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

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Abstract

The interaction of the components in the Ce–Pd–Ge system at 600°C was investigated over the whole concentration range by X-ray powder and monocrystal diffraction, metallography, and X-ray microprobe analysis. The formation of the previously reported phases, CePdGe and $CePd_2Ge_2$, was confirmed and 15 new ternary compounds were observed. The crystal structures of the compounds Ce_2PdGe_6, $Ce(Pd,Ge)_2$, $Ce_3Pd_{20}Ge_6$, $CePd_2Ge$, $Ce_7Pd_4Ge_2$ and $CePd_5Ge_3$ were determined.

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

1. Introduction

The ternary compounds RE–TM–X (RE, rare earth; TM, transition metal; X, Si or Ge) 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 has obtained data on the interaction of the components in the Ce–Pd–Ge ternary system and on the crystal structure of new ternary intermetallic compounds.

The three binary systems bounding the ternary system have been described in detail in the literature. The first investigation of the interactions in the Ce–Ge binary system was made by Gladyshewski [1]. The $CeGe_2$ binary phase was reported to exist at fixed composition based on X-ray powder and single crystal diffraction and microstructure data. In Ref. [2] the Ce–Ge binary system was investigated over the whole concentration range by X-ray powder diffraction, DTA and microstructure analyses. Six intermediate phases were found in this work: Ce_3Ge, Ce_5Ge_3, Ce_4Ge_3, Ce_5Ge_4, CeGe, and $CeGe_{2-x}$. Eremenko et al. [2] assumed that not $CeGe_2$ but $CeGe_{2-x}$ with two crystallographic modifications really exists. In the present investigation we have established that the alloy $Ce_{33}Ge_{67}$ crystallises in the α-$GdSi_2$-type structure and the $Ce_{38}Ge_{62}$ alloy crystallises in the α-$ThSi_2$-type structure. Therefore, we will construct the isothermal section of the Ce–Pd–Ge phase diagram under the supposition that both phases are present. The existence of other intermediate binary phases was confirmed in our investigation. According to Eremenko et al. [2], at 600°C, cerium and germanium do not dissolve any noticeable amount of the second component. The compounds CeGe and $CeGe_{2-x}$ exhibit homogeneity ranges, about 0.5 at.% for CeGe and 36–43 at.% Ce for $CeGe_{2-x}$. The compositions of the remaining intermediate phases are invariant. Crystal structure and lattice parameter data for the binary phases of the Ce–Ge system are summarized in Table 1 [3].

All previous reports on the interaction of the components in the Ce–Pd binary system were summarized and analyzed in the review of Okamoto [4]. There are eight intermediate phases in the Ce–Pd system [4]: Ce_7Pd_3, Ce_3Pd_2, CePd, Ce_3Pd_4, Ce_3Pd_5, $CePd_3$, $CePd_5$, $CePd_7$. Two of these, CePd and $CePd_5$, have low- and high-temperature modifications (α and β) of their crystal structure. At 600°C both exist in their low-temperature modifications. According to Bretschneider and Schaller [5] Pd dissolves up to 6.7 at.% Ce at 1000°C. This fact resulted from the concentration dependence of the lattice spacing of Pd solid solutions. Nevertheless, Okamoto reports that the homogeneity region of (Pd) alloys extends up to 13 at.% Ce at 1075°C, in accordance with the previous work reported by Sakamoto et al. [6]. Cerium does not dissolve any noticeable amount of palladium. As derived from X-ray powder diffraction and microstructure data, the homogeneity region of $CePd_3$ is about 1.4 at.% [4,5]. The other intermediate phases have fixed compositions. In our work the solubility of cerium in palladium

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Table 1
Crystal structure and lattice parameter data for the intermediate phases in the Ce–Ge system [3]

Phase	Composition (at.% Ge)	Space group	Prototype	Lattice parameters (nm)		
				a	*b*	*c*
Ce_3Ge	25	$P4_2/n$	Ti_3P[a]	1.224(3)		0.640(5)
Ce_5Ge_3	37.5	$P6_3/mcm$	Mn_5Si_3	0.887		0.6588
Ce_4Ge_3	42.9	$I\bar{4}3d$	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	$I4_1/amd$	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].

at 600°C was about 9 at.%. The homogeneity regions of the other intermediate phases are in accordance with literature data. Crystal structure and lattice parameter data for the binary phases of the Ce–Pd system are summarized in Table 2 [4].

