.94}Sn_{0.82}$) are characterized by Ge vacancies and positional disorder of Ge atoms in the central prism layers. In both structures, the disorder was modeled by splitting the Ge-atom position in the direction perpendicular to the prism axes. Such disorder can be explained by a shift from the ideal positions to compensate for ~30% of vacancies in the Ge-atom network, as it has been described for another related structure type, $PrGe_{1.91}$ [10]. Since the crystal structure of the ternary compound $Gd_2Ge_{2.94}Sn_{0.82}$ [3] was determined on a single crystal grown at high temperature (1100^0C) in molten Sn, and the structure of $Gd_2Ge_{2.91}Sn_{0.80}$ was determined on a bulk sample homogenized at 600^0C, polymorphism cannot be excluded.

Table 3

Experimental details and crystallographic data for the individual phases in the sample $Gd_{34.5}Ge_{51.5}Sn_{14}$

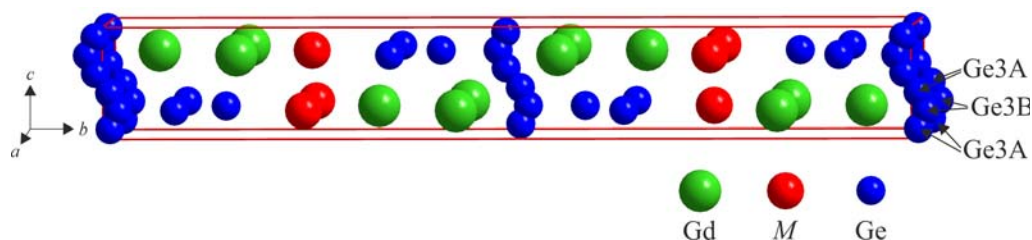| Phase		$Gd_2Ge_{2.91(4)}Sn_{0.80(2)}$	Sn
Content, wt.%		95.9(5)	4.1(2)
Structure type		$Gd_2Ge_{3.38}Bi_{0.42}$	Sn
Pearson symbol		$oS32$	$tI4$
Space group		$Cmcm$	$I4_1/amd$
Cell parameters:	a, Å	4.0445(6)	5.8286(11)
	b, Å	30.473(5)	−
	c, Å	4.1694(6)	3.1816(7)
Cell volume V, Å^3		513.87(14)	108.09(4)
Formula units per cell Z		4	4
Density D_X, g cm^{-3}		8.026	7.294
Preferred orientation: value / [direction]		0.917(9) / [101]	−
Reliability factors:	R_B	0.0752	−
	R_F	0.0767	−
Profile parameters:	U	0.321(9)	
	V	0.036(6)	
	W	0.061(4)	
Shape parameter		0.807(15)	
Asymmetry parameters		0.094(10), 0.0105(19)	
Reliability factors:	R_p	0.0330	
	R_{wp}	0.0419	
	χ^2	1.11	

Fig. 6. Cell content of the ternary compound $Gd_2Ge_{2.91}Sn_{0.80}$

Table 4

Atomic coordinates, site occupancies and isotropic displacement parameters for $Gd_2Ge_{2.91(4)}Sn_{0.80(2)}$ ($Gd_2Ge_{3.38}Bi_{0.42}$, $oS32$, $Cmcm$, a=4.0445(6), b=30.473(5), c=4.1694(6) Å)

Site	Wyckoff position	x	y	z	B_{iso}, Å^2
Gd1	4c	0	0.4368(2)	1/4	0.64(3)
Gd2	4c	0	0.83393(17)	1/4	0.62(3)
Ge1	4c	0	0.0887(9)	1/4	1.02(8)
Ge2	4c	0	0.6444(4)	1/4	1.11(6)
Ge3A (occ.=0.15(2))	8f	0	0.0086(12)	0.0887(18)	1.0
Ge3B (occ.=0.41(3))	4c	0	0.0183(7)	1/4	1.0
M (0.20(2)Ge+0.80(2)Sn)	4c	0	0.2483(2)	1/4	0.86(3)

