Journal of Alloys and Compounds 365 (2004) 168–172

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Sm–Ru–Ge system at 1070 K

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Received 5 November 2002; received in revised form 16 June 2003; accepted 16 June 2003

Abstract

Phase equilibria in the Sm–Ru–Ge system were investigated by X-ray powder diffraction and the isothermal section at 1070 K was obtained. We confirmed the compounds $CeGa_2Al_2$-type $SmRu_2Ge_2$ [$a = 0.4229(1)$ nm, $c = 0.9933(2)$ nm, space group $I4mmm$, No. 139], $Y_3Co_4Ge_{13}$-type $Sm_3Ru_4Ge_{13}$ [$a = 0.9016(1)$ nm, space group $Pm3n$, No. 223], $La_3Ni_2Ga_2$-type $Sm_3Ru_2Ge_2$ [$a = 0.5620(1)$ nm, $b = 0.7808(1)$ nm, $c = 1.3567(2)$ nm, space group $Pbcm$, No. 57], $U_2Co_3Si_5$-type $Sm_2Ru_3Ge_5$ [$a = 0.9878(6)$ nm, $b = 1.2437(8)$ nm, $c = 0.5791(4)$ nm, space group $Ibam$, No. 72] and Zr_2CoSi_2-type Sm_2RuGe_2 [$a = 1.0948(3)$ nm, $b = 1.0839(3)$ nm, $c = 0.4302(1)$ nm, $\gamma = 123.23(2)^\circ$, space group $B2/m$, No. 12-1]. We found the following new compounds: TiNiSi-type SmRuGe [$a = 0.7165(1)$ nm, $b = 0.4476(1)$ nm, $c = 0.7152(1)$ nm, space group $Pnma$, No. 62], $CeRh_{1-x}Ge_{2+x}$-type Sm_2RuGe_{5-x} [$a = 0.4061(2)$ nm, $b = 0.4179(2)$ nm, $c = 1.6226(7)$ nm, space group $Pmmn$, No. 59-2], Cr_5B_3-type Sm_5Ru_2Ge [$a = 0.7736(4)$ nm, $c = 1.3426(8)$ nm, space group $I4/mcm$, No. 140] and $Tb_3Co_2Ge_4$-type $Sm_3Ru_2Ge_4$ [$a = 1.0899(9)$ nm, $b = 0.8139(8)$, $c = 0.4319(3)$ nm, $\gamma = 109.29(7)^\circ$, space group $B2/m$, No. 12-1]. The melting temperature for $Sm_2Ru_3Ge_5$ [T_m=1760(10) K], $Sm_3Ru_4Ge_{13}$ [$T_m = 1600(10)$ K], $Sm_3Ru_2Ge_2$ [$T_m = 1560(10)$ K] and Sm_2RuGe_2 [$T_m = 1750(10)$ K] were measured.

Keywords: Rare earth compounds; Transition metal compounds; Phase diagram; Crystal structure; X-ray diffraction

1. Introduction

The Ru–Ge, Sm–Ge and Sm–Ru binary systems have been studied in Refs. [1–12] (Table 1). The $SmRu_2Ge_2$, $Sm_3Ru_4Ge_{13}$, $Sm_2Ru_3Ge_5$, $Sm_3Ru_2Ge_2$ and Sm_2RuGe_2 ternary compounds have been studied in Refs. [13–18] (Table 2). The interaction of components at 870 K were studied in Ref. [18].

The goal of the present work was the updating the crystallographic data of Ref. [18] using Rietveld refinement [19,20] and the investigation of the phase equilibria in the Sm–Ru–Ge systems at 1070 K.

