The structure and magnetic properties of the ternary intermetallic compounds $La_2Co_{17-x}Ta_x$

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Abstract

Novel ternary intermetallic compounds $La_2Co_{17-x}Ta_x$ ($x = 0.5$ and 0.6) with the Th_2Zn_{17}-type structure were synthesized with Ta as a stabilizing element, and their crystal structures and magnetic properties were investigated by x-ray powder diffraction and magnetic measurement. The lattice parameters are $a = 8.5092$, $c = 12.3575$ Å for $x = 0.5$, and $a = 8.5104$, $c = 12.3591$ Å for $x = 0.6$. Rietveld refinement of the crystal structure reveals that Ta atoms occupy exclusively $6c$ crystallographic positions. The preferential occupation of Ta atoms can be understood in terms of the site volume and enthalpy of mixing. These compounds exhibit favourable uniaxial magnetocrystalline anisotropy parallel to c-axis. The Curie temperature T_C and saturation moment M_S are 1032 K and 104.3 A m^2 kg^{-1} for $x = 0.5$, and 1020 K and 98.5 A m^2 kg^{-1} for $x = 0.6$, respectively.

1. Introduction

R_2Co_{17} (R = rare-earth elements) compounds have been studied extensively because of their high saturation magnetizations and Curie temperatures which lead to permanent-magnet applications. However, the isostructural 2:17 compound for La, La_2Co_{17}, does not exist in the La–Co binary system. In our previous work, a series of novel ternary compounds $La_2Co_{17-x}M_x$ (M = Ti, V, Mn, Nb, Mo) were reported by adding a small amount of M as the stabilizing element [1–3]. These compounds have attracted our interest because of their uniaxial anisotropy. In this work, we have successfully synthesized new compounds $La_2Co_{17-x}Ta_x$, with a small amount of Ta as a stabilizing element. Here we consider the structural and magnetic properties of these compounds. Due to a large difference between the atomic scattering factors of Ta and Co, the preferential occupancies of Ta on different crystallographic positions in the structure of $La_2Co_{17-x}Ta_x$ are successfully determined by Rietveld refinement of x-ray powder diffraction data.

2. Experimental procedure

$La_2Co_{17-x}Ta_x$ compounds ($x = 0.0, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8\ 1.0$) were prepared by arc-melting of an appropriate amount of metallic La, Co and Ta with purity >99.0% in an argon atmosphere under ambient pressure. The weight loss of the samples during melting was less than 1.0%. After arc melting, the samples were annealed in vacuum at 1273 K for one month. Phase identification of the samples was carried out by x-ray powder diffraction (XRD). XRD data were collected by a Rigaku D/max -2500 diffractometer with Cu Kα radiation and a graphite monochromator, operating at a step-scan mode with a scanning step of $2\theta = 0.02°$ and a sampling time of 2 s per step. The temperature dependence of magnetization (M–T curves) in the temperature range of 300–1123 K was measured by using a Faraday balance and a vibrating sample magnetometer. The Curie temperatures were determined from the M–T curves. Magnetization (M–H) curves were measured at 1.5 K by use of an extraction sample magnetometer in a magnetic field ranging from 0 to 6.5 T. Saturation magnetization was derived according to the law of approach to saturation. The easy magnetization direction (EMD) was identified based on the x-ray diffraction pattern of magnetically aligned samples. The aligning was done by mixing fine particles of a sample with epoxy resin and allowing them to harden in a magnetic field of 1 T.

3. Results and discussion

Figure 1 shows the XRD patterns of the annealed samples of $La_2Co_{17-x}Ta_x$ ($x = 0.0, 0.3, 0.4, 0.5, 0.6, 0.8$). It can be seen from figure 1 that in the binary La–Co system there exists no trace of the 2:17 phase. When adding a small amount of Ta, say, $x = 0.3$, the $La_2Co_{17-x}Ta_x$ compound can be crystallized. As x reaches 0.5, the alloy is almost single phase crystallized in the Th_2Zn_{17}-type structure with a very small amount of $LaCo_{13}$ and $LaCo_5$ as impurities. A further increase of the Ta content, x, leads to the formation of Co_2Ta as an impurity phase. These observations and thermomagnetic measurements indicate that the homogenous range of the $La_2Co_{17-x}Ta_x$ phase is very narrow, i.e. probably $0.5 \leqslant x \leqslant 0.6$.

