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Subsolidus phase relations of the La–Co–Cu system and crystal structure of $LaCoCu_{12}$

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Abstract

The subsolidus phase relations of the La–Co–Cu ternary system in the La-poor region on annealing at 800 °C were investigated by X-ray powder diffraction. A new ternary intermetallic compound was discovered. The crystal structure of $LaCoCu_{12}$ was refined by the Rietveld profile fitting technique.

Keywords: Subsolidus phase relations; Crystal structure; X-ray powder diffraction

1. Introduction

$LaCo_{13}$ has a large magnetization and a high Curie temperature, $4\pi M_s = 13$ kG and $T_C = 1318$ K, because of its high content of 3d metals [1,2]. It is the only stable compound with $NaZn_{13}$-type structure of all the binary rare earth–transition metal (Fe, Co or Ni) systems. Unfortunately, $LaCo_{13}$ with $NaZn_{13}$-type structure is cubic and lacks significant anisotropy. Therefore, it cannot be used for permanent magnets. Many researchers [2–5] have found it interesting to substitute other elements M (M≡Al, Si, Fe, Ni, Zn etc.) for part of the transition metal Co, expecting to lower the symmetry of $LaCo_{13-x}M_x$ compounds and increase the magnetic anisotropy. In this paper, we report our study on the subsolidus phase relations of the La–Co–Cu ternary system in the La-poor region and the crystal structure of $LaCo_{13-x}Cu_x$.

2. Experiments

Twenty alloy samples of $LaCo_{13-x}Cu_x$ (the compositions are shown in Table 1) were prepared by arc melting appropriate amounts of starting materials in a non-self-consuming furnace under an ultrapure Ar atmosphere. The purity of the starting materials was better than 99.9%. In order to ensure homogeneity of the samples, the ingots were turned upside down and melted several times. The weight loss of the sample during arc melting was less than 1%. Thus, the nominal composition can be considered as the real composition. To achieve equilibrium, the samples were sealed in

Table 1
The composition, phase and lattice parameter of the cubic phase in $LaCo_{13-x}Cu_x$

Composition x	Phases	a (Å)
0	$LaCo_{13}$	11.350(2)
0.5	$LaCo_{13}+LaCo_5+Co$	11.354(2)
1.0	$LaCo_{13}+LaCo_5+Co$	11.367(1)
1.5	$LaCo_{13}+LaCo_5+Co$	11.369(4)
2.0	$LaCo_{13}+LaCo_5+Co$	11.351(4)
2.5	$LaCo_{13}+LaCo_5+Co$	11.353(4)
3.0	$LaCo_5+Co$	–
4.0	$LaCo_5+Co$	–
5.0	$LaCo_5+Co$	–
6.0	$LaCo_5+Co$	–
7.0	$LaCoCu_{12}+LaCu_6+Co$	11.581(4)
8.0	$LaCoCu_{12}+LaCu_6+Co$	11.575(3)
9.0	$LaCoCu_{12}+LaCu_6+Co$	11.563(2)
10.0	$LaCoCu_{12}+LaCu_6+Co$	11.569(3)
10.5	$LaCoCu_{12}+LaCu_6+Co$	11.564(1)
11.0	$LaCoCu_{12}+LaCu_6+Co$	11.574(3)
11.5	$LaCoCu_{12}+LaCu_6+Co$	11.566(3)
12.0	$LaCoCu_{12}+LaCu_6$	11.565(2)
12.5	$LaCoCu_{12}+LaCu_6+Cu$	11.573(2)
13.0	Cu	–

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quartz tubes and vacuum annealed at 1073 K for 1 month, then slowly cooled to room temperature.

Phase identification of the samples was carried out using X-ray powder diffraction, with a four-layer monochromatic focusing Guinier-de Wolff camera and Co Kα radiation. Pure Si powder was used as an inner standard for determination of the lattice parameters. The X-ray diffraction data used for crystal structure refinement were collected by an automatic X-ray diffractometer with a rotation anode. Graphite-monochromated Cu Kα radiation was used. The scan step width of 2θ was 0.02° and the sampling time for each result was 2 s. The magnetic properties of the samples were simply examined using a magnet.

3. Results and discussions

3.1. Subsolidus phase relations of the La–Co–Cu ternary system

Based on phase identification of the samples (Table 1), the subsolidus phase relations of the La–Co–Cu ternary system in the La-poor region can be constructed, as shown in Fig. 1, which consists of five three-phase regions and four two-phase regions (Table 2). In the Cu-rich region a new ternary intermetallic compound $LaCoCu_{12}$ was discovered.