2. Experimental

The present study was carried out on about 20 alloys (Fig. 1). The alloys were made in an electric arc furnace under an argon atmosphere using a nonconsumable tungsten electrode and a water-cooled copper tray. Samarium, ruthenium and germanium (purity of each component ≥99.99%) were used as starting components. Titanium was used as a getter during the melting process. The alloys were remelted twice in order to achieve complete fusion and a homogeneous composition. The melted alloys were subjected to an anneal in evacuated quartz ampoules containing titanium chips as a getter. The ampoules were placed in a resistance furnace. The alloys were annealed at 1070 K for 2 weeks. The samples were quenched from the annealing temperature in ice-cold water. The phase equilibria in the Sm–Ru–Ge system were determined using X-ray phase analysis and microprobe X-ray analysis. X-ray data were obtained on a diffractometer Dron-3.0 (CuKα radiation, $2\theta = 20$–70°, step 0.05°, for 5 s per step). The diffractograms obtained were identified by means of calculated patterns using the RIETAN program [19,20] in the isotropic approximation. A ‘Camebax’ microanalyser was employed to perform microprobe X-ray spectral analyses of the samples.

The high temperature differential thermal analysis of the compounds was carried out on an VDTA-8M2 (Institute of metallophysic of the Ukraine). The samples were heated in helium (10^5 Pa) twice in order to achieve an accurate value of the melting temperature. The heating rate was kept constant for all samples (80 K/min). The investigation was carried out with a ZrO_2 crucible. The temperature was measured with

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doi:10.1016/S0925-8388(03)00652-2

Table 1
Crystallographic data and temperature of the phase transition of compounds in the Sm–Ru, Sm–Ge and Ru–Ge systems. The reliability factors are $R_{\mathrm{F}} = 100 \cdot (\Sigma_{\mathrm{k}}|(I_{\mathrm{k}}^{\mathrm{obs}})^{1/2} - (I_{\mathrm{k}}^{\mathrm{cal}})^{1/2}|)/\Sigma_{\mathrm{k}}|(I_{\mathrm{k}}^{\mathrm{obs}})^{1/2}|)\%(I_{\mathrm{k}}^{\mathrm{obs}}$ is the integrated intensity evaluated from summation of contribution of the kth peaks to net observed intensity, $I_{\mathrm{k}}{}^{\mathrm{cal}}$ is the integrated intensity calculated from refined structural parameters)

