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Peculiarities of the interaction of the components in the Gd–Cu–Sn ternary system at 670 K and 770 K

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Isothermal sections of the phase diagram of the Gd–Cu–Sn ternary system were constructed at 770 K and 670 K in the whole concentration range using X-ray, metallographic, and differential thermal analyses. The interaction of the components in the Gd–Cu–Sn system at 670 K results in the existence of five ternary compounds, while at 770 K only four intermediate phases were observed. Detailed crystal structure investigations were performed for the $GdCu_5Sn$ ($CeCu_6$-type) and $Gd_2Cu_3Sn_6$ ($Sm_2Cu_4Sn_5$-type) compounds. The existence of a substitutional solid solution $GdCu_{5-x}Sn_x$ (up to 5 at.% Sn) was observed at both temperatures.

Intermetallics / Phase diagrams / Crystal structure / X-ray diffraction / Rare earth system

1. Introduction

The formation and characterization of intermediate ternary phases formed in *R*–*Me*–Sn systems (*R* = rare earth, *Me* = 3*d*-metal) are often studied within the framework of the determination of the corresponding phase diagram. It is very convenient to study for each phase its stability (limits of the composition range, temperature of formation), influence of the size factor, and preparation methods. Previous investigations of *R*–*Me*–Sn systems where *R* belongs to the yttrium group (*R* = Dy, Er, Lu) [1-3] have shown a decreasing number of formed compounds down to three for the Lu–Cu–Sn system; however, ten intermediate phases were found in the Yb–Cu–Sn system at 673 K [4]. A detailed investigation of the Dy–Cu–Sn system at both 670 and 770 K showed the influence of the heat treatment on the number of formed ternary phases, especially at high Sn content [5]. The influence of the temperature on the crystal structure of the $R_3Cu_4Sn_4$ compounds (*R* = Tm, Lu), which are characterized by two structural modifications (monoclinic $Tm_3Cu_4Sn_4$-type and orthorhombic $Gd_3Cu_4Ge_4$-type), was studied in [6].

With regard to the work in progress on *R*–Cu–Sn ternary systems formed by rare earths of the yttrium group, it was decided to study the Gd–Cu–Sn system at different temperatures, especially in the Cu- and Sn-rich region. The first results of the investigation of the Gd–Cu–Sn ternary system at 670 K were reported in [7]. Six ternary compounds were found, but crystallographic data were given only for three of them: GdCuSn, $Gd_6Cu_8Sn_8$, and $Gd_2Cu_4Sn_5$.

In the present paper the results of an X-ray analysis of the phase equilibria in the Gd–Cu–Sn system at 670 K and 770 K, and crystal structure refinements of some of the ternary compounds, are reported. Data concerning the Gd–Sn binary system were taken from [7,8], and data for the Gd–Cu and Cu–Sn systems were found in [8,9].

2. Experimental details

The samples were prepared by direct twofold arc melting of the constituent elements (gadolinium, purity 99.9 wt.%; copper, purity 99.99 wt.%; and tin, purity 99.999 wt.%) under high-purity Ti-gettered argon atmosphere on a water-cooled copper crucible. The weight losses of the initial total mass were lower than 1 wt.%. Two pieces of the as-cast buttons were annealed separately for one month at 670 K and at 770 K in evacuated silica tubes and then water-quenched.

Phase analysis was performed using X-ray powder diffraction (RKD-57, Cr *K* radiation; DRON-2.0M, Fe K_α radiation). X-ray examination was carried out at the same time for the samples annealed at 670 and 770 K. The observed diffraction intensities were compared with reference powder patterns of known binary and ternary phases. The compositions of the samples were examined by Scanning Electron

Table 1 Phase compositions (at.%) of selected samples in the Gd–Cu–Sn ternary system at 670 K and 770 K (unit cell parameters in nm).

