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Isothermal cross-section of the Ce–Ru–Ge phase diagram at 600°C

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Abstract

The interaction of the components of the Ce–Ru–Ge system at 600°C was investigated over the whole concentration range by X-ray powder and X-ray microprobe analysis. The formation of the previously reported phases, $CeRu_2Ge_2$ and $Ce_2Ru_3Ge_5$, was confirmed and five new ternary compounds were observed. The crystal structures of $CeRuGe_3$ and CeRuGe were determined.

Keywords: Phase equilibria; Rare earth ruthenium germanides; Ternary system

1. Introduction

This work is the latest contribution of our investigations of ternary systems RE–TM–X (RE, rare earth; TM, transition metal, X=Si or Ge). The interaction of the components in such systems results in ternary intermetallic compounds which are known to exhibit a number of interesting properties such as heavy-fermion superconductivity, Kondo behavior, anomalous magnetism, and/or intermediate valency. The present investigation provided data on the interaction of the components in the Ce–Ru–Ge ternary system and on the crystal structure of two new ternary intermetallic compounds.

The binary systems bounding the ternary system have been described in detail in the literature. Seven intermediate phases occur in the Ce–Ge system [1–3]: Ce_3Ge, Ce_5Ge_3, Ce_4Ge_3, Ce_5Ge_4, CeGe, $CeGe_{2-x}$ and $CeGe_2$ (Table 1). Two of them, namely CeGe and $CeGe_{2-x}$, exhibit homogeneity ranges that are about 0.5 at.% for CeGe and x=0.36–0.43 for $CeGe_{2-x}$ (1 at.%) [3]. The compositions of other phases are invariant.

The interaction of the components in the Ce–Ru binary system was studied in detail by Palenzona [4]. There are five intermediate phases in the Ce–Ru system: $CeRu_2$, Ce_4Ru_3, $Ce_{16}Ru_9$, Ce_7Ru_3 and Ce_3Ru. All intermediate phases form peritectically and exist at fixed compositions. Both Ce and Ru do not dissolve any noticeable amount of the second component. Crystal structure and lattice parameter data for the binary phases of the Ce–Ru system are summarized in Table 2 [4].

The binary phase diagram Ru–Ge was investigated in Ref. [5]. There are two intermediate phases in this system, Ru_2Ge_3 and RuGe, which exist at fixed compositions. Both ruthenium and germanium do not dissolve a second component. Crystal structure and lattice parameter data for the intermediate Ru–Ge phases are shown in Table 3 [6].

Before our work no systematic studies of the ternary Ce–Ru–Ge system throughout the whole concentration range had been performed. Information on two ternary compounds only, $CeRu_2Ge_2$ and $Ce_2Ru_3Ge_5$, was reported. The crystallographic data that has been published for these two phases are given in Table 4 with references.

2. Experimental details

The present investigation was carried out with 114 samples having masses of about 1 g. They were prepared in an electric arc furnace under an argon atmosphere with a nonconsumable tungsten electrode and a water-cooled copper hearth. The purity of cerium was 99 at.%, the purity of ruthenium and germanium was >99.9 at.%. Titanium was used as a getter during melting. The alloys were remelted two times in order to achieve complete fusion and homogeneity. Alloys with melting losses not exceeding 1 wt.% were chosen for the experiments. All alloys after melting were subjected to a homogenizing anneal in

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Table 1
Crystal structure and lattice parameter data for the intermediate phases in the Ce–Ge system [2]

Phase	Composition (at.% Ge)	Space group	Prototype	Lattice parameters (nm)		
				a	*b*	*c*
Ce_3Ge	25	*P4₂/n*	Ti_3P [a]	1.224(3)		0.640(5)
Ce_5Ge_3	37.5	*P6₃/mcm*	Mn_5Si_3	0.887		0.6588
Ce_4Ge_3	42.9	*I43d*	Th_3P_4	0.9214(4)		
Ce_5Ge_4	44.5	*Pnma*	Sm_5Ge_4	0.795(2)	1.522(3)	0.806(2)
CeGe	50	*Pnma*	FeB	0.8354(5)	0.4082(3)	0.6033(3)
α-$CeGe_{2-x}$	61.1–62.12	*Imma*	α-$GdSi_2$	0.4355	0.4247	1.4054
β-$CeGe_{2-x}$	61.6–62.12 62.12	*I4₁/amd*	α-$ThSi_2$	0.4248		1.4186
$CeGe_2$ [b]	66.7	*Imma*	α-$GdSi_2$ [b]	0.4202		1.4153

[a] From Ref. [2].
[b] From Ref. [1].