$Gd_2Ge_{2.91}Sn_{0.80}$
(structure type $Gd_2Ge_{3.38}Bi_{0.42}$)
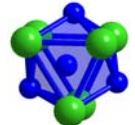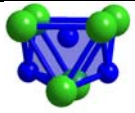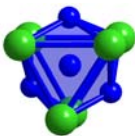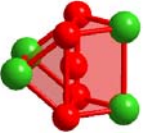
$Gd_2Ge_{2.94}Sn_{0.82}$
(own structure type)
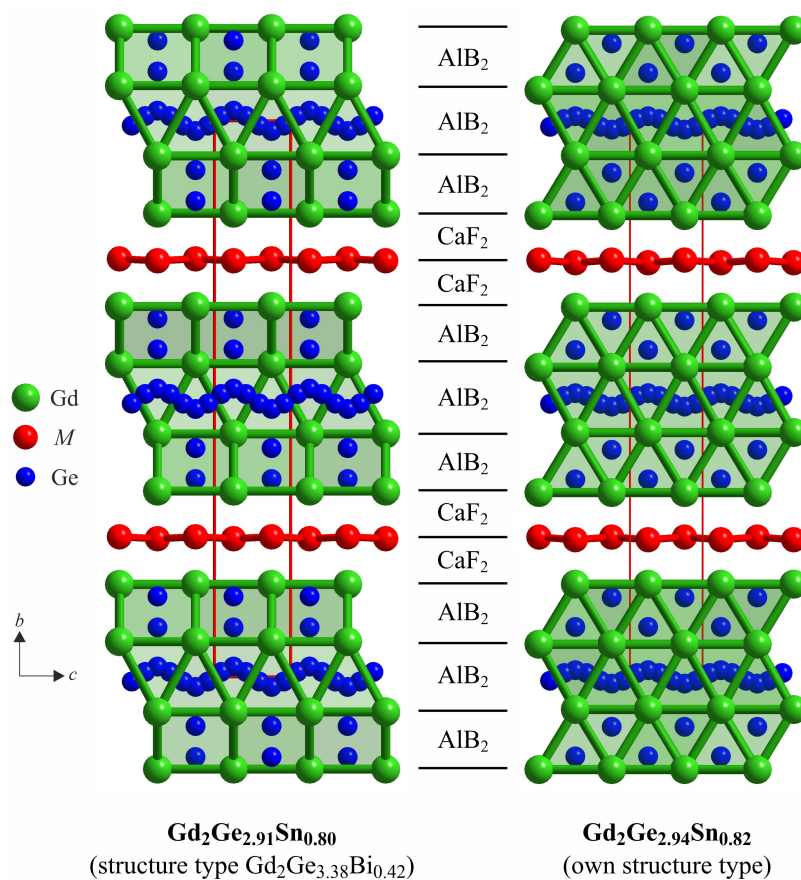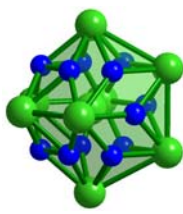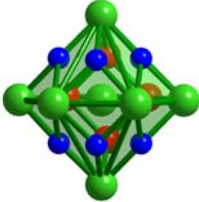
Fig. 7. Stacking of trigonal prisms and square-mesh nets in the structures of $Gd_2Ge_{2.91}Sn_{0.80}$ and $Gd_2Ge_{2.94}Sn_{0.82}$ along the crystallographic direction [010]. AlB$_2$- and CaF$_2$-type slabs are indicated

Table 5

Interatomic distances (d) within the coordination polyhedra of atoms and coordination numbers (CN) in the structure of $Gd_2Ge_{2.91(4)}Sn_{0.80(2)}$ (ST $Gd_2Ge_{3.38}Bi_{0.42}$, PS $oS32$, SG $Cmcm$)

Atoms		δ, Å	CN	Polyhedra
Gd1	− 4 Ge1	3.007(7)	20	$\underline{Gd1}Ge_{12}Gd_8$
	(4 Ge3A [a])	(3.055(4))		
	− 2 Ge3B [a]	3.203(17)		
	(4 Ge3A [a])	(2.974(3))		
	− 4 Ge3B [a]	3.211(9)		
	(4 Ge3A [a])	(3.802(3))		
	− 2 Ge2	3.236(10)		
	− 2 Gd2	3.730(7)		
	− 2 Gd1	4.044(1)		
	− 2 Gd1	4.169(1)		
	− 2 Gd1	4.380(8)		
Gd2	− 4 Ge2	2.979(3)	16	$\underline{Gd2}Ge_6M_4Gd_6$
	− 2 Ge1	3.15(2)		
	− 2 M [b]	3.260(6)		
	− 2 M [b]	3.301(6)		
	− 2 Gd1	3.730(7)		
	− 2 Gd2	4.044(1)		
	− 2 Gd2	4.169(1)		
Ge1	− 1 Ge3B [a]	2.15(4)	9	$\underline{Ge1}Gd_6Ge_3$
	(2 Ge3A [a])	(2.53(3))		
	− 2 Ge2	2.640(19)		
	− 4 Gd1	3.007(7)		
	− 2 Gd2	3.15(2)		
Ge2	− 2 Ge1	2.640(19)	8	$\underline{Ge2}Gd_6Ge_2$
	− 4 Gd2	2.979(3)		
	− 2 Gd1	3.236(10)		
Ge3B [a]	− (2 Ge3A [a])	(0.734(9))	9	$\underline{Ge3B}Gd_6Ge_3$
	− 1 Ge1	2.15(4)		
	(2 Ge3A [a])	(1.634(11))		
	− 2 Ge3B	2.364(14)		
	(2 Ge3A [a])	(2.877(6))		
	− 4 Gd1	3.203(17)		
	− 2 Gd1	3.211(9)		
M [b]	− 4 M [b]	2.906(1)	8	$\underline{M}Gd_4M_4$
	− 2 Gd2	3.260(6)		
	− 2 Gd2	3.301(6)		

Notes: [a] − partially occupied sites; [b] − M=0.20(2)Ge+0.80(2)Sn.