N	Nominal alloy composition (at.%)			Phases											
				1st phase				2nd phase				3rd phase			
	Gd	Cu	Sn	Gd	Cu	Sn	Phase	Gd	Cu	Sn	Phase	Gd	Cu	Sn	Phase
1	25	70	5	17.1	82.9		$GdCu_5$ *a*=0.7060	33.67	66.33		$GdCu_2$	32.7	32.9	34.4	GdCuSn
2	17	78	5	16.9	78.3	4.8	$GdCu_{5-x}Sn_x$ *a*=0.7115								
3	10	82.5	7.5	16.10	68.85	15.05	$GdCu_5Sn$ *a*=0.8237 *b*=0.4993 *c*=1.0586				Cu *a*=0.362	15.1	84.9		$GdCu_6$
4	55	30	15	52.08	47.92		GdCu *a*=0.3505	63.21		36.79	Gd_5Sn_3				
5	40	40	20	33.48	66.52		$GdCu_2$ *a*=0.434 *b*=0.684 *c*=0.729	63.25		36.75	Gd_5Sn_3	32.33	34.35	33.32	GdCuSn
6	20	60	20	15.25	69.12	15.63	$GdCu_5Sn$ *a*=0.8238 *b*=0.4991 *c*=1.0587	32.34	34.35	33.31	GdCuSn	27.21	36.03	36.76	$Gd_3Cu_4Sn_4$
7	50	30	20	51.98	47.91	0.11	GdCu	63.22		36.78	Gd_5Sn_3 *a*=0.902 *c*=0.658	33.39	66.51	0.10	$GdCu_2$
8	10	70	20	13.67	63.05	23.28	$Gd_{1.9}Cu_{9.2}Sn_{2.8}$ *a*=0.5042 *c*=2.0451		78.79	21.21	$Cu_{41}Sn_{11}$				
9	15	65	20	13.57	62.90	23.53	$Gd_{1.9}Cu_{9.2}Sn_{2.8}$ *a*=0.5043 *c*=2.0451	14.78	70.09	15.13	$GdCu_5Sn$ *a*=0.826 *b*=0.501 *c*=1.061	27.49	36.33	36.18	$Gd_3Cu_4Sn_4$ *a*=0.446 *b*=0.693 *c*=1.472
10	45	30	25	31.55	33.77	34.68	GdCuSn *a*=0.4532 *c*=0.7365	33.63	66.37		$GdCu_2$	63.15		36.85	Gd_5Sn_3
11	25	45	30	27.17	35.59	37.24	$Gd_3Cu_4Sn_4$ *a*=1.4729 *b*=0.6934 *c*=0.4466	32.22	34.55	33.23	GdCuSn	14.97	68.95	16.08	$GdCu_5Sn$
12	15	50	35	27.12	37.22	35.66	$^*Gd_3Cu_4Sn_4$ $Gd_3Cu_4Sn_4$	0.78	74.23	24.99	Cu_3Sn Cu_3Sn	0.63	53.6	45.77	Cu_6Sn_5 Sn
13	31	29	40	34.08	31.64	34.28	GdCuSn *a*=0.4532 *c*=0.7365	26.99	37.13	35.88	$Gd_3Cu_4Sn_4$	34.11		65.89	$GdSn_2$
14	40	15	45	32.77	34.56	32.67	GdCuSn *a*=0.453 *c*=0.7361	32.87	0.61	66.52	$GdSn_2$	49.81	1.12	49.07	$Gd_{11}Sn_{10}$
15	15	35	50	19.88	26.45	53.67	$^*Gd_2Cu_3Sn_6$ Cu_3Sn	27.31	34.99	37.7	$Gd_3Cu_4Sn_4$ $Gd_3Cu_4Sn_4$	0.72	54.5	44.78	Cu_6Sn_5 Sn
16	25	15	60	24.12		75.88	$^*GdSn_3$ *a*=0.432 *b*=0.441 *c*=2.211 $GdSn_3$	19.11	26.99	53.9	$Gd_2Cu_3Sn_6$ $Gd_3Cu_4Sn_4$	26.77	35.46	37.77	$Gd_3Cu_4Sn_4$
17	15	35	55	19.23	27.35	53.42	$^*Gd_2Cu_3Sn_6$ *a*=0.4414 *c*=2.495				Sn				
18	32	4	64	31.61	5.35	63.04	$GdCu_xSn_2$ *a*=0.4425 *b*=1.672 *c*=0.4355								

*at 670 K

Table 2 Crystallographic data for the ternary compounds in the Gd–Cu–Sn system.

