Journal of Alloys and Compounds 488 (2009) 123–128

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Reinvestigation of the isothermal section of the Ce–Co–Ge ternary system, at 700 °C

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ARTICLE INFO

Article history:
Received 22 June 2009
Received in revised form 28 August 2009
Accepted 31 August 2009
Available online 15 September 2009

Keywords:
Intermetallics
X-ray diffraction
Metallography
Crystal structure
Heavy fermions

ABSTRACT

The solid state phase equilibria in the Ce–Co–Ge ternary system at 700 °C were investigated by means of X-ray diffraction and scanning electron microscope–energy dispersive X-ray spectroscopy. A total number of nine intermediate phases were characterized and the homogeneity ranges of the various ternary solid solutions of the binary boundary systems (Ce–Co, Ce–Ge and Co–Ge) were studied. The new ternary phase, $CeCo_{13-x}Ge_x$ ($4 \le x \le 4.5$) has been discovered. It crystallizes in the tetragonal space group *I*4/*mcm* (no. 140), with the cell parameters $a = 7.974(5)$ Å and $c = 11.856(5)$ Å for $x = 4$. $CeCo_9Ge_4$ derives from the $CeNi_{8.5}Si_{4.5}$-type, but, with a perfect ordering of the atoms on the crystallographic sites. The phase diagram comprises seven extensions of binaries into the ternary system, eight stoichiometric ternary phases, CeCoGe, $CeCo_2Ge_2$, $CeCoGe_3$, $Ce_2Co_3Ge_5$, Ce_2CoGe_3, Ce_3CoGe_2, Ce_5CoGe_2 and $Ce_5Co_4Ge_{13}$ and two intermediate solid solutions, $CeCo_{1-x}Ge_2$ ($0 \le x \le 0.24$) and $CeCo_{13-x}Ge_x$ ($4 \le x \le 4.5$).

1. Introduction

Cerium and uranium based intermetallics have been revealed to be a continuous source of intriguing compounds for the study of unusual electronic phenomena. However, the literature comprises numerous examples of conflicting or not fully reproducible results between various research groups, depending on the preparation of the samples. Small changes of the initial composition, which induce either a deviation of the chemical content within a homogeneity range, or the presence of foreign phases, as well as different heat-treatments of the samples, may yield significant discrepancies of the physical properties. Therefore, in addition to detailed studies of the electronic features, sound chemical, structural and thermodynamical investigations of the phases are required.

As part of our ongoing research project on the investigation of crystal-chemistry and electronic properties of ternary intermediate phases combining cobalt, germanium and an f-element having a particular electronic configuration (Ce or U), we present here, the experimental study of the phase relationships at 700 °C of the Ce–Co–Ge ternary system. The assessment of the isothermal section was carried out by means of X-ray diffraction (XRD) and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM–EDS), revealing the formation of a new intermediate phase, $CeCo_{13-x}Ge_x$ with $4 \le x \le 4.5$, but, preclude the formation of the previously reported individual compounds, Ce_3CoGe_6, $Ce_{15}Co_4Ge_{31}$ and Ce_5CoGe_4 [1].

2. Literature data

2.1. Binary systems

The binary boundary systems Ce–Ge, Ce–Co and Co–Ge were accepted from the compilation of binary alloy phase diagrams by Massalski et al. [2]. A total of twelve binary compounds and seven solid solutions are reported in these binary systems at 700 °C. In the Ce–Co system, six compounds are found to be stable: $CeCo_2$, $CeCo_3$, Ce_2Co_7, Ce_5Co_{19}, $CeCo_5$ and Ce_2Co_{17}. The Ce_2Co_7 compound displays two polymorphic forms but only the hexagonal one (Ce_2Ni_7-type) is stable at 700 °C. The Ce–Ge system comprises six phases: Ce_3Ge, Ce_5Ge_3, Ce_4Ge_3, Ce_5Ge_4 defined as line compounds, and CeGe and Ce_3Ge_5 having small homogeneity range of 50.0–50.5 at.% Ge and 61.1–62.0 at.% Ge, respectively. The Co–Ge system contains a total of seven intermediate phases; two well-defined compounds, Co_5Ge_7 and $CoGe_2$, three compounds with homogeneity domains, CoGe (48.9–51.1 at.% Ge), Co_5Ge_3 (34.9–41.6 at.% Ge), Co_3Ge (21.5–22.1 at.% Ge) and two separated solid solutions based on Co, in the range 0–11.4 at.% and 12.6–17.1 at.% Ge.