The structures of the three ternary compounds, $Gd_2Ge_{3.84}Sn_{0.92}$, $GdGe_{0.75-0.85}Sn_{1.25-1.15}$, $Gd_2Ge_{2.91}Sn_{0.80}$, which exist in the ternary system Gd−Ge−Sn at 600^0C, are closely related: they have the same space group $Cmcm$ and similar cell parameters a and c, but differ by the values of the cell parameter c. These structures derive from the binary structure type $ZrSi_2$, which is adopted by the solid solution $GdGe_{0-0.15}Sn_{2-1.85}$ based on the binary stannide $GdSn_2$. The structure type $ScCo_{0.25}Si_{1.75}$ (ternary compound $GdGe_{0.75-0.85}Sn_{1.25-1.15}$) is a ternary variant of $ZrSi_2$ with preferential substitution of Co atoms for Si atoms on one site. Both structures are built from layers of trigonal prisms and square-mesh nets, alternating along

the crystallographic direction [010]. Replacement of the single layers of trigonal prisms in the structure type $ScCo_{0.25}Si_{1.75}$ by slabs of triple layers of trigonal prisms leads to the structure type $Gd_2Ge_{3.38}Bi_{0.42}$ ($Gd_2Ge_{2.91}Sn_{0.80}$), and, finally, the replacement of the single square-mesh nets by slabs of double square-mesh nets leads to the $Nd_2Ge_{3.55}Sn_{1.24}$-type structure ($Gd_2Ge_{3.84}Sn_{0.92}$). In the structures of the ternary compounds $Gd_2Ge_{3.84}Sn_{0.92}$, $GdGe_{0.75-0.85}Sn_{1.25-1.15}$, and $Gd_2Ge_{2.91}Sn_{0.80}$, the trigonal prisms are formed by Gd atoms and preferentially centered by Ge atoms, whereas the square-mesh nets are essentially formed by Sn atoms. The relationship between the structures of $GdGe_{0.75-0.85}Sn_{1.25-1.15}$ and $Gd_2Ge_{3.84}Sn_{0.92}$ is further described in ref. [4].

Conclusions

The ternary system Gd−Ge−Sn at 600^0C is characterized by the existence of two continuous solid solutions $Gd_5Ge_{4-x}Sn_x$ ($x=0−4$, structure type Sm_5Ge_4) and $Gd_5Ge_{3-x}Sn_x$ ($x=0−3$, structure type Mn_5Si_3), limited solid solutions based on the binary compounds $Gd_{11}Ge_{10}$ (6 at.% Sn), $GdSn_3$ (5.5 at.% Ge), Gd_3Sn_7 (2 at.% Ge), $GdSn_2$ (5 at.% Ge), $Gd_{11}Sn_{10}$ (3.5 at.% Ge), and three ternary compounds, $Gd_2Ge_{3.84}Sn_{0.92}$ (structure type $Nd_2Ge_{3.55}Sn_{1.24}$), $GdGe_{0.75-0.85}Sn_{1.25-1.15}$ (structure type $ScCo_{0.25}Si_{1.75}$), and $Gd_2Ge_{2.91}Sn_{0.80}$ (structure type $Gd_2Ge_{3.38}Bi_{0.42}$). The ternary phases are characterized by partial disorder of Ge and Sn atoms. The crystal structures of the ternary compounds are closely related and are built from alternating slabs formed by Ge-centered (in part Sn-centered) Gd_6 trigonal prisms, and square-mesh nets of Sn atoms (in part replaced by Ge atoms).

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ПОТРІЙНА СИСТЕМА Gd–Ge–Sn ПРИ 600^0C