The resulting binary phase diagram for Pd–Ge was reported in Ref. [7]. There are six intermediate binary phases in the Pd–Ge system: Pd_5Ge, Pd_3Ge, $Pd_{25}Ge_9$, $Pd_{21}Ge_8$, Pd_2Ge, and PdGe. Pd_5Ge has high- and low-temperature crystal structure modifications. Palladium does not dissolve germanium; the solubility of palladium in germanium has not been studied. All intermediate phases have homogeneity regions: Pd_5Ge 1 at.%, Pd_3Ge 1.1 at.%, $Pd_{25}Ge_9$ 1 at.%, $Pd_{21}Ge_8$ 1.2 at.%, Pd_2Ge 2 at.%, and PdGe 2.3 at.%. Crystal structure and lattice parameter data for the intermediate Pd–Ge phases are summarized in Table 3. The X-ray powder diffraction data of the present investigation correspond to the data reported in the previous publications. The solubility of Pd in Ge was found to be <2 at.%.

Table 2
Crystal structure and lattice parameter data for the intermediate phases in the Ce–Pd system [4–6,8,9]

Phase	Composition (at.% Pd)	Space group	Prototype	Lattice parameters (nm)		
				a	*b*	*c*
Ce_7Pd_3	30	$P6_3mc$	Fe_3Th_7	1.0222		0.6441
Ce_3Pd_2	40					
α-CePd	50	*Cmcm*	CrB	0.3890	1.0910	0.4635
β-CePd	50	*Pnma*	FeB			
Ce_3Pd_4	57.1					
Ce_3Pd_5	62.5	$P\bar{6}2m$	Th_3Pd_5			
$CePd_3$	74.8–76.2	$Pm\bar{3}m$	Cu_3Au	0.4160		
α-$CePd_5$	83.3	*Pnma*		0.5700	0.4062	0.8462
β-$CePd_5$	83.3	*cub*		0.4055		
$CePd_7$	87.5	*Fm3m*	Pt_7Cu	0.80805		

Table 3
Crystal structure and lattice parameter data for the intermediate phases in the Pd–Ge system [8]

Phase	Composition (at.% Ge)	Space group	Prototype	Lattice parameters (nm)		
				a	*b*	*c*
α-Pd_5Ge	16.7	*C2*	Pd_5As	0.5509	0.7725, $\beta = 98.09°$	0.8375
β-Pd_5Ge	16.7	*Im3m*	W	0.3137		
Pd_3Ge	25					
$Pd_{25}Ge_9$	26.3	$P\bar{3}$	$Pd_{25}Ge_9$	0.7351		1.0605
$Pd_{21}Ge_8$	27.6	$I4_1/a$	$Al_{21}Pt_8$	1.3067		1.0033
Pd_2Ge	33.3	$P\bar{6}2m$	Fe_2P	0.6712		0.3408
PdGe	50	*Pnma*	MnP	0.5782	0.3481	0.6259

Table 4
Published crystal structure and lattice parameter data for two of the ternary intermediate phases of the Ce–Pd–Ge system [10,11]

Phase	Space group	Prototype	Lattice parameters (nm)		
			a	*b*	*c*
CePdGe	*Imma*	KHg_2	0.44875	0.73001	0.76759
$CePd_2Ge_2$	*I4/mmm*	$CeAl_2Ga_2$	0.4369		1.0055

Systematic studies of the ternary Ce–Pd–Ge system over the whole concentration range have not been performed. Nevertheless, some information has been reported concerning the crystallographic and physical properties of two ternary compounds, $CePd_2Ge_2$ and CePdGe. 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 performed with 153 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 the cerium was 99 at.% and the purity of the palladium and germanium was better than 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 evacuated double-walled quartz ampoules containing titanium chips as getters. Annealing was performed in a resistance furnace at 600°C for 720 h with a subsequent quench in ice water.