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doi:10.1016/j.jallcom.2009.08.158

Table 1
Single crystal X-ray diffraction details for $CeCo_9Ge_4$.

Empirical formula	$CeCo_9Ge_4$
Molecular weight ($g\,mol^{-1}$)	960.85
Crystal system, space group	Tetragonal, $I4/mcm$ (no. 140)
Lattice parameters (Å)	$a = 7.969(5)$ Å $c = 11.856(5)$ Å
Volume ($Å^3$)	753.86
Z, calculated density (g/cm^3)	4/8.477
Absorption coefficient (mm^{-1})	40.75
Crystal size (mm^3)	$0.016 \times 0.052 \times 0.035$
Crystal colour	Black
θ range (°)	3.44–42.03
$h\,k\,l$ range	$-14 \le h \le 14$ $-13 \le k \le 15$ $-20 \le l \le 22$
Collected/unique reflections	7236/738
Absorption correction	Numerical (ANALYTICAL)
R (int)	0.0697
Refined parameters	25
G.O.F.	1.125
wR_2 $[I > 2\sigma(I)]$	0.0700
R_1 $[I > 2\sigma(I)]$	0.0335
Extinction coefficient	0.0015(2)
Holes/residual peaks ($\bar{e}\,Å^{-3}$)	−2.256/3.274

$R(F) = \sum ||F_0| - |F_c|| / \sum |F_0|$, $wR_2 = [\sum w(F_0^2 - F_c^2)^2 / w F_0^4]^{1/4}$, where $w^{-1} = [\sigma^2(F_0^2) + (aP)^2 + bP]$, $P = [\max(F_0^2, 0) + 2F_c^2]/3$, goodness-of-fit (G.O.F.) $= (F_0^2 - F_c^2)^2/(n-p)^{1/2}$, n = number of reflections, p = parameters used.

2.2. *Ternary compounds and phase relations*

The following ternary intermetallic compounds are known from the literature: Ce_2CoGe_3 (hexagonal, AlB_2-type) [3], $CeCo_2Ge_2$ (tetragonal, $CeGa_2Al_2$-type) [4], $CeCoGe_3$ (tetragonal, $BaNiSn_3$-type) [5], $CeCo_{1-x}Ge_2$ (tetragonal, $CeNiSi_2$-type), with homogeneity range of $0 < x < 0.14$ according to [6] and $0 \le x \le 0.22$ according to [7], $Ce_2Co_3Ge_5$ (orthorhombic, $U_2Co_3Si_5$ [8] or monoclinic, $Lu_2Co_3Si_5$-type [1]) but no precision is given about a possible polymorphic transformation or about the crystallographic form stable at 700 °C, CeCoGe (tetragonal, PbFCl-type) [9], Ce_3CoGe_2 (orthorhombic, La_3NiGe_2-type) [1], Ce_5CoGe_2 presents two polymorphic forms: a low temperature form observed in samples annealed at 600 °C (orthorhombic, Y_2HfS_5-type) and a high temperature form observed at temperatures above 1100 °C (hexagonal Mn_5Si_3-type) [10], and the very recently reported compound $Ce_5Co_4Ge_{13}$ (orthorhombic, new structure type, which can be viewed as a ternary filled version of the Nb_5Ga_{13}-type) [11] found in an as-cast sample.

Partial isothermal sections at 600 °C, for the composition range 0–50 at.% Ce and at 400 °C, for the composition range 50–100 at.% Ce, are also available in the literature [1]. The existence and the crystallographic data about most of the ternary phases, listed above, were confirmed. However, limited or discordant results appear for several cases, such as, the crystalline form of $Ce_2Co_3Ge_5$, and the chemical and structural characterizations of the compounds identified with approximate compositions $\sim Ce_5CoGe_4$, $\sim Ce_3CoGe_6$ and $\sim Ce_{15}Co_4Ge_{31}$. A complete reinvestigation of the Ce–Co–Ge ternary system found therefore further motivation.

Table 2
Atomic parameters for $CeCo_9Ge_4$. Atomic positions were standardized using the Structure Tidy software [17].