Table 2
Crystal structure and lattice parameter data for the intermediate phases in the Ce–Ru system [4]

Phase	Composition, (at.% Ru)	Space group	Prototype	Lattice parameters (nm)		
				a	*b*	*c*
Ce_3Ru	25	*Pnma*	Fe_3C	0.7242	0.9863	0.6419
Ce_7Ru_3	30	*P6₃ mc*	Th_7Fe_3	0.9802		0.6261
$Ce_{16}Ru_9$	36	*R3m*	$Ce_{16}Ru_9$	1.3645		2.2742
Ce_4Ru_3	42.9	*C2/m*	Ce_4Ru_3	0.8400	1.3837	0.5985
$CeRu_2$	66.7	*Fd3m*	$MgCu_2$	0.7545		

Table 3
Crystal structure and lattice parameter data for the intermediate phases in the Ru–Ge system [6]

Phase	Composition (at.% Ge)	Space group	Prototype	Lattice parameters (nm)		
				a	*b*	*c*
RuGe	50	*P2₁3*	FeSi	0.4846		
Ru_2Ge_3	60	*Pbcn*	Ru_2Si_3	1.1436	0.9238	0.5716

evacuated double-walled quartz ampoules containing titanium chips as getters. Annealing was performed in a resistance furnace at 600°C for 720 h with subsequent quench into ice water.

X-ray powder diffraction and electron probe X-ray analyses were used in the present investigation. X-ray phase analyses were performed with an URS-60 generating unit with Cr Kα radiation (λ=0.229092 nm) for RKD-57 cameras having asymmetric film loading. For precision lattice parameters, one of the following was used: ''DRON-2.0'' with Fe Kα radiation, λ=0.193728 nm; ''DRON-3.0'' with Cu Kα radiation, λ=0.154178 nm.

Table 4
Crystal structure and lattice parameter data published for two of the ternary intermediate phases of the Ce–Ru–Ge system

Phase	Space group	Prototype	Lattice parameters (nm)			Ref.
			a	*b*	*c*	
$CeRu_2Ge_2$	*I4/mmm*	$CeAl_2Ga_2$	0.4270		1.0088	[8]
$Ce_2Ru_3Ge_5$	*Ibam*	$U_2Co_3Si_5$	0.9919	1.238	0.5887	[9]

Calculations needed for the analysis of the X-ray experiments were performed with CSD programs of Ref. [7]. Electron probe X-ray analyses were performed with a ''Comebax Microbeam'' analyzer. This device was used for phase identification of the individual grains in the microstructure by energy dispersive analyses of secondary electrons in combination with determination of the position and intensity of characteristic X-ray wavelengths.

3. Results and discussion

The isothermal cross-section of the Ce–Ru–Ge phase diagram at 600°C has been constructed by using data obtained in the present work. The existence of the two phases known before was confirmed, and we found the formation of at least five new ternary compounds (Fig. 1).

The binary phase α-$CeGe_{2-x}$ has an extension into the ternary space of the diagram up to 5 at.% Ru. The other