	Compound	Space group	Structure type	a (nm)	b (nm)	c (nm)	R_{F} (%)	T[b] (K)	Refs.
1	Sm[a]	$R3m$	α-Sm	0.3621		2.625		1190	[1]
	Sm[a]	$R3m$	α-Sm	0.3611(4)		2.622(3)	3.6		–[c]
	Sm	$Im3m$	W	0.407				***1350***	[1]
2	Ru[a]	$P6_3/mmc$	Mg	0.27058		0.42811		***2583***	[1]
	Ru[a]	$P6_3/mmc$	Mg	0.2696(1)		0.4269(2)	4.4		–[c]
3	Ge[a]	$Fd3m$	C	0.565754				***1210.6***	[1]
	Ge[a]	$Fd3m$	C	0.5621(1)			5.6		–[c]
4	RuGe[a]	$P2_13$	FeSi	0.4846				~***1670***	[2,3]
	RuGe[a]	$P2_13$	FeSi	0.4839(3)			5.1		–[c]
5	Ru_2Ge_3 (HT)	$P4c2$	Ru_2Sn_3	0.5739		0.9952		~***1670***	[2,3]
	Ru_2Ge_3 (LT)[a]	$Pbcn$	Ru_2Si_3	1.1436	0.9238	0.5716			[2]
	Ru_2Ge_3 (LT)	$Pbcn$	Ru_2Si_3	1.144(2)	0.9237(7)	0.5719(8)	2.2		–[c]
6	$SmGe_{1.63}$[a]	$I4_1/amd$	$ThSi_2$	0.4183		1.3810		1030	[7–9]
7	$SmGe_{1.5}$[a]	$P6/mmm$	AlB_2	0.4005		0.4250		1020	[7,9]
	$SmGe_{1.5}$[a]	$P6/mmm$	AlB_2	0.4002(1)		0.4244(1)	2.6		–[c]
	$SmGe_{1.5}$ (HT1)	...						1360	[9]
	$SmGe_{1.5}$ (HT2)	...						**1630**	[9]
8	SmGe[a]	$Cmcm$	CrB	0.4374	1.0885	0.3996		**1670**	[2,6,9]
	SmGe[a]	$Cmcm$	CrB	0.4366(3)	1.0853(3)	0.3985(1)	4.9		–[c]
9	Sm_5Ge_4[a]	$Pnma$	Sm_5Ge_4	0.774	1.495	0.784		**1770**	[2,5,9]
	Sm_5Ge_4[a]	$Pnma$	Sm_5Ge_4	0.777(1)	1.5146(2)	0.783(1)	1.9		–[c]
10	Sm_5Ge_3[a]	$P6_3/mcm$	Mn_5Si_3	0.866		0.649		***1970***	[2,4,9]
	Sm_5Ge_3[a]	$P6_3/mcm$	Mn_5Si_3	0.8607(2)		0.6497(2)	4.3		–[c]
11	Sm_3Ru[a]	$Pnma$	Fe_3C	0.733	0.9508	0.6361		**1090**	[2,12]
12	Sm_5Ru_2[a]	$C2/c$	Mn_5C_2	1.6083	0.6438 $\beta = 96.89^{\circ}$	0.7314		**1180**	[2,12]
13	$Sm_{44}Ru_{25}$[a]	$Pnma$	$Y_{44}Ru_{25}$					**1220**	[11]
	$Sm_{44}Ru_{25}$[a]	$Pnma$	$Y_{44}Ru_{25}$	2.276(2)	1.509(1)	1.5033(9)	6.1		–[c]
14	$SmRu_2$ (HT)	$Fd3m$	$MgCu_2$	0.7577				***2310***	[2,10]
	$SmRu_2$ (LT)[a]	$P6_3/mmc$	$MgZn_2$	0.5282		0.8854			[2,10]
	$SmRu_2$ (LT)[a]	$P6_3/mmc$	$MgZn_2$	0.5287(2)		0.8940(2)	5.3		–[c]

[a] Compounds belongs to the isothermal cross-section at 1070 K.

[b] The temperatures listed refer to a solid-phase transition (normal font), to the melting temperature (italic bold font) or to the melting temperature for peritectic (bold font).

[c] This work.

a W–W (20% Re) thermocouple. As reference we used the melting temperature of Cu (1356 K) and the phase transitions temperatures of Fe (1041, 1183, 1663, 1812 K). The purity of all standard metals was 99.999% at. The accuracy of the temperature measurements was ±10 K.

3. Results and discussion

The results obtained were used in the construction of the isothermal section of the Sm–Ru–Ge system at 1070 K, presented in Fig. 2.

Crystallographic data and the temperature of the phase transition of the binary compounds in the Sm–Ru, Sm–Ge and Ru–Ge systems and the crystallographic data of the binary compounds that were detected in the isothermal section at 1070 K are shown in Table 1. A high-temperature $MgCu_2$-type modification of $SmRu_2$ was found in which Ge substitutes for Ru, leading to the $Sm_{33}Ru_{52}Ge_{15}$ compound (Table 2). The other binary compounds do not show any visible solubility.

The compounds $SmRu_2Ge_2$, $Sm_2Ru_3Ge_5$, $Sm_3Ru_4Ge_{13}$, $Sm_3Ru_2Ge_2$, Sm_2RuGe_2 and the new compounds SmRuGe, Sm_5Ru_2Ge and Sm_2RuGe_{5-x} were detected in the isothermal section at 1070 K (Table 2).

The SmRuGe compound belongs to the well-known TiNiSi-type structure. We have not detected the CeFeSi-type SmRuGe compound [17] in the present work.