Atom	Wyck.	x	y	z	U_{eq} ($Å^2$)
Ce_1	4a	0	0	1/4	0.0105(1)
Co_1	4d	0	1/2	0	0.0091(2)
Co_2	16k	0.06704(6)	0.20074(6)	0	0.0102(1)
Co_3	16l	0.62198(4)	0.12198(4)	0.17752(4)	0.0096(1)
Ge_1	16l	0.17377(3)	0.67377(3)	0.12530(4)	0.0102(1)

Table 3
Selected interatomics distances of $CeCo_9Ge_4$.

Ce_1	8 Co_1	3.282(2)	Co_2	2 Co_2	2.387(2)
	8 Ge_1	3.297(2)		1 Co_1	2.445(2)
	8 Co_2	3.411(2)		2 Ge_1	2.554(1)
				2 Co_3	2.573(1)
				1 Co_2	2.619(2)
				2 Ge_1	2.626(1)
				1 Co_2	3.375(1)
Ge_1	1 Co_3	2.385(2)	Co_3	1 Ge_1	2.385(2)
	1 Co_3	2.410(1)		1 Ge_1	2.410(1)
	1 Co_1	2.459(1)		2 Ge_1	2.473(2)
	2 Co_3	2.473(2)		1 Co_1	2.514(1)
	2 Co_2	2.554(1)		2 Co_2	2.573(1)
	2 Co_2	2.626(1)		2 Co_3	2.596(1)
	1 Ge_1	2.971(1)		1 Co_3	2.751(2)
	2 Ce_1	3.297(2)			
Co_1	4 Co_2	2.445(2)			
	4 Ge_1	2.459(1)			
	4 Co_3	2.514(1)			

2.3. *Liquid phase*

In the Ce-rich corner, the liquid phase can cover a significant surface in the ternary system. Its extension was evaluated according to the liquid phase expansions of the binary systems Ce–Co and Ce–Ge, and the temperature of 700 °C has been chosen to minimize its area. The relations between the solid phases and the liquid phase have not been studied in the present investigation.

3. Experimental details

Samples were prepared by melting calculated amounts of the elements in an arc furnace under a residual atmosphere of high purity argon. The starting materials were used in form

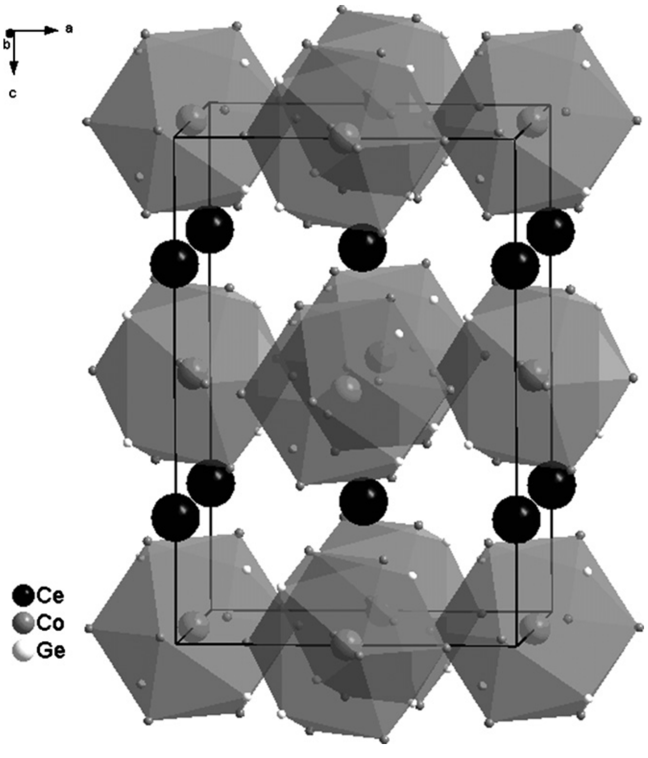

Fig. 1. Perspective view of the crystal structure of $CeCo_9Ge_4$.