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Ізотермічний переріз при 600^0C діаграми стану потрійної системи Gd−Ge−Sn побудовано в повному концентраційному інтервалі, використовуючи рентгенівську порошкову дифракцію та енергодисперсійну рентгенівську спектроскопію. Встановлено утворення неперервних рядів твердих розчинів $Gd_5Ge_{4-x}Sn_x$ ($x=0−4$, структурний тип Sm_5Ge_4, символ Пірсона $oP36$, просторова група *Pnma*, $a=7,8565(12)−8,040(2)$, $b=14,812(2)−15,552(3)$, $c=7,7781(12)−8,201(2)$ Å) *mcm*, $a=8,5702(8)−9,0306(13)$, $c=6,4305(5)−6,5941(10)$ Å) та обмежених твердих розчинів на основі бінарних сполук $Gd_{11}Ge_{10}$ (6 ат.% Sn), $GdSn_3$ (5,5 ат.% Ge), Gd_3Sn_7 (2 ат.% Ge), $GdSn_2$ (5 ат.% Ge) і $Gd_{11}Sn_{10}$ (3,5 ат.% Ge). У системі при 600^0C встановлено існування трьох тернарних сполук: $Gd_2Ge_{3.84}Sn_{0.92}$, $GdGe_{0.75-0.85}Sn_{1.25-1.15}$ і $Gd_2Ge_{2.91}Sn_{0.80}$. Використовуючи рентгенівську порошкову дифракцію визначено кристалічну структуру двох тернарних сполук: $GdGe_{0.75-0.85}Sn_{1.25-1.15}$, структурний тип $ScCo_{0.25}Si_{1.75}$, $oS12$, *Cmcm*, $a=4,3035(4)−4,3206(4)$, $b=16,4433(14)−16,4824(15)$, $c=4,0961(4)−4,1270(4)$ Å і $Gd_2Ge_{2.91}Sn_{0.80}$, структурний тип $Gd_2Ge_{3.38}Bi_{0.42}$, $oS32$, *Cmcm*, $a=4,0445(6)$, $b=30,473(5)$, $c=4,1694(6)$ Å. Кристалічна структура третьої сполуки, $Gd_2Ge_{3.84}Sn_{0.92}$, належить до структурного типу $Nd_2Ge_{3.55}Sn_{1.24}$. Кристалічні структури є близько спорідненими та побудовані з шарів тригональ-

них призм Gd_6, центрованих атомами Ge (чи частково атомами Sn) і квадратних сіток атомів Sn (чи частково атомів Ge), що чергуються вздовж кристалографічного напряму [010]. Спостерігається часткове невпорядкування атомів Ge і Sn.

Ключові слова: гадоліній, германій, олово, рентгенівська порошкова дифракція, діаграма стану, твердий розчин, тернарна сполука, кристалічна структура.

THE TERNARY SYSTEM Gd−Ge−Sn AT 600⁰C

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The isothermal section at 600⁰C of the phase diagram of the ternary system Gd−Ge−Sn was constructed in the whole concentration range, based on X-ray powder diffraction and energy-dispersive X-ray spectroscopy. The formation of two continuous solid solutions, $Gd_5Ge_{4-x}Sn_x$ (x=0−4, structure type Sm_5Ge_4, Pearson symbol $oP36$, space group *Pnma*, a=7.8565(12)−8.040(2), b=14.812(2)−15.552(3), c=7.7781(12)−8.201(2) Å) and $Gd_5Ge_{3-x}Sn_x$ (x=0−3, structure type Mn_5Si_3, $hP16$, $P 6_3/mcm$, a=8.5702(8)−9.0306(13), c=6.4305(5)−6.5941(10) Å), and limited solid solutions based on the binary compounds $Gd_{11}Ge_{10}$ (6 at.% Sn), $GdSn_3$ (5.5 at.% Ge), Gd_3Sn_7 (2 at.% Ge), $GdSn_2$ (5 at.% Ge), and $Gd_{11}Sn_{10}$ (3.5 at.% Ge) was established. Three following ternary compounds were found in the system at 600⁰C: $Gd_2Ge_{3.84}Sn_{0.92}$, $GdGe_{0.75-0.85}Sn_{1.25-1.15}$, and $Gd_2Ge_{2.91}Sn_{0.80}$. The detailed crystal structures of two of them were refined on X-ray powder diffraction data: $GdGe_{0.75-0.85}Sn_{1.25-1.15}$, structure type $ScCo_{0.25}Si_{1.75}$, $oS12$, *Cmcm*, a=4.3206(4)−4.3035(4), b=16.4824(15)−16.4433(14), c=4.1270(4)−4.0961(4) Å and $Gd_2Ge_{2.91}Sn_{0.80}$, structure type $Gd_2Ge_{3.38}Bi_{0.42}$, $oS32$, *Cmcm*, a=4.0445(6), b=30.473(5), c=4.1694(6) Å. The third compound, $Gd_2Ge_{3.84}Sn_{0.92}$, adopts the structure type $Nd_2Ge_{3.55}Sn_{1.24}$. The crystal structures are closely related and are built from layers of Gd_6 trigonal prisms centered by Ge atoms (or in part by Sn atoms) and square-mesh nets of Sn atoms (or in part Ge atoms), which alternate along the crystallographic direction [010]. Partial disorder of Ge and Sn atoms is observed.

Keywords: gadolinium; germanium; tin; X-ray powder diffraction; phase diagram; solid solution; ternary compound; crystal structure.

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