Table 2

Crystallographic data and the melting temperature T_m of compounds in the Sm–Ru–Ge systems. The reliability factors are $R_F = 100 \cdot (\Sigma_k|(I_k^{obs})^{1/2} - (I_k^{cal})^{1/2}|)/\Sigma_k|(I_k^{obs})^{1/2}|)\%(I_k^{obs}$ is the integrated intensity evaluated from summation of contribution of the kth peaks to net observed intensity, $I_k{}^{cal}$ is the integrated intensity calculated from refined structural parameters)

	Compound	Space group	Structure type	a (nm)	b (nm)	c (nm)	R_F (%)	T_m (K)	Refs.
1	$SmRu_2Ge_2$	$I4/mmm$	$CeGa_2Al_2$	0.4236		0.9944			[13]
	$SmRu_2Ge_2$	$I4/mmm$	$CeGa_2Al_2$	0.4229(1)		0.9933(2)	5.4	>2000	–[a]
2	$Sm_2Ru_3Ge_5$	$Ibam$	$U_2Co_2Si_3$	0.9867	1.244	0.579			[14]
	$Sm_2Ru_3Ge_5$	$Ibam$	$U_2Co_2Si_3$	0.9878(6)	1.2437(8)	0.5791(4)	1.8	1760(10)	–[a]
3	$Sm_3Ru_4Ge_{13}$	$Pm3n$	$Y_3Co_4Ge_{13}$	0.9020					[15]
	$Sm_3Ru_4Ge_{13}$	$Pm3n$	$Y_3Co_4Ge_{13}$	0.9016(1)			3.4	1600(10)	–[a]
4	Sm_2RuGe_{5-x}	$Pmmn$	$CeRh_{1-x}Ge_{2+x}$	0.4061(2)	0.4178(2)	1.6223(7)	6.3		
5	Sm_2RuGe_2	$B2/m$	Zr_2CoSi_2	1.0948(3)	1.0839(3)	0.4302(1) $\gamma = 123.23(2)^\circ$	1.8	1750(10)	–[a]
6	SmRuGe	$P4/nm$	CeFeSi	0.4244		0.6711			[17]
	SmRuGe	$Pnma$	TiNiSi	0.7165(1)	0.4476(1)	0.7152(1)	6.2		–[a]
7	$Sm_3Ru_2Ge_2$	$Pbcm$	$La_3Ni_2Ga_2$	0.5611	0.7818	1.3473			[16]
	$Sm_3Ru_2Ge_2$	$Pbcm$	$La_3Ni_2Ga_2$	0.5620(1)	0.7808(1)	1.3567(2)	4.6	1560(10)	–[a]
8	Sm_5Ru_2Ge	$I4/mcm$	Cr_5B_3	0.7736(4)		1.3426(8)	2.0		–[a]
9	$Sm_{33}Ru_{52}Ge_{15}$	$Fd3m$	$MgCu_2$	0.7557(1)			3.6		–[a]
10	$Sm_3Ru_2Ge_4$	$B2/m$	$Tb_3Co_2Ge_4$	1.0899(9)	0.8139(8)	0.4319(3) $\gamma = 109.29(7)^\circ$	6.9		–[a]

[a] This work.

The Sm_2RuGe_{5-x} compound forms in the $Sm_3Ru_4Ge_{13}$–$SmGe_{1.5}$–$Sm_2Ru_3Ge_5$ domain of the Sm–Ru–Ge system after annealing at 1070 K. The Sm_2RuGe_{5-x} compound belongs to the orthorhombic structure type. The $CeRh_{1-x}Ge_{2+x}$-type structure [21] is the best model for this compound.

Substitution of Ge for Ru in the Mn_5Si_3-type Sm_5Ge_3 compound leads to the formation of the Cr_5B_3-type Sm_5Ru_2Ge compound.

We have detected the $Tb_2Co_3Ge_4$-type [22] $Sm_3Ru_2Ge_4$ compound (Table 2) as an admixture phase with the SmGe, $Sm_2Ru_3Ge_5$ and Sm_2RuGe_2 compounds in a sample of the composition $Sm_{33}Ru_{22}Ge_{44}$. Obviously, the $Tb_3Co_2Ge_4$-type $Sm_3Ru_2Ge_4$ compound is this intermediate (nonstable) phase.