Metallography, X-ray powder and monocrystal diffraction, and electron probe X-ray analyses were used in the present investigation. In the metallographic studies, Pd-rich samples (>60 at.% Pd) were etched in a HNO_3+HCl (1:1) solution. A HNO_3+H_2O (2:1) mixture was used for etching alloys with <50 at.% Ce. Ce-rich samples (>50 at.% Ce) were etched by highly dilute HNO_3. Microstructures were examined with a ''Neophot 32'' microscope at magnifications of 200× and 250×.

X-ray phase analyses were performed with a 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;
''DRON-4.0'' with Co Kα radiation, λ=0.179020 nm;
FR-552 focusing monochromator camera with Cu Kα1 radiation, λ=0.154051 nm, and Ge as an internal standard.

X-ray monocrystal analyses were first carried out photographically with RKV-86 or RGNS-2 cameras and Mo Kα radiation, then with an Enraf-Nonius CAD-4 autodiffractometer and Mo Kα radiation. Calculations were performed with the CSD programs of Ref. [12].

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 the determination of the position and intensity of characteristic X-ray wavelengths.

DTA experiments were executed on high temperature VDTA-8M_2 equipment (W–W/Re thermocouples) in a BeO crucible. Pure Fe, Cu, and Pt metals were used as calibration standards.

3. Results and discussion

Results from the present measurements were used in the construction of the isothermal cross-section of the Ce–Pd–Ge phase diagram at 600°C (Fig. 1). The two intermediate phases listed in Table 4 were also found. $CePd_3$, Ce_3Pd_5, Ce_3Pd_4, Ce_7Pd_3, Ce_4Ge_3, Ce_5Ge_4, CeGe and $CeGe_{2-x}$ all have noticeable extensions into the ternary system. The binary phases of the Pd–Ge system and the remaining binary phases in the other two systems dissolve <5 at.% of the third component. The interaction of Ce, Pd and Ge leads to the formation of at least 17 ternary phases, including the two phases already reported. The crystallographic data obtained for the ternary compounds are given in Table 5. The powder diffraction method was applied for

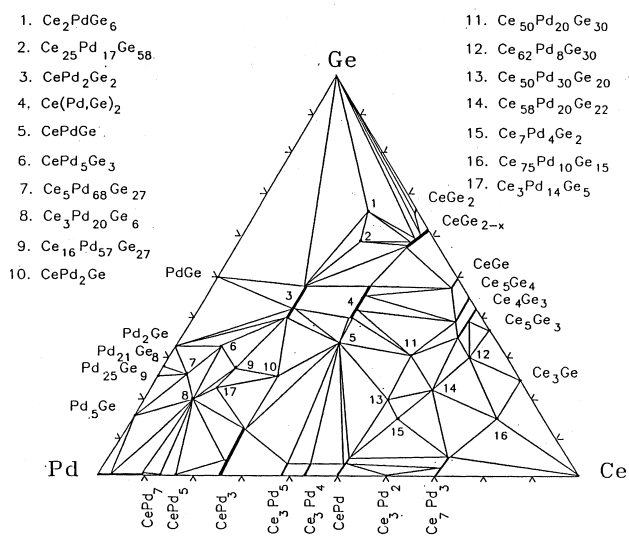

Fig. 1. Isothermal cross-section of the Ce–Pd–Ge system at 600°C.

