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Phase equilibria in systems Ce–*M*–Sb (*M* = Si, Ge, Sn) and superstructure $Ce_{12}Ge_{9-x}Sb_{23+x}$ ($x = 3.8 \pm 0.1$)

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ABSTRACT

Phase relations in the ternary systems Ce–*M*–Sb (*M* = Si, Ge, Sn) in composition regions $CeSb_2$–Sb–*M* were studied by optical and electron microscopy, X-ray diffraction, and electron probe microanalysis on arc-melted alloys and specimens annealed in the temperature region from 850 to 200 °C. The results, in combination with an assessment of all literature data available, were used to construct solidus surfaces and a series of isothermal sections. No ternary compounds were found to form in the Ce–Si–Sb system whilst $Ce_{12}Ge_{9-x}Sb_{23+x}$ ($3.3 < x < 4.2$) and $CeSn_xSb_2$ ($0.1 < x < 0.8$) participate in phase equilibria in the composition region investigated. Crystallographic parameters for the ternary compound $Ce_{12}Ge_{9-x}Sb_{23+x}$ ($x = 3.8 \pm 0.1$) were determined from X-ray single crystal and powder diffraction. For the binary system Ge–Sb a eutectic was defined $L \Leftrightarrow$(Ge)+(Sb) at 591.6 °C and 22.5 at%. Ge EPMA revealed a maximal solubility of 6.3 at% Ge in (Sb) at the eutectic temperature.

1. Introduction

Following our general interest in phase equilibria in binary and ternary systems formed by rare earths (RE) with p^2 elements (Si, Ge, Sn) and/or with antimony, the ternary systems Ce–*M*–Sb were investigated as a logical continuation of our previous studies [1–4]. Literature information on ternary compounds in these systems is available from [5–10], whereas phase relations were only reported for the Ce–Sb–Ge system for which an isothermal section at 400 °C has been determined [6] revealing three ternary compounds: Ce_2GeSb_3 (super structure of $ThGe_2$-type), $Ce_5Ge_3Sb_2$ (unknown structure) and Ce_3GeSb (La_3GeIn-type). A subsequent investigation [7] of ternary rare earth germanium antimonides prepared from Sb-flux yielded the formation of isotypic compounds $RE_6Ge_{5-x}Sb_{11+x}$ (*RE* = La, Ce, Pr, Nd, Sm, Gd, Tb and Dy) crystallizing in the orthorhombic space group *Immm* ($La_6Ge_{2.8}Sb_{13.2}$ structure type). A detailed structural characterization by X-ray single crystal techniques was performed for $La_6Ge_{2.8(1)}Sb_{13.2(1)}$ and $Nd_6Ge_{4.3(1)}Sb_{11.7(1)}$, whereas for the other representatives of the $La_6Ge_{2.8}Sb_{13.2}$ structure type only lattice parameters were given [7].

Equilibrium phase diagrams Ce–Sn–Sb and Ce–Si–Sb have not been constructed so far, however, ternary compounds with composition $RESn_xSb_2$ (*Cmcm*, $LaSn_{0.75}Sb_2$ type, *RE* = La, Ce, Pr, Nd and Sm) were reported by [5,10].

With respect to the limited information on phase equilibria in the ternary systems Ce–*M*–Sb (*M* = Si, Ge, Sn), and in view of the contradiction concerning the formation of $Ce_6Ge_{5-x}Sb_{11+x}$ [7] (not mentioned by [6]) the ternary systems Ce–*M*–Sb (*M* = Si, Ge, Sn) became the subject of our studies in the region $CeSb_2$–Sb–*M* (Ge, Sn, Si). Furthermore details will be elucidated for the structures of $Ce_6Ge_{5-x}Sb_{11+x}$ (found to be a superstructure with formula $Ce_{12}Ge_{9-x}Sb_{23+x}$ in current work) and $CeSn_xSb_2$.