For the annealed samples, X-ray powder diffraction patterns indicated that a single-phase sample with cubic $NaZn_{13}$-type structure was obtained only in the sample with $x=0$, and other phases ($LaCo_5$, Co) were observed in the sample with $x=0.5$, which implies that the solubility limit of Cu in $LaCo_{13}$ is less than $x=0.5$. The

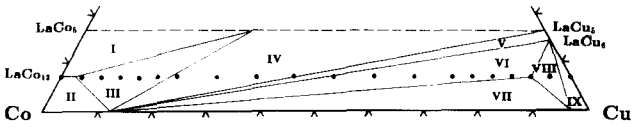

Fig. 1. Subsolidus phase relations of the La–Co–Cu ternary system in the La-poor region.

Table 2
Three-phase regions and two-phases regions in the La–Co–Cu ternary system

Region	Phases
I	$LaCo_{13}+La(Co,Cu)_5$
II	$LaCo_{13}+Co$
III	$LaCo_{13}+La(Co,Cu)_5+Co$
IV	$La(Co,Cu)_5+Co$
V	$LaCu_5+LaCu_6+Co$
VI	$LaCu_6+LaCoCu_{12}+Co$
VII	$LaCoCu_{12}+Co+Cu$
VIII	$LaCoCu_{12}+LaCu_6+Cu$
IX	$LaCu_6+Cu$

dependence on composition of the lattice parameter of the cubic phase in $LaCo_{13-x}Cu_x$ is shown in Fig. 2. The lattice parameter increases with increasing Cu content x, which can be attributed to the difference in the atomic radius of Cu (1.28 Å) and Co (1.25 Å). Based on Vegard's law and the data shown in Fig. 2, the solubility of Cu in $LaCo_{13}$ can be estimated to be about $x=0.46$, which coincides well with our experimental result.

For the samples with $x\geqslant 7.0$, the appearance of another new phase with $NaZn_{13}$-type structure reveals that the substitution of Co for some Cu can stabilize the metastable compound $LaCu_{13}$ [6] at room temperature in the form of $LaCoCu_{12}$.

The samples except those with $x\geqslant 12$ were found to be magnetic when examined simply by a magnet. This phenomenon can be easily explained by the phase relations shown in Fig. 1. The magnetism of the samples ($x=0$–11.5) arises from $LaCo_{13}$, or Co, or both, which are present in the samples.

3.2. Crystal structure of $LaCoCu_{12}$

In order to determine the crystal structure of the new compound, diffraction intensity data of the sample $LaCo_{0.5}Cu_{12.5}$, in which the main contribution to the X-ray diffraction pattern is attributed to the new compound, were collected by a diffractometer. The X-ray diffraction pattern of the annealed sample was successfully indexed by an f.c.c. lattice with $a=11.569(1)$ Å. The space group of the compound was derived as $Fm3c$ based on the reflection conditions that h, k, l are all even or odd for (hkl), and $l=2n$ for (hhl). Therefore, the new compound is isomorphous with $LaCo_{13}$, with $NaZn_{13}$-type structure.

There are two kinds of crystallographically inequivalent position in a ratio 1:12 which Co can occupy in the $LaCo_{13}$ structure. In Wyckoff notation, they are represented by the symbols 8(b) and 96(i). La atoms

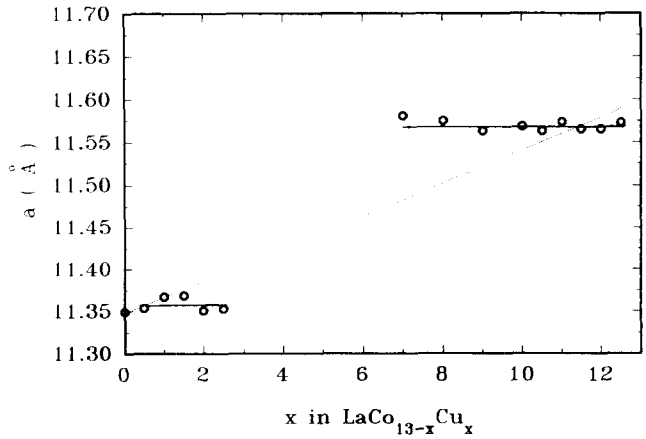

Fig. 2. Dependence on composition of the lattice parameter of the cubic phase in $LaCo_{13-x}Cu_x$. The dashed line was calculated based on Vegard's model.

occupy 8(a) positions. Each unit cell comprises eight formula units of $LaCo_{13}$ in the structure. For $LaCoCu_{12}$, La atoms with the larger atomic radius can be expected to remain in the 8(a) position. However, there are two possible atomic positions for Co atoms and Cu atoms: (i) 8Co and 96Cu occupy 8(b) and 96(i) positions randomly; (ii) 8Co and 96Cu occupy 8(b) and 96(i) positions orderly. To decide between these two possibilities, the intensities of the X-ray diffraction patterns were calculated and compared with the experimental data (Fig. 3). The arrow in Fig. 3 indicates the position of the (400) reflection. The (400) reflection disappears in (i), but appears in both (ii) and (iii). The agreement of pattern (ii) with the experimental pattern (iii) implies that there is a preference of atomic ordering of Co and Cu in the structure of the new compound.