The atomic position parameters of the ternary compounds of the Sm–Ru–Ge system are shown in Table 3.

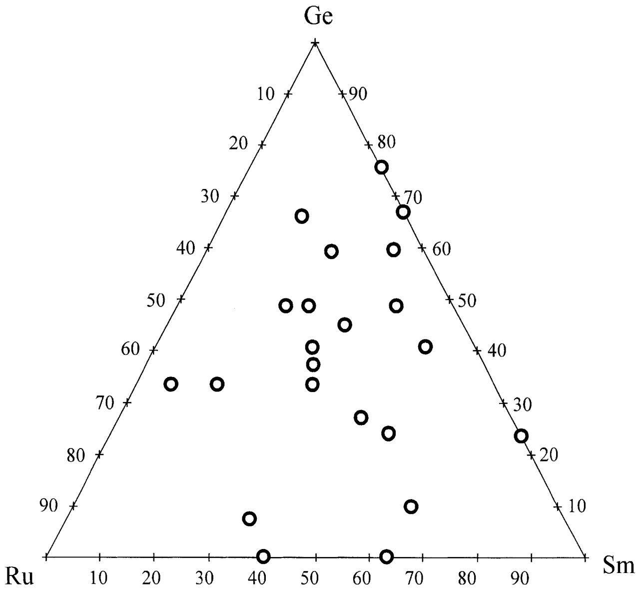

Fig. 1. Composition of samples investigated in the Sm–Ru–Ge system.

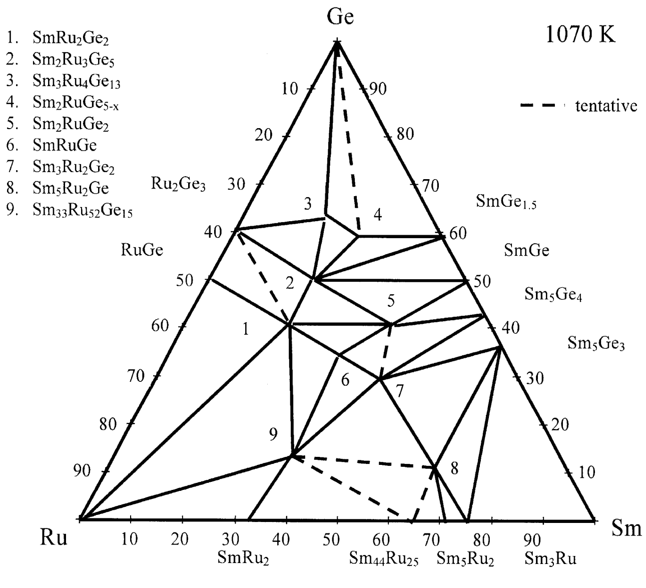

Fig. 2. Isothermal section of the Sm–Ru–Ge system at 1070 K.