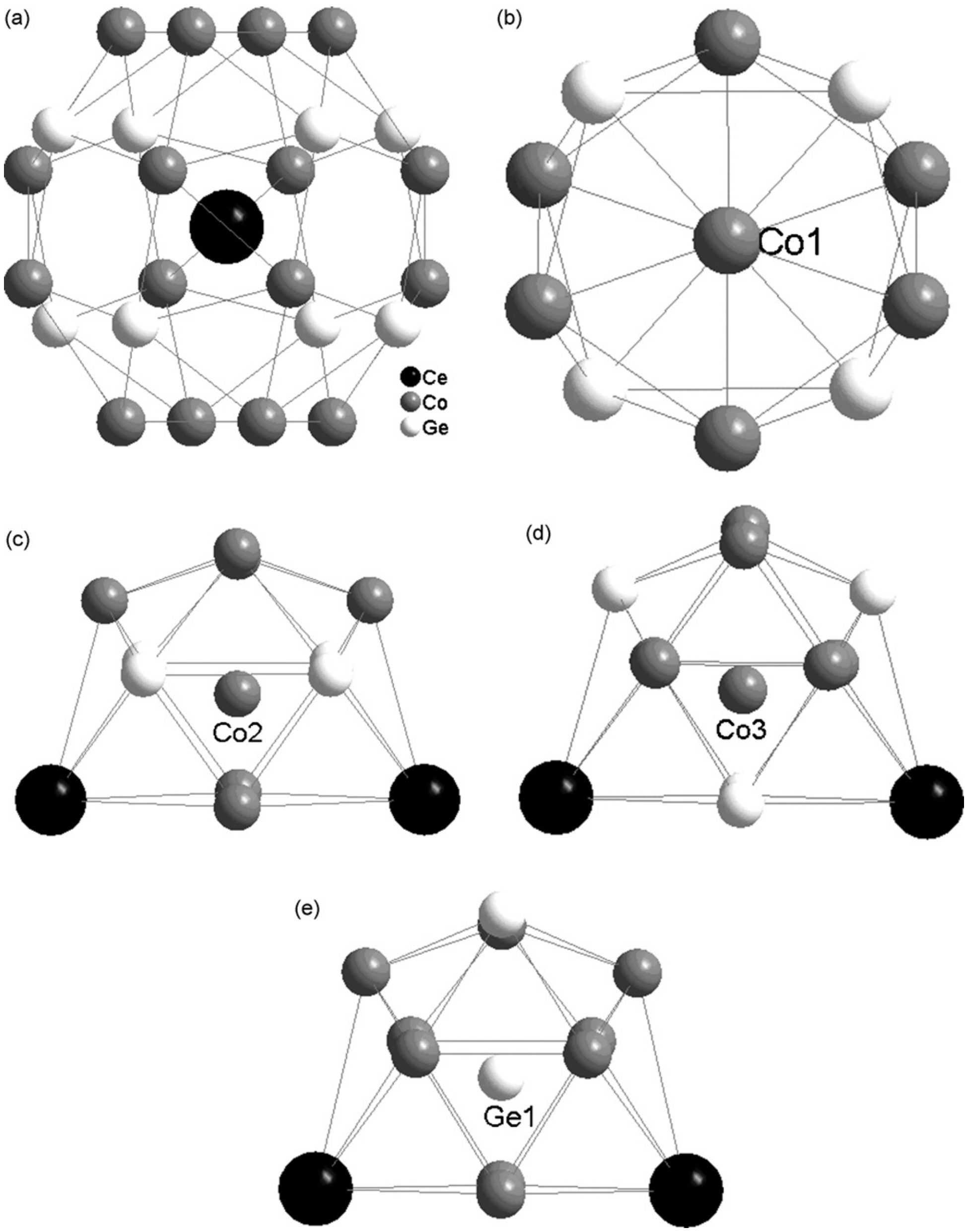

Fig. 2. Coordination polyhedron around the independent atoms of the structure of $CeCo_9Ge_4$, (a) around Ce_1 atom, (b) around Co_1, (c) around Co_2, (d) around Co_3, and (e) around Ge_1.

of pieces of high purity elements: Ce (99.9%), Co (99.9%) and Ge (99.999%). The weight losses were generally less than 1%. The samples were annealed at 700 °C for 3 weeks in sealed silica tubes, followed by air quenching down to room temperature.

All samples were analyzed by XRD on powder with an Inel CPS 120 diffractometer using a CoKα radiation (λ = 1.789 Å). The POWDERCELL software [12] was used, to compare the experimental diffractograms with the calculated ones, from the known structures and to evaluate the unit-cell parameters. The microstructure was studied on thoroughly polished surfaces of the samples with the use of a Jeol JSM 6400 Scanning Electron Microscope (SEM). The composition of the phases was analyzed by energy dispersive X-ray spectroscopy (EDS) with an Oxford Link-Isis Si/Li analyzer.