№	Compound	Structure type	Space group	Unit cell parameters, nm		
				a	*b*	*c*
1	$GdCu_5Sn$	$CeCu_6$	*Pnma*	0.82397(4)	0.49905(2)	1.05877(6)
2	$Gd_{1.9}Cu_{9.2}Sn_{2.8}$	$Dy_{1.9}Cu_{9.2}Sn_{2.8}$	$P6_3/mmc$	0.50429(1)		2.0451(1)
3	$GdCuSn$	$CaIn_2$	$P6_3/mmc$	0.4532(3)		0.7365(2)
4	$Gd_3Cu_4Sn_4$	$Gd_3Cu_4Ge_4$	*Immm*	1.4729(1)	0.6935(7)	0.4468(4)
5	$Gd_2Cu_3Sn_6$	$Sm_2Cu_4Sn_5$	*I*4*mm*	0.44141(1)		2.4950(1)

The compound numbers correspond to the labels in the phase diagrams (Figs. 1, 2).

Table 3 Composition and cell parameters of the $GdCu_{5-x}Sn_x$ solid solution.

Composition	Unit cell parameter, nm	Cell volume, nm^3
$GdCu_5$	0.7060(2)	0.3518
$Gd_{17}Cu_{81}Sn_2$	0.7085(3)	0.3556
$Gd_{17}Cu_{79}Sn_4$	0.7110(2)	0.3594
$Gd_{17}Cu_{78}Sn_5$	0.7115(3)	0.3602
$Gd_{17}Cu_{77}Sn_6$	0.7116(3)	0.3603

Microscopy (SEM) using a JEOL-840A scanning microscope. Quantitative electron probe microanalysis (EPMA) of the phases was carried out using an energy-dispersive X-ray analyser with the pure elements as standards (the acceleration voltage was 20 kV; *K*- and *L*-lines were used). Data for the crystal structure refinements were collected at room temperature on a Bruker D8 diffractometer (graphite monochromator, Cu $K_{\alpha 1}$ radiation, 20-100° 2θ range with scanning step 0.02° and 20 s exposure time). Calculations of the unit cell parameters and theoretical patterns were performed using the CSD and WinPLOTR program packages [10,11].

A differential thermal analysis (DTA, NETZSCH device, Al_2O_3 as a reference material) was performed on the $Gd_2Cu_3Sn_6$ compound to check the limits of the temperature range. The sample was heated up to 770 K at a rate of 10 K/min.

3. Results and discussion

According to previously published data [7], three ternary compounds with unknown structure were observed in the Cu-rich corner of the Gd–Cu–Sn system. Further investigation of the Cu-rich corner of the *R*–Cu–Sn ternary systems, where *R* = Y, La-Yb, showed the formation of ternary phases at the composition $R_{15}Cu_{70}Sn_{15}$, crystallizing with $CeCu_5Au$- or $CeCu_6$-type structure [12,13]. Recently, we studied the crystal structure of a new series of isotypic $R_{1.9}Cu_{9.2}Sn_{2.8}$ compounds, found at 870 K, where *R* = Y, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu [14]. This structure is a partly disordered substitution variant of the $CeNi_5Sn$ structure type (space group $P6_3/mmc$). Further investigation showed that these phases are formed also at 670 and 770 K. Thus, it was decided to perform a detailed study of this range of the Gd–Cu–Sn system at 670 K and of the interaction of the components at 770 K to check the formation of the above-mentioned compounds and the influence of the heat treatment on the character of the phase equilibria.

The phase equilibria in the Gd–Cu–Sn phase diagram were investigated at 670 K and at 770 K, carrying out X-ray and metallographic analyses of 20 binary and 115 ternary alloys, annealed at both temperatures. The resulting isothermal sections are presented in Figs. 1 and 2. The phase compositions of selected samples at 670 and 770 K are given in Table 1, and SEM pictures of some alloys are shown in Fig. 3. The compositions and the crystallographic parameters of the compounds are listed in Table 2.