2. Experimental

All samples, each of a total amount of ca. 1 g, were prepared in an electric arc furnace under Ti-gettered argon with a non-consumable tungsten electrode on a water cooled copper heath. The purity of cerium was 99.5 mass%, the purity of antimony, germanium, silicon and tin was better than 99.9%. The alloys were remelted three times in order to achieve complete fusion and homogeneity. Weight losses were found to be less than 1–2 mass% and were attributed to most volatile elements Sb and Sn. Final decision on phase solubilities and extent of phases was based on electron probe micro-analyses (EPMA) data (see below). After melting, alloys were subjected to annealing in evacuated quartz tubes with subsequent quenching in water. Alloys for the systems Ce–Ge–Sb and Ce–Si–Sb were annealed at 400 (30 days) and

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600 °C (14 days) and alloys for the Ce–Sn–Sb system were annealed at 200 (90 days) and 400 °C (14 days).

X-ray powder diffraction data from as-cast and annealed alloys were collected with a Guinier–Huber image plate system (Cu$K\alpha_1$ or Fe$K\alpha_1$; $8° < 2\theta < 100°$). Precise lattice parameters were calculated by least-squares fits to indexed 2θ-values employing Ge as internal standard ($a_{Ge} = 0.565791$ nm).

To determine the crystal structure of $Ce_{12}Ge_{9-x}Sb_{23+x}$, a single crystal fragment, suitable for X-ray structure determination was broken from an arc-melted sample with nominal composition $Ce_{25}Sb_{62.5}Ge_{12}$, which had been vacuum-sealed in a quartz tube and annealed for 14 days at 600 °C prior to quenching in cold water. Inspection on an AXS-GADDS texture goniometer assured high crystal quality, unit cell dimensions and Laue symmetry of the specimens prior to X-ray intensity data collection on a four-circle Nonius Kappa diffractometer equipped with a CCD area detector and employing graphite monochromated Mo$K\alpha$ radiation ($\lambda = 0.071073$ nm). Orientation matrix and unit cell parameters for an orthorhombic system were derived using the program DENZO [11]. No absorption correction was necessary because of the rather regular crystal shape and small dimensions of the investigated specimen. The structure was solved by direct methods and refined with the SHELXL-97 and SHELXS-97 programs [12].

The as cast and annealed samples were polished using standard procedures and were examined by optical metallography and scanning electron microscopy (SEM). Compositions for Ce–Si–Sb and Ce–Ge–Sb alloys were determined via EPMA on a Carl Zeiss DSM 962 equipped with a Link EDX system operated at 20 kV and 60 μA and on a Carl Zeiss EVO 40 equipped with a Pentafet Link EDX system operated at 20 kV. Binary compounds $CeSb_2$ and CeSb were used as EPMA standards. Difference between measured values and nominal compositions were found to be within 3 at%.

Isothermal reaction temperatures were derived from thermal arrests determined in a calibrated Netzsch STA 409 PG/4/G Luxx Differential Scanning Calorimeter (DSC) employing a heating rate of 5 K/min in Al_2O_3 crucibles under a stream of 6N argon. Prior to DTA the alloys were annealed at 520 °C for 5–7 days.

3. Results and discussions

3.1. Binary boundary systems

Information regarding the binary boundary systems was taken from [13] as well as from [14] on the existence of two modifications for $CeSb_2$. Crystallographic data for the relevant solid phases from literature and/or from our current work are summarized in Table 1. During our investigation we came across two conflicting situations concerning (i) the constitution of the Ge–Sb phase diagram and (ii) the crystal structure of $Ce_{12}Ge_{9-x}Sb_{23+x}$.

3.1.1. The binary phase diagram germanium–antimony

The binary Ge–Sb phase diagram as a result of our investigation is shown in Fig. 1a. It differs from the phase diagram given in [13] (compilation of data of various authors [15–19]) by two major facts: (i) eutectic composition (85.5 at% Sb after [13] and 77.5 at% Sb (this work)) and (ii) maximal solubility of Ge in Sb (no solubility after [13] and 6.3 at% Ge at 592 °C (this work)).