Single crystals of $CeCo_9Ge_4$ for X-ray diffraction experiments were obtained from samples with the nominal composition, heated in an induction furnace up to the melting temperature and then slowly cooled down to room temperature. X-ray diffraction intensities were collected on a Nonius Kappa CCD four circle diffractometer working with MoKα radiation (λ = 0.71073 Å). The orientation matrix and the unit-cell parameters were derived from the first 10 measured frames of the data using the DENZO software [13]. The scaling and merging of redundant measurements of the different data sets as well as the cell refinement was performed using DENZO-ScalePack. Semi-empirical absorption corrections were made with the use of the MULTISCAN software [14]. Structural model was determined by direct methods using SIR-97 [15]. All structures refinements and Fourier syntheses were made with the help of SHELXL-97 [16]. The occupancy rate of each of the independent atoms was successively allowed to vary in order to check a possible substitution mechanism between Co and Ge atoms. Atomic positions have been standardized with the help of STRUCTURE TIDY [17].

4. Results

4.1. Crystal structure of $CeCo_9Ge_4$

The existence of this new phase was revealed by means of both X-ray powder patterns and SEM–EDS analyses carried out on a sample with starting composition of Ce:Co:Ge of 10:60:30. Besides the diffraction peaks of the body centred tetragonal structure of $CeCo_2Ge_2$, the additional peaks could be successfully indexed on the basis of a body centred tetragonal unit-cell related to the $CeFe_{8.5}Si_{4.5}$-type [18]. Precise determination of the crystallographic parameters was carried out by single crystal X-ray diffraction experiments. Details of the data collection and crystallographic data are summarized in Table 1. Successive refinements of the occupancy parameters, treated separately, revealed full occupancy for all Wyckoff sites, confirming that $CeCo_9Ge_4$ adopts the $CeFe_{8.5}Si_{4.5}$-type, with ordered atom network, as observed for $LaFe_9Si_4$ [19]. The atomic parameters are listed in Table 2, and interatomic distances are given in Table 3. This structure, which derives from the cubic $NaZn_{13}$-type, is characterized by a perfect ordering of the Co and Ge atoms in the unit-cell, as established by the structural refinement. Fig. 1 represents a perspective view of the crystal structure of $CeCo_9Ge_4$, which can be described as an alternation of Co and Ge icosahedra layers with Ce atoms layers along the *c*-axis [20]. Such a description readily emphasis intralayer interactions between the Ce atoms, but does not reflect perfectly the strong three-dimensional character of the structure, as it is well illustrated by the high coordination number around the atoms and the short Co–Co and Co–Ge bond distances. Ce environment (Fig. 2a) is constituted of a 24 atoms: 8 Co_1, 8 Ge_1 and 8 Co_2 and the distances with the Ce atom are respectively 3.282(2) Å, 3.297(2) Å and 3.411(2) Å. The coordination polyhedra around the three Co atoms and Ge_1 are distorted icosahedra. As an example of short contacts, Co_1 environment (Fig. 2b) is composed of 4 Co_3, 4 Co_2 and 4 Ge_1 and the distances with the central atom are respectively 2.541 Å, 2.445 Å and 2.459 Å, which are shorter than the sum of the elemental radius [21]. The coordination polyhedra about Co_2, Co_3 and Ge_1 atoms are presented respectively in Fig. 2c–e.

4.2. The isothermal section of the phase diagram of Ce–Co–Ge at 700 °C

The isothermal section at 700 °C of this ternary system is shown in Fig. 3. It has been constructed by using our experimental results obtained by comparison of the X-ray diffraction patterns, scanning electron micrography and EDS-analysis. The twelve binary phases, stable at 700 °C, have been confirmed. It has to be noted than, in agreement with Massalski et al. [2], no doubt remains about the formation and crystal structure of the binary compound Ce_5Co_{19} which has been observed in the present investigation carried out at 700 °C. The solubility of Ce in all the Co–Ge phases is below the detection limit of EDS analyses. Substitution mechanism engages the almost equally sized atom species cobalt and germanium (rCo ~1.25 Å [21], rGe ~1.23 Å [22]) as reflected by the homogeneity ranges of the equilibrium phases Co–Ge binary subsystem and the extensions into the ternary system of two binary subsystems Ce–Co and Ce–Ge. In agreement with the previous study [3], six significant binary extensions are observed. Their observed crystallographic structure and homogeneity ranges are compiled in Table 4. Evaluation of the solubility of Ge in the binary phase Ce_5Co_{19} was severely hampered by the proximity of the Ce_2Co_7 phase, yielding phase-fields of extremely narrow area. The homogeneity range of the binaries $CeGe_{2-x}$ shows a maximum phase width of 5% at Co, with a unique crystallographic form based on the $GdSi_2$ structure type. It has to be noted, that neither the $ThSi_2$-type nor the Y_3Ge_5-type has been observed into the ternary system.