In order to confirm further the crystal structure of $LaCoCu_{12}$, the X-ray diffraction data of the compound were fitted by the Rietveld refinement technique. All the refinement calculations were carried out on a personal computer using the program DBWS 3.2S-PC-9005. The X-ray diffraction pattern of the cubic phase and the difference curve of calculated and experimental patterns are shown in Fig. 4. The satisfactory refinement gives $a = 11.569(1)$ Å, a pattern R-factor $R_p = \Sigma|y_i - y_{ci}|/\Sigma|y_i| = 3.058\%$, and a weighted pattern R-factor $R_{wp} = [\Sigma W_i(y_i - y_{ci})^2/\Sigma w_i y_i^2]^{1/2} = 4.481\%$, where y_i and y_{ci} are observed and calculated intensities at θ_i respectively, w_i is the weighted factor. The atomic positions and isotropic temperature factors derived by Rietveld refinement are listed in Table 3. They are similar to the atomic parameters in the structure of $LaCo_{13}$. The bond lengths between atoms and the nearest coordination number of atoms are given in Table 4.

It should be mentioned that refinement of the composition of the compound converged to $LaCoCu_{12}$, which is in agreement with the ratio of the numbers of three kinds of inequivalent positions 8(a), 8(b) and 96(i).

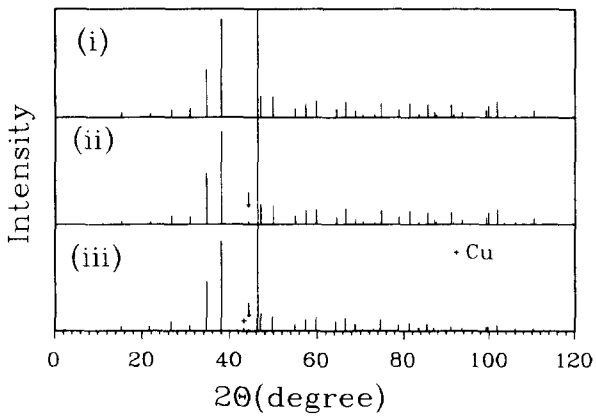

Fig. 3. Calculated X-ray diffraction intensities for two different atomic occupancies (see text) and the experimental X-ray diffraction intensity of $LaCoCu_{12}$.

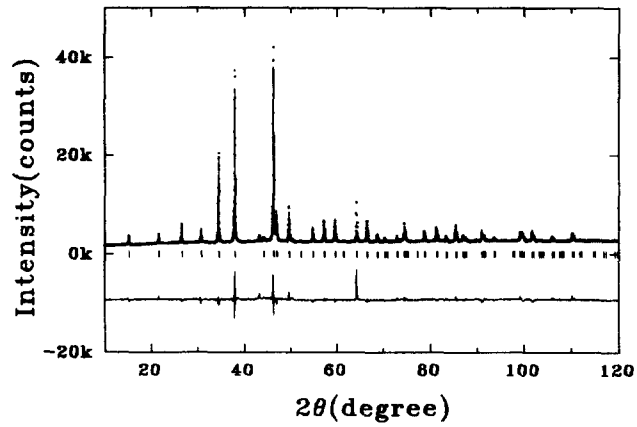

Fig. 4. Result of Rietveld fitting of the X-ray diffraction pattern of $LaCoCu_{12}$. The solid line indicates the calculated pattern, the crosses are experimental intensities, and the bars indicate the Bragg positions. The difference curve is shifted downward for clarity.

Table 3
Atomic positions and isotropic temperature factors B derived by Rietveld refinement

Atom	Site	x	y	z	B(Å^2)	N
La	8a	0.25	0.25	0.25	0.39(5)	8
Co	8b	0	0	0	–	8
Cu	96i	0	0.1803(1)	0.1177(1)	0.26(4)	96

Table 4
The bond length and the nearest coordination number of atoms in the cubic $LaCoCu_{12}$ structure

Atom	Atom	Bond length (Å)	N
La	Cu	3.370	24
Co	Cu	2.491	12
Cu	2La	3.370	12
	Co	2.491	
	Cu	2.723	
	4Cu	2.594	
	2Cu	2.512	
	2Cu	2.447	

4. Conclusions

The subsolidus phase relations of the La–Co–Cu ternary system in the La-poor region were determined by X-ray powder diffraction. This region can be divided into five three-phase regions and four two-phase regions. A new ternary intermetallic compound was discovered. The solubility limit of Cu in $LaCo_{13}$ is $x < 0.5$. In the Cu-rich region, the metastable compound $LaCu_{13}$ can be stabilized at room temperature in the form of $LaCoCu_{12}$. The structure of $LaCoCu_{12}$ is $NaZn_{13}$ type ($Fm3c$); La, Co and Cu atoms occupy orderly 8(a), 8(b) and 96(i) positions respectively.

Acknowledgment

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