According to [7] the formation of ternary phases was observed at the compositions $Gd_{15}Cu_{70}Sn_{15}$, $Gd_{15}Cu_{65}Sn_{20}$, and $Gd_{10}Cu_{70}Sn_{20}$ in the copper-rich corner of the Gd–Cu–Sn ternary system at 670 K. The phase analysis of the powder patterns of ingots annealed at 670 and 770 K revealed the formation of a substitutional solid solution $GdCu_{5-x}Sn_x$ up to about 5 at.% Sn based on the binary compound $GdCu_5$ ($AuBe_5$-type), at both temperatures (Table 3). A detailed crystal structure investigation performed on the sample $Gd_{15}Cu_{70}Sn_{15}$ showed that the $GdCu_5Sn$ compound exists in the temperature range from 670 K to 870 K and confirmed that it belongs to the structure type $CeCu_6$ (space group *Pnma*, *a* = 0.82397(4), *b* = 0.49905(2), *c* = 1.05877(6) nm) with a (Cu,Sn) statistical distribution in the 8*d* atomic position. The final atomic parameters, refined to $R_p = 0.113$, $R_{wp} = 0.154$, $R_{Bragg} = 0.056$, are listed in Table 4. The observed, calculated, and difference X-ray patterns for the sample $Gd_{15}Cu_{70}Sn_{15}$ are presented in Fig. 4. The presence of the Cu-phase in the diffraction pattern may be explained by the existence of some liquidus region near the $GdCu_5Sn$ phase.

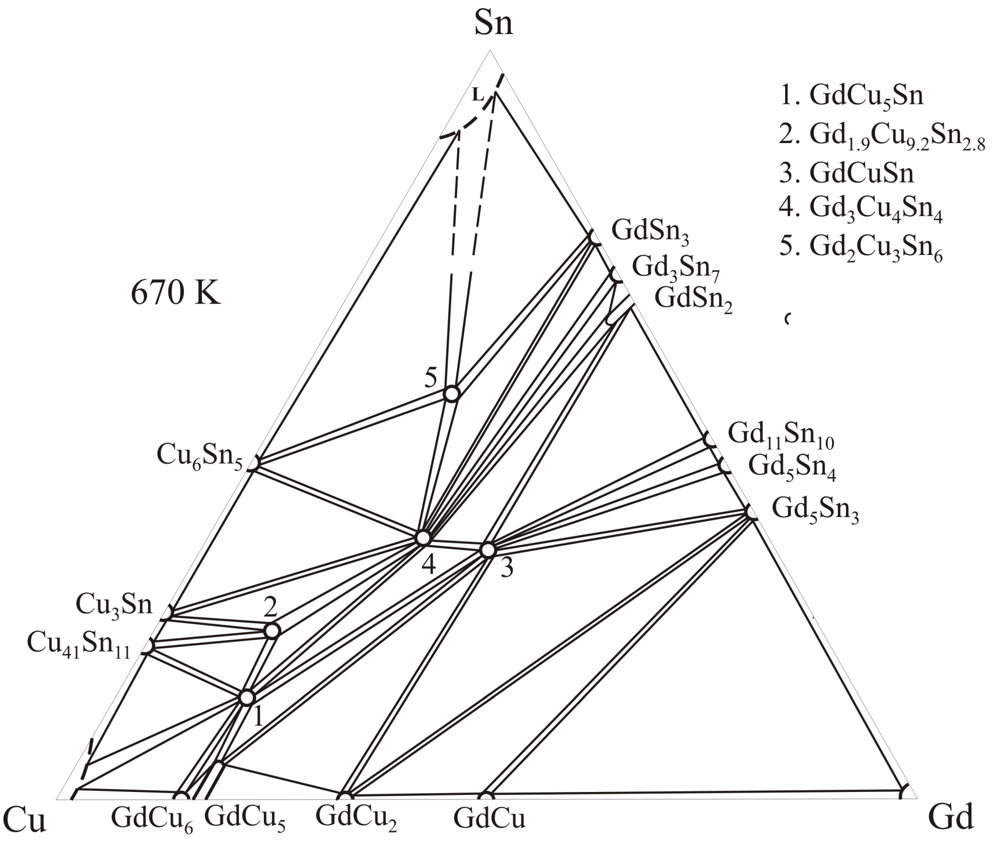


Fig. 1 Isothermal section for the Gd–Cu–Sn system at 670 K.