Table 3
Atomic position parameters of ternary compounds in the Sm–Ru–Ge system

Atom	Type of position	x/a	y/b	z/c	Occupation factor
(a)					
Sm	2(*a*)	0	0	0	
Ru	4(*d*)	0	1/2	1/4	
Ge	4(*e*)	0	0	0.3664(6)	
(b)					
Sm	8(*j*)	0.266(1)	0.137(1)	0	
Ru1	4(*a*)	0	0	1/4	
Ru2	8(*j*)	0.092(2)	0.354(2)	0	
Ge1	4(*b*)	1/2	0	1/4	
Ge2	8(*g*)	0	0.204(2)	1/4	
Ge3	8(*j*)	0.324(2)	0.415(2)	0	
(c)					
Sm	6(*b*)	1/4	1/2	0	
Ru	8(*c*)	1/4	1/4	1/4	
Ge1	2(*a*)	0	0	0	
Ge2	24(*f*)	0	0.318(1)	0.160(1)	
(d)					
Sm1	2(*c*)	1/4	1/4	0.148(2)	1.00
Sm2	2(*c*)	1/4	3/4	0.651(2)	1.00
T1*	2(*c*)	1/4	1/4	0.949(6)	1.00
T2	2(*c*)	1/4	3/4	0.293(6)	1.00
Ge1	2(*c*)	1/4	1/4	0.793(7)	1.00
Ge2	2(*c*)	1/4	1/4	0.494(5)	1.00
Ge3	2(*c*)	1/4	3/4	0.008(5)	1.00
Ge4	2(*c*)	1/4	3/4	0.436(9)	0.20(1)
(e)					
Sm1	4(*j*)	0.176(1)	0.677(1)	0	
Sm2	4(*j*)	0.421(1)	0.111(1)	0	
Ru	4(*j*)	0.144(2)	0.370(2)	0	
Ge1	4(*j*)	0.424(2)	0.575(2)	0	
Ge2	4(*j*)	0.127(2)	0.125(2)	0	
(f)					
Sm	4(*c*)	0.482(1)	1/4	0.314(1)	
Ru	4(*c*)	0.149(1)	1/4	0.563(1)	
Ge	4(*c*)	0.808(2)	1/4	0.600(2)	
(g)					
Sm1	8(*e*)	0.154(2)	0.100(2)	0.102(1)	
Sm2	4(*d*)	0.624(4)	0.244(3)	1/4	
Ru	8(*e*)	0.350(4)	0.470(2)	0.090(1)	
Ge1	4(*d*)	0.141(7)	0.378(4)	1/4	
Ge2	4(*c*)	0.618(8)	1/4	0	
(h)					
Sm	8(*a*)	0	0	0	
$Ru_{0.77}Ge_{0.23}$	16(*d*)	1/8	1/8	1/8	
(i)					
Sm1	4(*i*)	0.379(5)	0.301(4)	0	
Sm2	2(*a*)	0	0	0	
Ru	4(*i*)	0.685(6)	0.303(6)	0	
Ge1	4(*i*)	0.122(9)	0.376(8)	0	
Ge2	4(*i*)	0.739(7)	0.069(9)	0	

*, $T1 = T2 = Ru_{0.4}Ge_{0.6}$.

[a] $CeGa_2Al_2$-type $SmRu_2Ge_2$ compound [$a = 0.4229(1)$ nm, $c = 0.9933(2)$ nm, space group $I4/mmm$, No. 139].

[b] $U_2Co_3Si_5$-type $Sm_2Ru_3Ge_5$ compound [$a = 0.9878(6)$ nm, $b = 1.2437(8)$ nm, $c = 0.5791(4)$ nm, space group *Ibam*, No. 72].

[c] $Y_3Co_4Ge_{13}$-type $Sm_3Ru_4Ge_{13}$ compound [$a = 0.9016(1)$ nm, space group $Pm3n$, No. 223].

[d] $CeRh_{1-x}Ge_{2+x}$-type Sm_2RuGe_{5-x} compound [$a = 0.4061(2)$ nm, $b = 0.4178(2)$ nm, $c = 1.6223(7)$ nm, space group *Pmmn*, No. 59-2].

[e] Zr_2CoSi_2-type Sm_2RuGe_2 compound [$a = 1.0948(3)$ nm, $b = 1.0839(3)$ nm, $c = 0.4302(1)$ nm, $\gamma = 123.23(2)^\circ$, space group $B2/m$, No. 12-1].

[f] TiNiSi-type SmRuGe compound [$a = 0.7165(1)$ nm, $b = 0.4476(1)$ nm, $c = 0.7152(1)$ nm, space group *Pnma*, No. 62].

[g] $La_3Ni_2Ga_2$-type $Sm_3Ru_2Ge_2$ compound [$a = 0.5620(1)$ nm, $b = 0.7808(1)$ nm, $c = 1.3567(2)$ nm, space group *Pbcm*, No. 57].