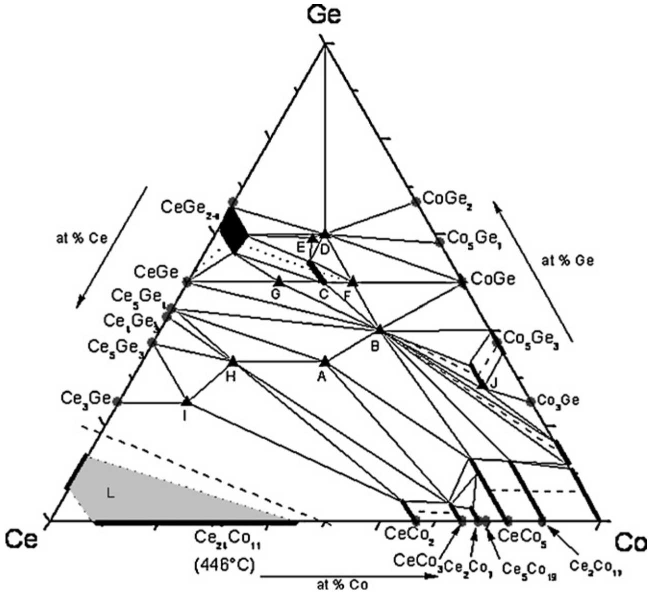

Fig. 3. Isothermal section at 700 °C of the Ce–Co–Ge system. (A) CeCoGe, (B) $CeCo_2Ge_2$, (C) $CeCo_{1-x}Ge_2$, (D) $CeCoGe_3$, (E) $Ce_5Co_4Ge_{13}$, (F) $Ce_2Co_3Ge_5$, (G) Ce_3CoGe_2, (H) Ce_3CoGe_2, (I) Ce_5CoGe_2, and (J) $CeCo_{13-x}Ge_x$.

The isothermal section at 700 °C presents ten intermediate phases, including eight well-defined compounds: CeCoGe, $CeCo_2Ge_2$, $Ce_2Co_3Ge_5$, Ce_2CoGe_3, $Ce_5Co_4Ge_{13}$, $CeCoGe_3$, Ce_3CoGe_2 and Ce_5CoGe_2 and two intermediate solid solutions; $CeCo_{1-x}Ge_2$ and the new phase $CeCo_{13-x}Ge_x$. Compositions, homogeneity ranges and crystallographic data of the intermediate phases are gathered in Table 5. The present results for the ternary $CeCo_{1-x}Ge_2$ ($0 \leq x \leq 0.24$) phase, which crystallizes with orthorhombic $CeNiSi_2$-type (space group *Cmcm*, no. 63) was found to exhibit a slightly longer homogeneity range than in the preceding study ($0 \leq x \leq 0.22$) [7]. However, the observed mechanism based on vacancies on the 3*d* metal site (*x*) remains unchanged. The substitution mechanism for $CeCo_{13-x}Ge_x$ with $4 \leq x \leq 4.5$ is based on the mutual substitution of Co/Ge, presumably on the 16*l* Wyckoff site of the tetragonal space

Table 4
Crystalline forms, lattice parameters and homogeneity domains of the ternary extensions of the binary compounds in the Ce–Co–Ge system.

Binary compound	Structure type	Space group	Solid solution range	Lattice parameters (Å) for the lowest and highest limit of solubilities.		
				a	*b*	*c*
$CeCo_2$	$MgCu_2$	$Fd\bar{3}m$	4 at.% Ge	7.161–7.220	–	–
$CeCo_3$	$PuNi_3$	$R\bar{3}m$	3 at.% Ge	4.955–4977	–	24.720–24.840
Ce_2Co_7	Ce_2Ni_{17}	$P6_3/mmc$	2.5 at.% Ge	4.980–4.935	–	24.520–24.446
Ce_5Co_{19}	Ce_5Co_{19}	$R\bar{3}m$	Not determined	4.954	–	48.718
$CeCo_5$	$CaCu_5$	$P6/mmm$	12 at.% Ge	4.928–4.958	–	4.018–4.061
Ce_2Co_{17}	Th_2Ni_{17}	$P6_3/mmc$	10 at.% Ge	8.388–8.473	–	8.144–8.205
$CeGe_{2-x}$	$GdSi_2$	$Imma$	5 at.% Co	4.260–4.216	4.347–4.192	14.087–14.379

Table 5
Crystalline forms, lattice parameters and homogeneity domains of the ternary compounds in the Ce–Co–Ge system.