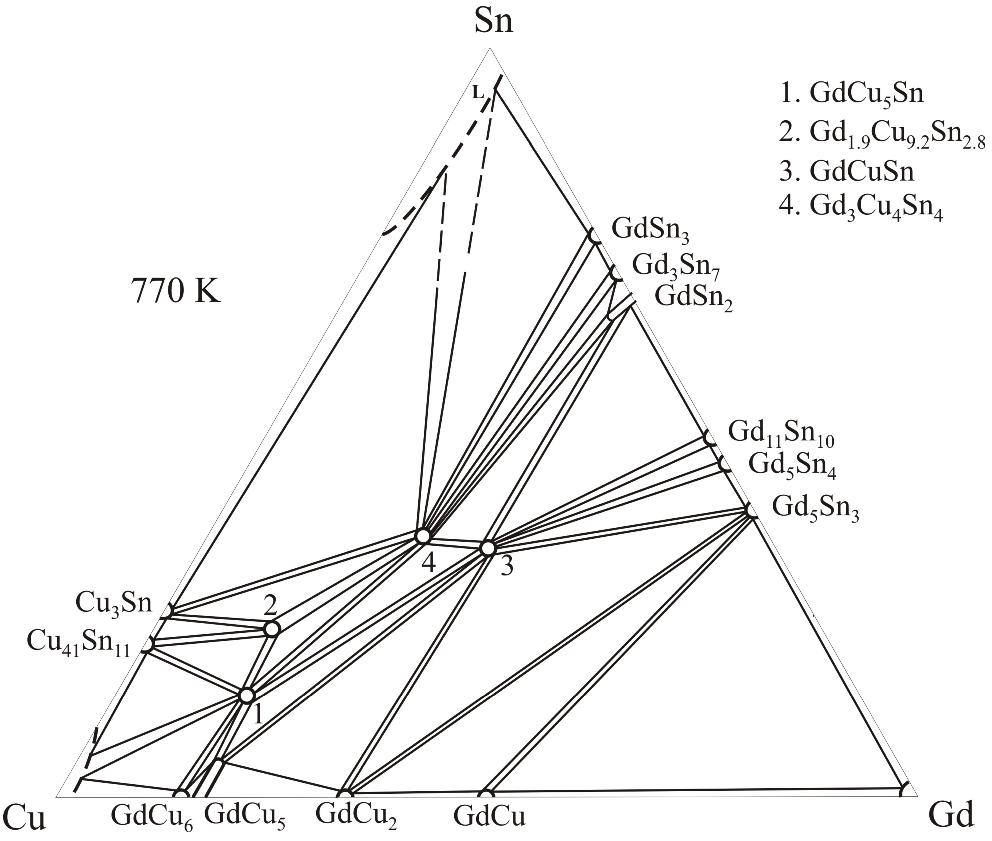
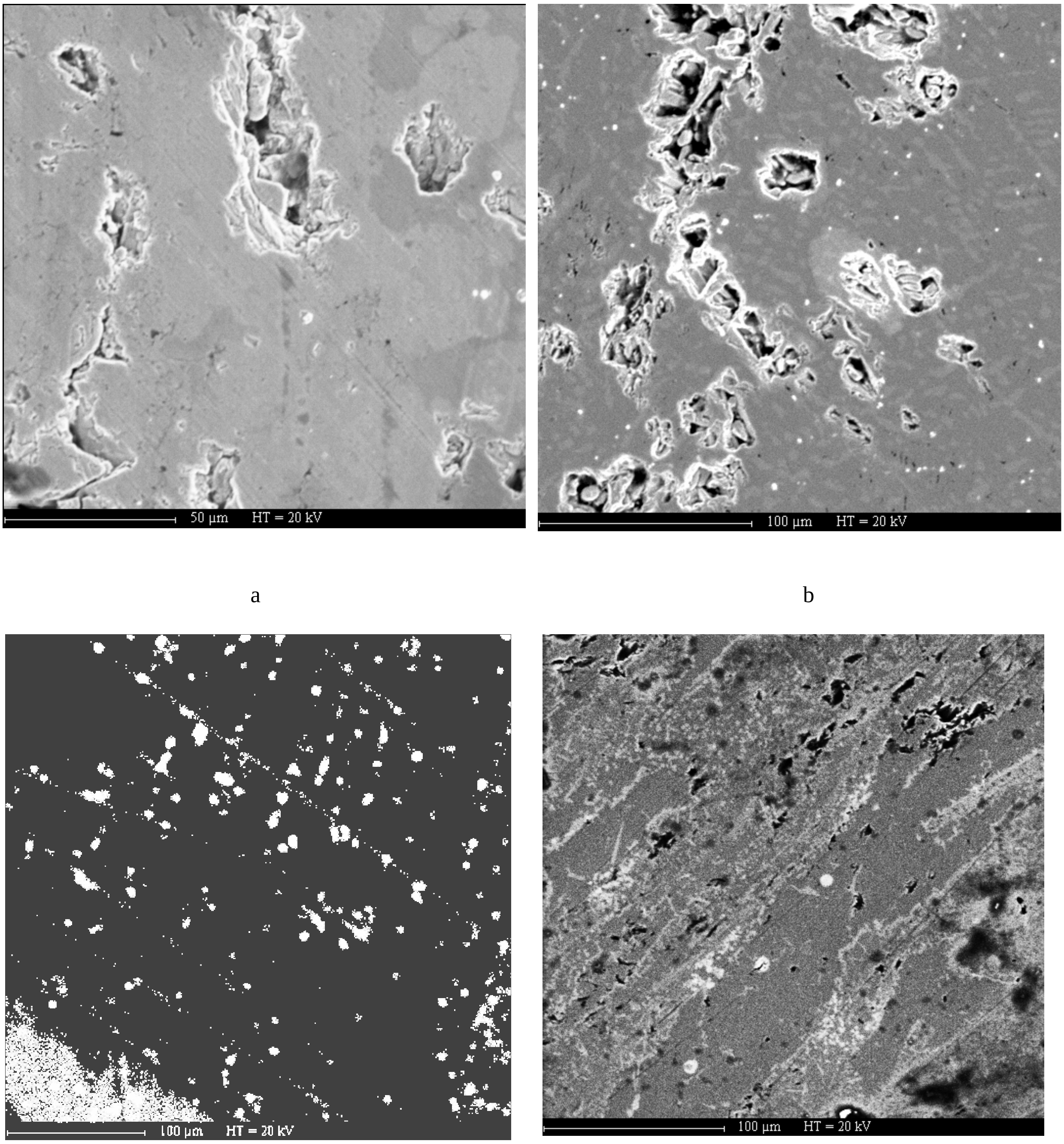