Six alloys Ge_xSb_{100-x} (for $x = 2.5$, 5, 10, 15, 22 and 30 at%) were investigated in the as-cast state and after anneal at 400 (45 days), 500 (7 days), 520 (7 days) and 580 °C (2 days). The binary as-cast alloys with germanium content lower than 22 at% show primary crystallization of antimony containing up to 6.3 at% Ge as well as a eutectic with composition $Ge_{22.5}Sb_{77.5}$ (Fig. 1b). Alloys with higher germanium content reveal primary grains of germanium and the eutectic at $Ge_{22.5}Sb_{77.5}$ (Fig. 1c). The solubility of Ge in primary grains of Sb increases with the overall germanium content of the samples.

In order to determine the exact solubility limits of Ge in antimony at sub-solidus temperatures the sample Ge_5Sb_{95} was annealed at 580, 500 and 400 °C for 2, 7 and 45 days, respectively. After annealing at 400 and 500 °C the sample shows grains of Sb with a maximal solubility of 2.3 and 2.8 at% Ge at 400 and 500 °C, respectively. At 580 °C the sample looks almost single phase with traces of (Ge) consistent with a maximal solubility of 4.1 at% germanium in antimony. EPMA measurements recorded from grains of the Sb-based solution are plotted in Fig. 1a in order to define the solubility range of (Sb). Compositional dependences of lattice parameters of (Sb) as shown in Fig. 1d reveal some deviation from linearity in the higher solubility range. The maximum solubility of Ge in Sb (6.3 at%) at the eutectic temperature (592 °C) is measured by EPMA on big primary grains of Sb in the alloy with 22 at% Ge and 78 at% Sb; Fig. 1b. The puzzling non-linearity of unit cell dimensions vs. composition for more than 5 at% Ge can neither be explained by tiny Ge-precipitates in the ss-(Sb) (see inset in Fig. 1b) nor by a retrograde solidus of the (Sb)-phase (lattice parameters and EPMA data of hypo- and hyper-eutectic alloys are the same!). On Ge/Sb

Table 1
Crystal structure data for relevant solid phases in the systems Ce–Sb–M (M = Ge, Si, Sn).

Phase	Pearson symbol	Space group	Structure type	Lattice parameters			Reference
				a (nm)	b (nm)	c (nm)	
(Sb)	hR2	$R\bar{3}m$	As	a = 0.45067	$\alpha = 57.11$		[13]
				0.43084	–	1.1274	[13]
(Si)	cF8	$Fd\bar{3}m$	C	0.54306	–	–	[13]
(Ge)		$Fd\bar{3}m$	C	0.56574	–	–	[13]
(Sn)	tI2	$I4_1/amd$	βSn $I4_1/amd$	0.58318	–	0.31818	[13]
CeSb	cF8	$Fm\bar{3}m$	NaCl	0.6407			[26]
α-$CeSb_2$	oC24	$Cmca$	$SmSb_2$	0.6295(6)	0.6124(6)	1.821(2)	[26]
β-$CeSb_2$	–	–	Unknown	–	–	–	[14]
SbSn	hR2	Rhomb.	Distorted, NaCl	0.4326	–	1.0693	[24]
HP-SbSn	cF8		NaCl	0.5880(4)	–	–	[21][a]
Sb_2Sn_3	cF8	$Fm\bar{3}m$	NaCl	0.615	–	–	[20]
$CeSn_3$	cP4	$Pm\bar{3}m$	$AuCu_3$	0.47214(2)	–	–	[26]
$Ce_6Ge_{5-x}Sb_{11+x}$	oI48	$Immm$	$La_6Ge_{2.8}Sb_{13.2}$	0.42972(7)	1.0740(1)	2.6791(4)	[7]
$Ce_{12}Sb_{23+x}Ge_{9-x}$	oC184	$C222$	$Ce_{12}Sb_{23+x}Ge_{9-x}$	0.86075(2)	2.15154(4)	2.68227(5)	This work; $x = 3.8 \pm 0.1$
$CeSn_xSb_2$	oC28	$Cmcm$	$LaSn_{0.75}Sb_2$	0.4228(1)	2.2868(4)	0.4478(1)	[5] for $x = 1$
				0.42370(1)	2.2834(1)	0.44594(2)	This work for $x = 0.8$

[a] Unit cell dimension given at 7.5 GPa.