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

N	Phase	Space group	Prototype	Lattice parameters (nm)		
				a	*b*	*c*
1	Ce_2PdGe_6	*Amm2*	Ce_2CuGe_6	0.4163(2)	0.4089(2)	2.196(2)
2	$Ce_{25}Pd_{17}Ge_{58}$					
3	$CePd_2Ge_2$	*I4/mmm*	$CeAl_2Ga_2$	0.4359(4)		1.001(1)
4	$Ce(Pd,Ge)_2$	*P6/mmm*	AlB_2	0.43464(8)		0.4033(3)
5	CePdGe	*Imma*	KHg_2	0.4480(4)	0.7288(5)	0.7672(4)
6	$CePd_5Ge_3$	*Pnma*	YNi_5Si_3	2.024(1)	0.4122(1)	0.7244(3)
7	$Ce_5Pd_{68}Ge_{27}$					
8	$Ce_3Pd_{20}Ge_6$[a]	*Fm3m*	$Ce_3Pd_{20}Ge_6$	1.24453(4)		
9	$Ce_{16}Pd_{57}Ge_{27}$					
10	$CePd_2Ge$	*Pnma*	Fe_3C	0.6980(7)	0.7702(7)	0.5789(6)
11	$Ce_{50}Pd_{20}Ge_{30}$					
12	$Ce_{62}Pd_8Ge_{30}$					
13	$Ce_{50}Pd_{30}Ge_{20}$					
14	$Ce_{58}Pd_{20}Ge_{22}$					
15	$Ce_7Pd_4Ge_2$[b]	$P2_1/n$	$Ce_7Pd_4Ge_2$	0.9315(2)	1.2277(7), $\beta = 114.31°$	1.2698(3)
16	$Ce_{75}Pd_{10}Ge_{15}$					
17	$Ce_3Pd_{14}Ge_5$	*Orthorhombic*		0.4517(2)	0.9082(3)	1.8142(5)

[a]Ref. [13].
[b]Ref. [14].

determining the structures of Ce_2PdGe_6, $CePd_2Ge_2$, $Ce(Pd,Ge)_2$, CePdGe and $CePd_2Ge$. The structures of $CePd_5Ge_3$, $Ce_3Pd_{20}Ge_6$, $Ce_7Pd_4Ge_2$ and $Ce_3Pd_{14}Ge_5$ were examined on monocrystals.

Investigation of the powder diffraction data of eight alloys with compositions $Ce_{25}Pd_{17}Ge_{58}$, $Ce_5Pd_{68}Ge_{27}$, $Ce_{16}Pd_{57}Ge_{27}$, $Ce_{50}Pd_{20}Ge_{30}$, $Ce_{62}Pd_8Ge_{30}$, $Ce_{50}Pd_{30}Ge_{20}$, $Ce_{58}Pd_{20}Ge_{22}$ and $Ce_{75}Pd_{10}Ge_{15}$ 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 belief in 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 the two-phase and three-phase regions. These results are presented in Table 6.

DTA experiments show the following compounds to be formed from the liquid together with the melting temperatures:

$Ce_3Pd_{20}Ge_6$	960°C
$CePd_5Ge_3$	920°C
$Ce_3Pd_{14}Ge_5$	850°C
$CePd_2Ge_2$	1480°C.

According to the microstructure analyses, the phases Ce_2PdGe_6, $Ce(Pd,Ge)_2$ and CePdGe also formed from the liquid phase but their melting temperatures were not established.

The complicated character of the interaction of the components in the ternary Ce–Pd–Ge system leads to the formation of 17 compounds. The presence of some of them, $CePd_2Ge_2$, Ce_2PdGe_6, $CePd_2Ge$, $Ce(Pd,Ge)_2$ and CePdGe, can be expected from the knowledge of analogous Ce–TM–X systems. Other compounds, $Ce_3Pd_{20}Ge_6$,

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

Alloy composition (at.%)			Number of phases	Composition of phases (at.%)		
Ce	Pd	Ge		Ce	Pd	Ge
15	52	33	3	12	57	31
				16	56	28
				21	41	38
7	69	24	2	5	68	27
				10	70	20
12	60	28	2	11	69	20
				11	58	31
15	58	27	1	16	57	27
23	57	20	3	14	64	22
				23	51	26
				25	60	15
50	15	35	3	33	25	42
				55	7	38
				49	22	29
55	30	15	1	53	32	15
45	35	20	3	30	34	36
				50	30	20
				49	46	5
65	12	23	2	58	20	22
				70	25	5
72	18	10	2	71	25	4
				75	10	15
25	20	55	3	21	31	48
				25	17	58
				36	7	57
63	12	25	3	62	8	30
				58	20	22
				75	10	15

$Ce_7Pd_4Ge_2$, $CePd_5Ge_3$ and $Ce_3Pd_{14}Ge_5$, have no analogs in such ternary systems.

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