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Phase relationships and crystallography of annealed alloys in the Ce_5Si_4–Ce_5Ge_4 pseudobinary system

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ABSTRACT

The phase relationships of annealed alloys in the $Ce_5Si_{4-x}Ge_x$ system were determined by X-ray powder diffraction (XRD). Two structurally distinct terminal phase regions were observed in this system: the Ce_5Si_4-based solid solution ($0 \le x < 2.85$) crystallizing in the Zr_5Si_4-type tetragonal structure with space group $P4_12_12$, and the Ce_5Ge_4-based solid solution ($3.35 < x \le 4$) crystallizing in the Sm_5Ge_4-type orthorhombic structure with space group *Pnma*. An intermediate phase, which has a narrow composition range with the monoclinic $Gd_5Si_2Ge_2$-type structure, space group $P112_1/a$, was found to exist at $x = 2.95 \pm 0.05$. The Rietveld powder diffraction profile fitting technique was used to refine the crystal structures, lattice parameters, and the atomic positions. The phase relationships of the $Ce_5Si_{4-x}Ge_x$ pseudobinary system after heat treatment were established from these data.

1. Introduction

The binary compounds R_5Si_4 and R_5Ge_4 were discovered by Smith et al. [1], where R is a rare earth metal. They reported that the germanides with R = Nd, Sm, Gd, Tb, Er, and Y and the silicides with R = Y, Tb and Er adopt the same Sm_5Ge_4 orthorhombic crystal structure [2], while Nd_5Si_4 crystallized in a tetragonal lattice. Later some authors reported that the R_5Si_4 phases with R = La, Ce, Pr and Nd have the tetragonal Zr_5Si_4-type structure, and those with R = Sm, Gd, Tb, Dy, Er and Y crystallize in the Sm_5Ge_4-type structure, and all R_5Ge_4 compounds (R = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu and Y) are also isostructural with the Sm_5Ge_4-type structure [3]. Soon after, Holtzberg et al. [4] confirmed that the 5:4 silicides and germanides for R = Gd, Tb, Dy, Ho and Er had the orthorhombic Sm_5Ge_4-type structure.

The discovery of the giant magnetocaloric effect (GMCE) in $Gd_5Si_2Ge_2$ [5] triggered a subsequent extensive investigation of the pseudobinary $R_5Si_xGe_{4-x}$ systems. In 1997, Pecharsky and Gschneidner [6] reported that there are three structurally distinct phase regions in the $Gd_5Si_xGe_{4-x}$ system: Gd_5Si_4-type orthorhombic ($2 < x \le 4$), Sm_5Ge_4-type orthorhombic ($0 < x \le 0.8$), and $Gd_5Si_2Ge_2$-type solid solution, which is a monoclinically distorted derivative of the two closely related orthorhombic structures ($0.96 \le x \le 2$). They also proposed that in the pseudobinary Gd_5Si_4–Gd_5Ge_4 system, the large differences in the magnetic properties [6,7], including the appearance of the GMCE, are intimately related to the crystallography of these three phases in the paramagnetic state.

Over the last few years, some results have been reported on most $R_5Si_xGe_{4-x}$ pseudobinary systems with R = La [8], Pr [9], Nd [8,10], Sm [11], Gd [12], Tb [13], Dy [8], Ho [14], Er [15], Yb [16], Lu [8], and Y [17]. Nevertheless, there are still other $R_5Si_xGe_{4-x}$ systems (R = Ce, Eu, and Tm) that have not been studied in any detail. For the Ce and Tm systems, only the terminal binary silicides and germanides have been reported [3,18], while Eu does not form an equilibrium 5:4 compound with either Si or Ge.

In 2002, Bulanova et al. [18] investigated the Ce–Si binary system and reported that Ce_5Si_4 adopts the tetragonal Zr_5Si_4-type structure. Later, Vejpravová et al. [19] studied the crystal structure and magnetic behaviors of Ce_5Si_4, they found a paramagnetic (PM)–antiferromagnetic (AFM) phase transition around $T_N = 5.6$ K. But neither the physical properties nor the phase relationships in the $Ce_5Si_{4-x}Ge_x$ system have been determined. In our work, we have investigated the phase relationships, the crystal structures, the magnetic and thermodynamic properties of the *as-cast* and annealed alloys in the $Ce_5Si_{4-x}Ge_x$ pseudobinary system. Here, we report the phase relationships and the crystal structures for alloys in the annealed condition in the $Ce_5Si_{4-x}Ge_x$ system, while the results for the *as-cast* alloys will be reported elsewhere.