Fig. 2 Isothermal section for the Gd–Cu–Sn system at 770 K.



a

b

c

d

Fig. 3 Electron micrographs of the alloys:
a) $Gd_{15}Cu_{35}Sn_{50}$ – $Gd_2Cu_3Sn_6$ (light gray phase), $Gd_3Cu_4Sn_4$ (dark gray phase), Cu_6Sn_5 (bright phase);
b) $Gd_{15}Cu_{65}Sn_{20}$ – $Gd_{1.9}Cu_{9.2}Sn_{2.8}$ (dark gray phase), $GdCu_5Sn$ (light gray phase), $Gd_3Cu_4Sn_4$ (bright phase);
c) $Gd_{10}Cu_{70}Sn_{20}$ – $Gd_{1.9}Cu_{9.2}Sn_{2.8}$ (black phase), $Cu_{41}Sn_{11}$ (white phase);
d) $Gd_{45}Cu_{30}Sn_{25}$ – GdCuSn (gray phase), $GdCu_2$ (white phase), Gd_5Sn_3 (black phase).

At higher Sn content the other ternary compound, $Gd_{1.9}Cu_{9.2}Sn_{2.8}$, was confirmed at the composition $Gd_{15}Cu_{65}Sn_{20}$. A previous crystal structure investigation performed on the $Gd_{15}Cu_{65}Sn_{20}$ sample has shown that the structure belongs to the structure type $Dy_{1.9}Cu_{9.2}Sn_{2.8}$ (space group *P*6$_3$/*mmc*) [14], a disordered substitution variant of the $CeNi_5Sn$ structure.