Compound	Structure type	Space group	Lattice parameters (Å)			Ref.
			a	*b*	*c*	
A: CeCoGe	PbFCl	*P4/nmm*	4.162	–	6.865	[1]
			4.180	–	6.865	This work
B: $CeCo_2Ge_2$	$CeGa_2Al_2$	*I4/mmm*	4.071	–	10.170	[1]
			4.067	–	10.1744	This work
C: $CeCo_{1-x}Ge_2$ $0 \leq x \leq 0.24$	$CeNiSi_2$	*Cmcm*	4.245	16.740	4.197	[1]
			4.268	16.780	4.199	This work
D: $CeCoGe_3$	$BaNiSn_3$	*I4mm*	4.319	–	9.830	[1]
			4.278	–	9.850	This work
E: $Ce_5Co_4Ge_{13}$	Nb_5Ga_{13}	*Cmmm*	4.265	45.175	4.293	[11]
			4.275	45.183	4.308	This work
F: $Ce_2Co_3Ge_5$	$U_2Co_3Si_5$	*Ibam*	9.814	11.840	5.862	[1]
			9.836	11.901	5.887	This work
$Ce_2Co_3Ge_5$	$Lu_2Co_3Si_5$	*C2/c*	11.376	5.847	11.796 $\gamma = 120.77^\circ$	[1]
				Not observed		This work
G: Ce_2CoGe_3	AlB_2	*P6/mmm*	4.182	–	4.151	[1]
			4.182	–	4.151	This work
H:Ce_3CoGe_2	La_3NiGe_2	*Pnma*	11.951	4.302	11.477	[1]
			11.951	4.32	11.42	This work
I: Ce_5CoGe_2 (LT)	Y_2HfS_5	*Pnma*	12.245	8.857	7.891	[10]
			12.270	8.857	7.958	This work
J: $CeCo_{13-x}Ge_x$ $4 \leq x \leq 4.5$	$LaFe_9Si_4$	*I4/mcm*	7.974	–	11.856	This work

group, *I4/mcm*, as observed for $La(Fe,Si)_{13}$ [23]. This new phase, $CeCo_{13-x}Ge_x$, which is in equilibrium with four phases, namely $CeCo_2Ge_2$, Co_5Ge_3, Co_3Ge and Co appears to be stable in a wide range of temperature, as it is observed in as-cast and annealed (700 °C) samples.

4.3. Discussion on the crystallographic data and phase formation

In order to eliminate contradicting information in the literature on the crystal structure of $Ce_2Co_3Ge_5$ compound, a careful examination of its crystal-chemistry behaviour was carried out. $Ce_2Co_3Ge_5$ adopts the orthorhombic $U_2Co_3Si_5$ structure type at 700 °C. Moreover, structural investigations performed on samples in as-cast state and after heat-treatment at various temperatures, revealed that only the orthorhombic form is observed and never the monoclinic one. The structural phase transition was confirmed for Ce_5CoGe_2, which presents the hexagonal Mn_5Si_3 structure type in as-cast samples whereas, the orthorhombic Y_2HfS_5 structure is found stable at 700 °C. Differential Thermal Analysis (DTA) measurements (Labsys-Setaram) revealed weak thermal effect between room temperature and 1400 °C which may be associated to this transition. The temperature of the structural phase transition is suggested to be about 830 °C.