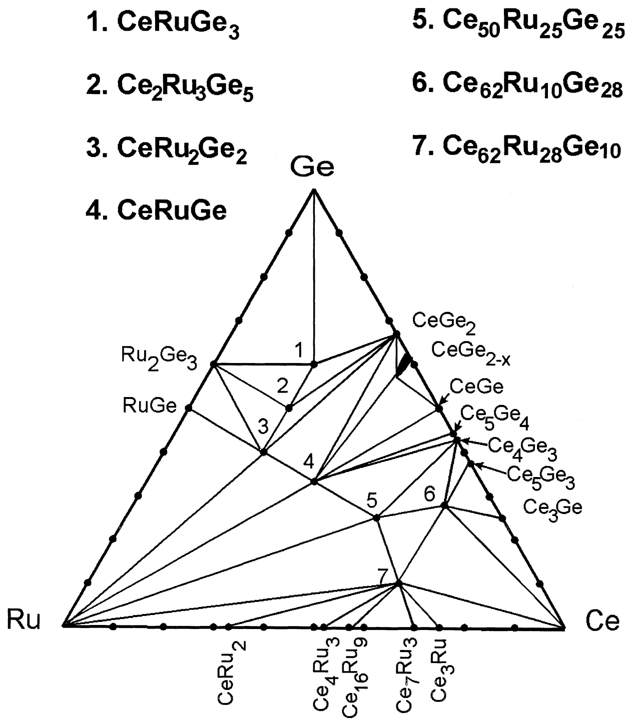

Fig. 1. Isothermal cross-section of the Ce–Ru–Ge system at 600°C.

Table 6
Results of microprobe X-ray analyses of some alloys from the Ce–Ru–Ge ternary system

Alloy composition (at.%)			No. of phases	Composition of phases (at.%)		
Ce	Ru	Ge		Ce	Ru	Ge
30	30	40	3	20	40	40
				33	0	67
				33	33	34
50	20	30	3	33	33	34
				50	25	25
				57	0	43
55	15	30	3	50	25	25
				62	10	28
				57	0	43
50	25	25	1	50	25	25
40	40	20	2	50	25	25
				0	100	0
50	30	20	3	0	100	0
				50	25	25
				62	28	10
60	20	20	3	50	25	25
				62	10	28
				62	28	10
45	45	10	3	0	100	0
				50	25	25
				62	28	10

binary compounds of the Ce–Ge, Ce–Ru and Ru–Ge systems exist at fixed compositions.

X-ray powder diffraction was used for determining the structure of $CeRu_2Ge_2$, $Ce_2Ru_3Ge_5$, $CeRuGe_3$ and CeRuGe. The crystallographic data obtained for the ternary compounds are given in Table 5.

Investigation of the powder diffraction data of alloys with compositions $Ce_{50}Ru_{25}Ge_{25}$, $Ce_{62}Ru_{28}Ge_{10}$ and $Ce_{62}Ru_{10}Ge_{28}$ leads to the speculation that even more ternary phases may exist at or near these compositions. However, no crystal structure determinations were performed because suitable monocrystals were not obtained. Support for our opinion about the existence of these additional phases is based on results of X-ray microprobe analyses of alloys with nearly single phase compositions, and of alloys corresponding to two-phase and three-phase regions. These results are presented in Table 6.

The interaction of the components in the ternary Ce–Ru–Ge system proceeds by a complicated path and leads to the formation of seven compounds. Unlike the ternary systems, in which the second component is Pt or Pd, in the Ce–Ru–Ge system compounds such as $(RE)_2$ $(TM)Ge_6$ with Ce_2CuGe_6 type structure and $Ce(Ru,Ge)_2$ with the AlB_2 type structure do not exist.

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Table 5
Crystal structure and lattice parameter data for the ternary intermediate phases in the Ce–Ru–Ge system

N Phase	Space group	Prototype	Lattice parameters (nm)		
			a	*b*	*c*
1. $CeRuGe_3$	*Cmmm*	$ScNiSi_3$	2.185(1)	0.4234(6)	0.4285(6)
2. $Ce_2Ru_3Ge_5$	*Ibam*	$U_2Co_3Si_5$	1.003(1)	1.204(1)	0.5895(5)
3. $CeRu_2Ge_2$	*I4/mmm*	$CeAl_2Ga_2$	0.42717(6)		1.0054(1)
4. CeRuGe	*P4/nmm*	PbFCl	0.4195(2)		0.6916(5)
5. $Ce_{50}Ru_{25}Ge_{25}$					
6. $Ce_{62}Ru_{10}Ge_{28}$					
7. $Ce_{62}Ru_{28}Ge_{10}$					

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