The existence of a ternary phase at the composition $Gd_{10}Cu_{70}Sn_{20}$ was not confirmed during our investigation at 670 and 770 K. According to the X-ray and microprobe analyses, the corresponding

Table 4 Atomic coordinates and isotropic displacement parameters for the $GdCu_5Sn$ compound.

Atom	Wyckoff position	*x/a*	*y/b*	*z/c*	$B_{iso}\cdot10^2$, nm^2
Gd1	4*c*	0.25350(8)	¼	0.43687(6)	0.82(2)
Sn2	4*c*	0.13784(7)	¼	0.14055(5)	0.41(2)
Cu3	4*c*	0.31526(14)	¼	0.75843(11)	0.58(3)
Cu4	4*c*	0.06292(15)	¼	0.89470(12)	0.58(3)
Cu5	4*c*	0.41429(14)	¼	0.97966(12)	0.58(3)
*M*6	8*d*	0.42740(11)	-0.0022(2)	0.19343(10)	1.40(4)

*M*6 = 0.98(Cu)+0.02(Sn)

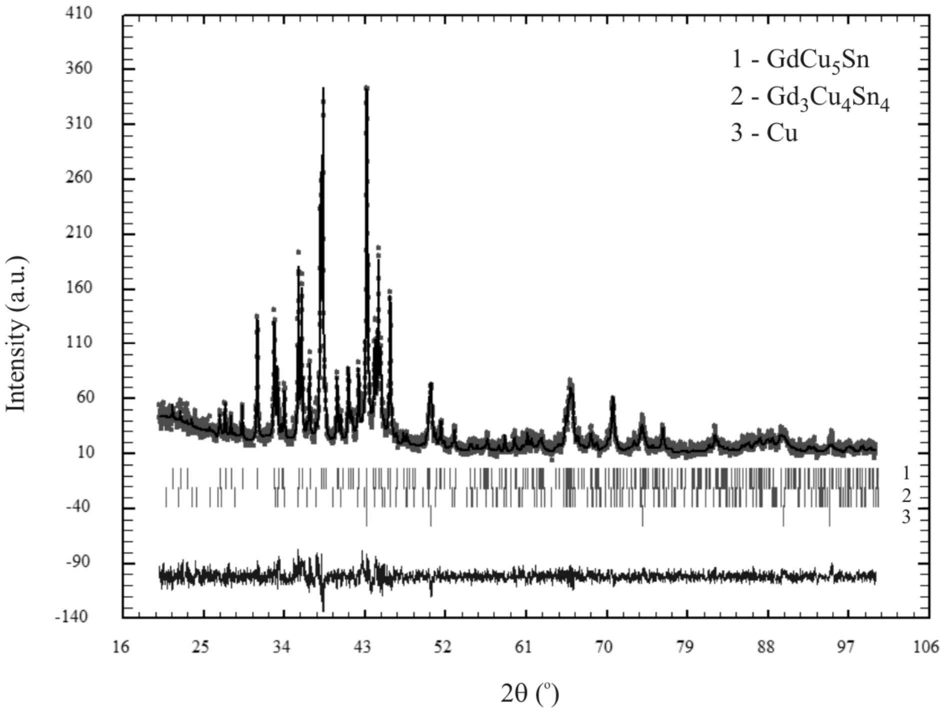


Fig. 4 Observed, calculated and difference X-ray patterns for the $Gd_{15}Cu_{70}Sn_{15}$ sample.

sample contained the phases $Gd_{1.9}Cu_{9.2}Sn_{2.8}$ and $Cu_{41}Sn_{11}$ (Fig. 3c).

Detailed crystal structure refinements were performed on the $Gd_{15}Cu_{35}Sn_{50}$ sample, using a starting model of the $Sm_2Cu_4Sn_5$ structure type (space group *I*4*mm*). Refinements of the site occupancies showed that one of the 2*a* positions of the Cu atoms in the starting model is here occupied by Sn atoms. The final atomic and isotropic displacement parameters are listed in Table 5 (a = 0.44141(1), c = 2.4950(1) nm, R_{Bragg} = 0.630, R_p = 0.142, R_{wp} = 0.189). Consequently, the chemical formula of the compound should be written as $Gd_2Cu_3Sn_6$, and is in good agreement with the microprobe analysis, which showed for this phase a composition richer in tin than $R_2Cu_4Sn_5$. Similar results were obtained in [15] for the $Nd_2Cu_3Sn_6$ compound.