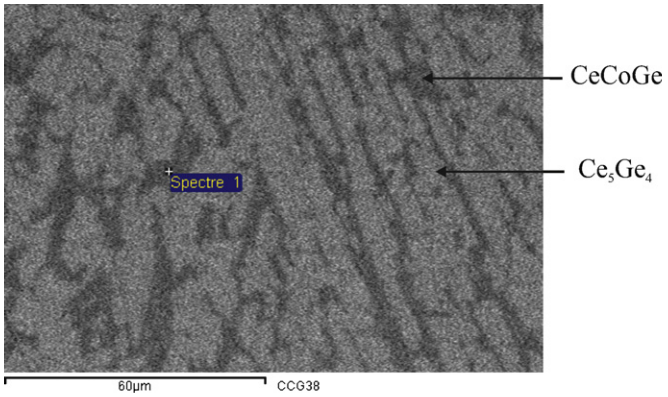

Fig. 4. Back scattered image of the microstructure of a sample of nominal composition Ce:Co:Ge of 5:1:4 annealed at 700 °C for 3 weeks. The grey area has an atomic composition in agreement with the binary Ce_5Ge_4 and the darker area presents an atomic composition in agreement with CeCoGe.

The formation of the ternary phases, namely Ce_3CoGe_6, $Ce_{15}Co_4Ge_{31}$ and Ce_5CoGe_4 reported in the previous study [1] of this system was not confirmed in the present investigation. Powder XRD analyses as well as metallographic observations on samples with initial compositions of Ce:Co:Ge of 3:1:6 and 15:4:31 revealed that these compositions belong to two-phases field and three-phases field involving $CeGe_{2-x}Co_x$, $CeCoGe_3$ and $CeGe_{2-x}Co_x$, $CeCoGe_3$ and $Ce_5Co_4Ge_{13}$ ternary phases, respectively.

Similarly a sample with nominal composition of Ce:Co:Ge of 5:1:4 has been melted and heat-treated at 700 °C. The microstructure as well as the X-ray powder pattern of the annealed and as-cast state of the sample, revealed a solid state equilibrium between the ternary compound CeCoGe and the binary compound Ce_5Ge_4. The microstructure and the powder pattern of the annealed sample are depicted in Figs. 4 and 5, respectively. The weak diffraction peaks non-indexed in the two previous unit-cells, can be attributed to a small amount of Ce_2O_3, as impurity. Changes around the initial composition yield samples in the three-phases field involving Ce_5Ge_4–CeCoGe–$CeCo_2Ge_2$ or

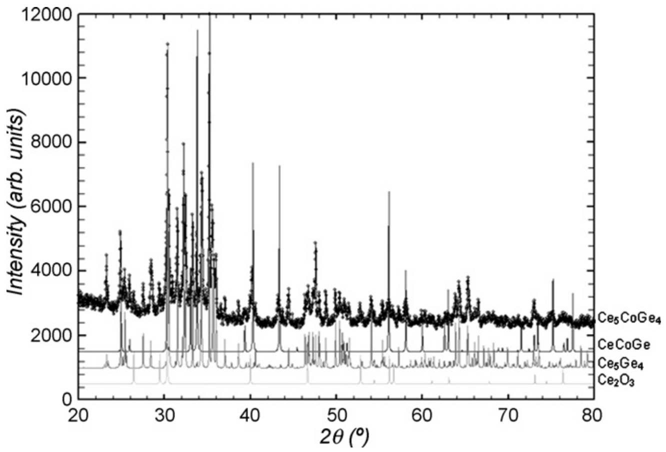

Fig. 5. X-ray powder pattern of a sample of nominal composition Ce:Co:Ge of 5:1:4 annealed at 700 °C for 3 weeks. All the diffraction peaks were indexed with both the tetragonal structure of PbFCl adopted by CeCoGe with the lattice parameters *a* = 4.189 Å; *c* = 6.863 Å (continuous line in dark grey—upper) and the orthorhombic structure Sm_5Ge_4 adopted by Ce_5Ge_4 with lattice parameters *a* = 7.985 Å; *b* = 15.295 Å; *c* = 8.085 Å (continuous line in medium grey—intermediaite).

Ce_5Ge_4–CeCoGe–Ce_3CoGe_2, confirming the absence of formation of Ce_5CoGe_4 compound.

Acknowledgements

This work was partially supported by the French–Polish Integrated Activity Program “POLONIUM” no. 20080PM (2008–2009). The authors acknowledge the use of the Nonius Kappa CCD diffractometer through the Centre de Diffraction X de l'Université de Rennes1 (CDIFX). We also thank Isabelle Peron, Caroline Leynia, Sandra Casale and the Centre de Microscopie Électronique à Balayage et microAnalyse (CMEBA) for the EDS-analysis.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jallcom.2009.08.158.

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