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Table 1
Lattice parameters and *R* factors of structure refinements for the annealed Ce_5Si_4, Ce_5SiGe_3 and Ce_5Ge_4 (a two-phase alloy) compositions.

	Ce_5Si_4	Ce_5SiGe_3		Ce_5Ge_4
Space group	$P4_12_12$	$P112_1/a + Pnma$		*Pnma*
a (Å)	7.9539(9)	7.9305(2)	7.9554(5)	7.9747(1)
b (Å)	7.9539(9)	15.2713(6)	15.2463(7)	15.2687(9)
c (Å)	15.0723(2)	8.0609(1)	8.0570(1)	8.0749(2)
V (Å^3)	953.5(6)	974.4(8)	977.2(4)	983.2(4)
γ (°)	90	93.452(7)	90	90
R_P (%)	7.31	9.83	9.83	10.98
R_{wp} (%)	9.31	12.89	12.89	14.20
R_{exp} (%)	6.58	6.38	6.38	6.53
Amt. phase present (vol.%)	~96[a]	27[a]	73[a]	~86[a]

[a] See text for details.

2. Experimental

A total of 17 alloys with the $Ce_5Si_{4-x}Ge_x$ stoichiometry, where *x* varies from 0 to 4 (see Table 3), were prepared by arc melting the mixtures of pure components on a water-cooled copper hearth under argon atmosphere. The Ce metal was prepared by the Materials Preparation Center of the Ames Laboratory [20] and it was 99.8 at.% (99.95 wt.%) pure with the major impurities, given as ppm at. (wt. ppm), as follows: O–201(23), N–110(11), C–199(17), Si–897(180) and Fe–30(10). The Si and Ge were purchased from CERAC Inc and were at least 99.9995 wt.% pure. Each alloy was melted six times with the button being turned over after each melting to ensure the homogeneity of the alloys. The weight losses after arc melting were negligible (<0.2 wt.%), and, therefore, the alloy compositions were accepted as nominally prepared. The *as-cast* alloys, which were sealed in quartz tubes backfilled with helium, were annealed at 1273 K for 1 week, followed by an ice-water quench.

The X-ray powder diffraction data were collected on a PANalytical X'Pert PRO diffractometer using monochromatic Cu Kα_1 radiation over a 2θ range of 20–80°. The Rietveld powder diffraction profile fitting technique was used to refine the crystal structures of the $Ce_5Si_{4-x}Ge_x$ compounds using the LHPM Rietica software [21].

3. Results and discussion

3.1. Crystallography of the annealed $Ce_5Si_{4-x}Ge_x$ alloys

In the *as-cast* $Ce_5Si_{4-x}Ge_x$ alloys, there are two distinct terminal phase regions as *x* varies from 0 to 4: the Ce_5Si_4-based solid solution alloys ($0 \le x < 2.15$) crystallize in the Zr_5Si_4-type tetragonal crystal structure, and the Ce_5Ge_4-based solid solution alloys ($2.4 < x \le 4$) crystallize in Sm_5Ge_4-type orthorhombic structure. When $2.15 \le x < 2.225$ the samples consist of two phases – the tetragonal phase and the $Gd_5Si_2Ge_2$-type monoclinic phase – and for $2.225 \le x \le 2.4$ the $Gd_5Si_2Ge_2$-type monoclinic phase coexists with Sm_5Ge_4-type orthorhombic phase. Thus, in the *as-cast* alloys, the monoclinic $Gd_5Si_2Ge_2$-type structure exists over a narrow composition at $x \approx 2.225$.

The X-ray powder diffraction investigation of the annealed alloys in the $Ce_5Si_{4-x}Ge_x$ pseudobinary system reveals that there are also two structurally distinct terminal phase regions in the system after heat treatment. The Ce_5Si_4-based solid solution alloys with *x* ranging from 0 to 2.85 crystallize in the tetragonal Zr_5Si_4-type structure with the space group $P4_12_12$, and the Ce_5Ge_4-based solid solution alloys with $3.35 < x \le 4$ crystallize in orthorhombic Sm_5Ge_4-type structure with space group *Pnma* [2]. The $Ce_5Si_{1.1}Ge_{2.9}$ alloy consists of two phases: the tetragonal phase and the $Gd_5Si_2Ge_2$-type monoclinic phase, while the alloys with $2.95 \le x \le 3.35$ are also two-phase alloys: the $Gd_5Si_2Ge_2$-type monoclinic phase and the Sm_5Ge_4-type orthorhombic phase. However, in comparison with the *as-cast* alloys, the boundaries of two-phase regions and Sm_5Ge_4-type orthorhombic phase region have been shifted toward the Ge-rich side after annealing. The XRD patterns of several representative annealed $Ce_5Si_{4-x}Ge_x$ samples with different Ge contents are shown in Fig. 1.