The phase analysis of the samples with a Sn content of more than 50 at.% confirmed the presence of the $Gd_2Cu_3Sn_6$ stannide at 670 K, while at 770 K in the corresponding region of the Gd–Cu–Sn system phase equilibria between Cu_3Sn, $Gd_3Cu_4Sn_4$ and Sn were observed. The differential thermal analysis showed temperature-induced transitions for the $Gd_2Cu_3Sn_6$ compound at about 225 and 400 K, which can be associated with the formation of the phase and its decomposition, respectively (Fig. 5). The limited temperature ranges observed for the compounds with a tin content higher than 50 at.% in the *R*–Cu–Sn systems is in accord with the binary Cu–Sn system [8], which is characterized by low-temperature formation of binary phases at more than 50 at.% Sn and by the presence of a low-temperature liquid ranging.

An interstitial solid solution $GdCu_xSn_2$, based on the binary compound $GdSn_2$ ($ZrSi_2$-type), was observed, similarly to [16,17]. The limiting composition of this solid solution is $GdCu_{0.16(2)}Sn_2$ ($Gd_{31.5}Cu_5Sn_{63.5}$, a = 0.4425(7), b = 1.672(3), c = 0.4355(5) nm) at both 670 and 770 K.

Table 5 Atomic coordinates and isotropic displacement parameters for the $Gd_2Cu_3Sn_6$ compound.

Atom	Wyckoff position	*x*/*a*	*y*/*b*	*z*/*c*	$B_{iso}\cdot 10^2$, nm^2
Gd1	2*a*	0	0	0^a	0.11(7)
Gd2	2*a*	0	0	0.6793(2)	0.11(7)
Cu1	4*b*	0	½	0.0938(7)	1.22(15)
Cu2	2*a*	0	0	0.2407(5)	1.22(15)
Sn1	4*b*	0	½	0.2930(3)	0.78(4)
Sn2	4*b*	0	½	0.4040(3)	0.78(4)
Sn3	2*a*	0	0	0.5212(3)	0.78(4)
Sn4	2*a*	0	0	0.1399(3)	0.78(4)

[a] fixed parameter

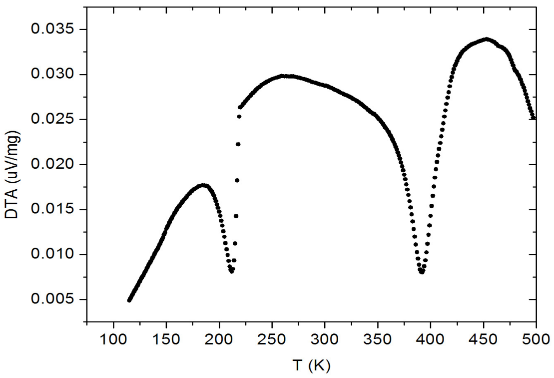


Fig. 5 DTA curve for the $Gd_2Cu_3Sn_6$ compound.

Comparing the present study of the Gd–Cu–Sn system with the data reported in [7] we may note the formation of four ternary phases at 770 K, but five ternary compounds at 670 K. The heat treatment is thus an important factor determining the formation of ternary phases at high Sn content. In this sense a close analogy was observed in the influence of the temperature on the character of the phase equilibria and number of formed compounds in the Gd–Cu–Sn and Dy–Cu–Sn ternary systems. The most remarkable difference between the *R*–Cu–Sn systems where *R* are rare earths of the yttrium group is related to the phases $R_2Cu_{4-x}Sn_{5+x}$, which were observed in the systems with *R* = Gd, Tb, and Dy at 670 K, while they have not been found in the systems where *R* = Y, Ho-Lu. However, phases *R*CuSn, $R_{1.9}Cu_{9.2}Sn_{2.8}$, $R_3Cu_3Sn_4$, and RCu_5Sn ($CeCu_6$-type) exist in all the systems of the Y-group, with the exception of a "$LuCu_5Sn$" phase in the Lu–Cu–Sn system.

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