[h] $MgCu_2$-type $Sm_{33}Ru_{52}Ge_{15}$ compound [$a = 0.7557(1)$ nm, space group *Fd3m*, No. 227-1].

[i] $Tb_3Co_2Ge_4$-type $Sm_3Ru_2Ge_4$ compound [$a = 1.0899(9)$ nm, $b = 0.8139(8)$ nm, $c = 0.4319(3)$ nm, $\gamma = 109.23(7)^\circ$, space group $B2/m$, No. 12-1].

The $SmRu_2Ge_2$ compound has the maximal melting temperature of all the ternary compounds of the Sm–Ru–Ge system (Table 2).

4. Conclusion

It is obvious that the phase equilibria in the {Y, Gd–Tm}–Ru–Ge systems will be close to those of the Sm–Ru–Ge system. So, we can detect compounds with the same structure type in the {Y, Gd–Tm}–Ru–Ge systems. Possibly, Cr_5B_3-type Gd_5Ru_2Ge or Tb_5Ru_2Ge may be interesting as magnetic materials.

References

[1] J. Emsley, The Elements, 2nd Edition, Clarendon Press, Oxford, 1991.
[2] Pearson’s Handbook of Crystallographic Data for Intermetallic Phases, American Society for Metals, Metals Park, OH, Vol. 3, 1985.
[3] E. Raub, W. Fritzsche, Z. Metallkd. 53 (12) (1962) 779–781.
[4] K.H.J. Buschow, I.F. Fast, Phys. Status Sol. 21 (1967) 593–600.
[5] G.S. Smith, Q. Johnson, A.G. Tharp, Acta Crystallgr. 22 (2) (1967) 269–272.
[6] A.G. Tharp, G.S. Smith, Q. Johnson, Acta Crystallgr. 20 (4) (1966) 583–585.
[7] I. Mayer, Y. Eshdat, Inorg. Chem. 7 (9) (1968) 1904–1908.
[8] K.H.J. Buschow, J.F. Fast, Phys. Status Sol. 16 (1966) 467–473.
[9] J. Ghosh, H.L. Lukas, L. Delaey, Calphad 12 (3) (1988) 295–299.
[10] J.F. Cannon, D.L. Robertson, H.T. Hall, J. Less-Common Met. 29 (2) (1972) 141–146.
[11] A. Palenzona, F. Canepa, J. Less-Common Met. 66 (2) (1979) L31–L33.
[12] A. Palenzona, J. Less-Common Met. 66 (2) (1979) 27–33.
[13] M. Francois, G. Venturini, J.F. Mareche, B. Malaman, B. Roques, J. Less-Common Met. 113 (2) (1985) 231–237.
[14] G. Venturini, M. Meot-Meyer, J.F. Mareche, B. Malaman, B. Roques, Mater. Res. Bull. 21 (1) (1986) 33–39.
[15] L. Serge, Ternary superconductors, in: Proc. Int. Conf., Lake Geneva, 1980, p. 243.
[16] O.I. Bodak, Izv.Akad.Nauk SSSR, Met. 5 (1990) 217–219, in Russian.
[17] R. Welter, G. Venturini, B. Malaman, E. Ressouche, J. Alloys Comp. 202 (1–2) (1993) 165–172.
[18] A.V. Morozkin, Yu.D. Seropegin, O.I. Bodak, J. Alloys Comp. 234 (1996) 143–150.
[19] F. Izumi, Rigaku J. 6 (N1) (1989) 10–19.
[20] F. Izumi, in: R.A. Young (Ed.), The Rietveld Method. Oxford University Press, Oxford, 1993, Chapter 13.
[21] B.I. Shapiev, Interaction of components in the Ce–{Ru,Rh}–(Si,Ge} systems at 870 K, Dissertation of candidate of chemical science, Moscow, MSU, 1988 (in Russian).
[22] P.K. Starodub, I.R. Mokraya, O.I. Bodak, V.K. Pecharskii, V.A. Bruskov, Kristallografiya 31 (1986) 394–396 (in Russian).