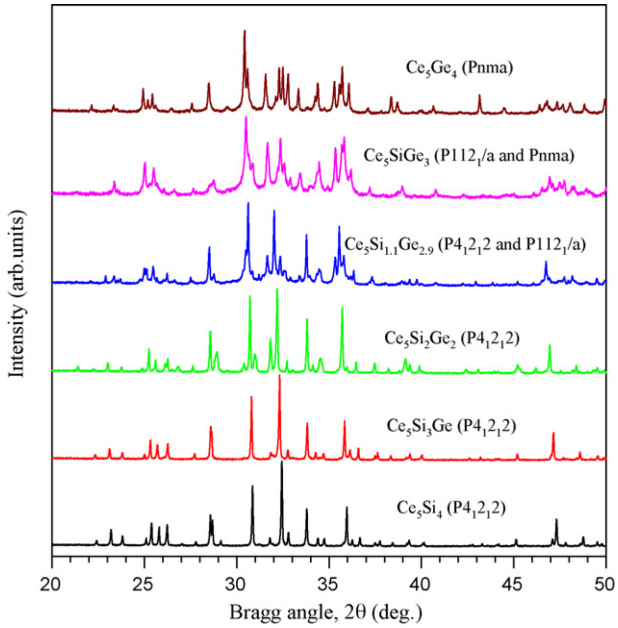

Fig. 1. The XRD patterns of six representative annealed $Ce_5Si_{4-x}Ge_x$ alloys with different Ge contents.

The crystal structures of the annealed Ce_5Si_4, Ce_5Ge_4 and Ce_5SiGe_3 alloys were refined by using the Rietveld powder diffraction profile fitting method and the comparison of the observed and calculated diffraction patterns is shown in Figs. 2–4. The lattice parameters of these compounds together with the *R* factors of the structure refinements are given in Table 1. The atomic parameters for the Zr_5Si_4-type tetragonal phase (Ce_5Si_4), the $Gd_5Si_2Ge_2$-type monoclinic phase (Ce_5SiGe_3), and the Sm_5Ge_4-type orthorhombic phase (Ce_5Ge_4) are listed in Table 2.

Ce_5Si_4 crystallizes in the tetragonal Zr_5Si_4-type structure with the space group $P4_12_12$. The Ce atoms occupy three crystallographic positions (Table 2): two 8*b* and one 4*a*, while the Si atoms are distributed over two 8*b* positions. In addition, a small amount

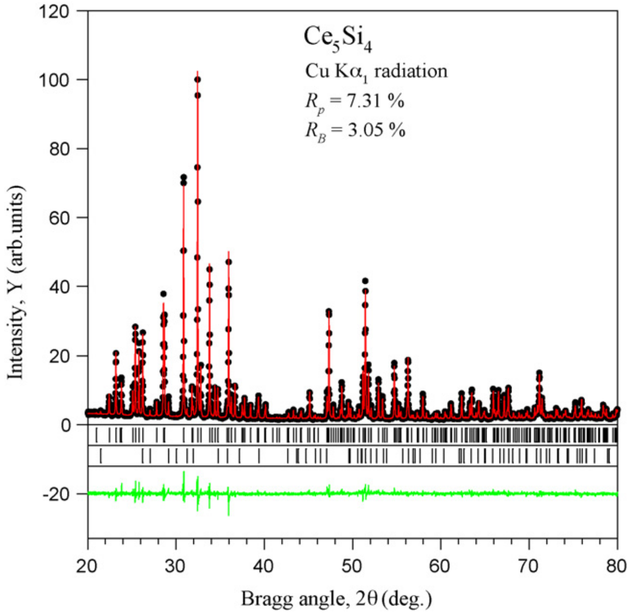

Fig. 2. The observed (dots) and calculated intensities (line drawn through the data points) of the full refined powder diffraction pattern of annealed Ce_5Si_4. The upper set of vertical bars indicates the calculated positions of the Bragg peaks of the tetragonal Ce_5Si_4 phase with the Zr_5Si_4-type structure, while the lower set of bars corresponds to the calculated positions of the Bragg peaks of the CeSi impurity. The difference, $Y_{obs} - Y_{calc}$, is shown at bottom of the plot. R_P is profile residual and R_B is derived Bragg residual.