The Rietveld powder diffraction profile fitting technique [4] was adopted to refine the crystal structure of $La_2Co_{17-x}Ta_x$ ($x = 0.5$) based on the Th_2Zn_{17}-type structure (space group $R\bar{3}m$) by using the program DBW-9411 [5]. $LaCo_{13}$ and $LaCo_5$ were included as the second and third phase in the XRD profile fitting. Due to large difference between the atomic scattering factors of Ta and Co, the preferential occupation of Ta on different crystallographic positions in the structure can be determined successfully by Rietveld refinement of x-ray powder diffraction data. During the refinement, we put Ta atoms on all possible sites ($9d$, $18f$, $18h$, $6c$), and then refine the occupancies on these sites as free parameters. The results show that Ta atoms occupy exclusively the $6c$ crystallographic positions. The final refinement results are listed in table 1. According to the refinement results, the chemical composition of the compound is $La_2Co_{16.52}Ta_{0.48}$ for the sample $La_2Co_{16.5}Ta_{0.5}$. The Ta content in the compound derived from the Rietveld refinement of the XRD data is equal to the nominal composition within the experimental error. This suggests that the refinement results of Ta preferential occupation are reliable. Figure 2 shows the Rietveld refinement results of XRD patterns of sample $La_2Co_{16.5}Ta_{0.5}$, including the experimental and calculated patterns as well as the difference of the intensities between the experimental and calculated data. The pattern factor R_p, the weighted pattern factor R_{wp}, and the expected pattern factor R_{exp} are 8.74%, 11.74% and 6.13%, respectively. The lattice parameters of $La_2Co_{17-x}Ta_x$ are $a = 8.5092$, $c = 12.3575$ Å for $x = 0.5$, and $a = 8.5104$, $c = 12.3591$ Å for $x = 0.6$ from Rietveld refinement results.

Since neither La_2Co_{17} nor La_2Ta_{17} are stable, the occurrence of the $La_2Co_{17-x}Ta_x$ phase
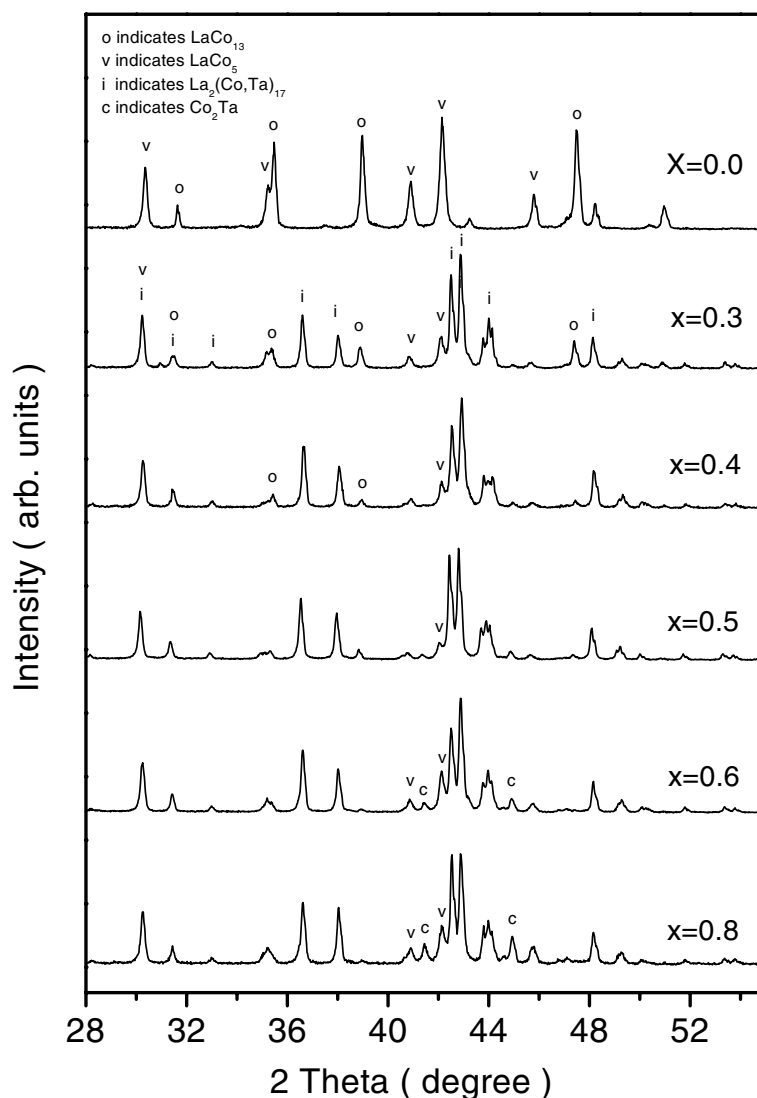
Figure 1. XRD patterns of annealed La$_2$Co$_{17-x}$Ta$_x$ samples ($x = 0.0, 0.3, 0.4, 0.5, 0.6, 0.8$).

with the Th$_2$Zn$_{17}$-type structure implies that it has to be regarded as a ternary intermetallic compound. The ternary character of the compound is further evidenced by the fact that the Ta atoms preferentially occupy only one type of the available atomic sites (18f, 18h, 9d and 6c), i.e. 6c positions based on Rietveld refinement results. The reasons why the Ta atoms occupy the 6c sites and stabilize these ternary compounds can be understood in consideration of the site volume and the enthalpy of mixing. Similar effects were also observed and discussed in our previous work [3] and in [6].

The atomic coordination (neighbour) and the average distance of a site to the neighbouring Co are listed in table 1. The average distance and coordinating number for the 6c site are the largest, indicating that the largest site volume is around the 6c site. So this site is expected to be preferentially occupied by large Ta atoms (compared with Co atoms).
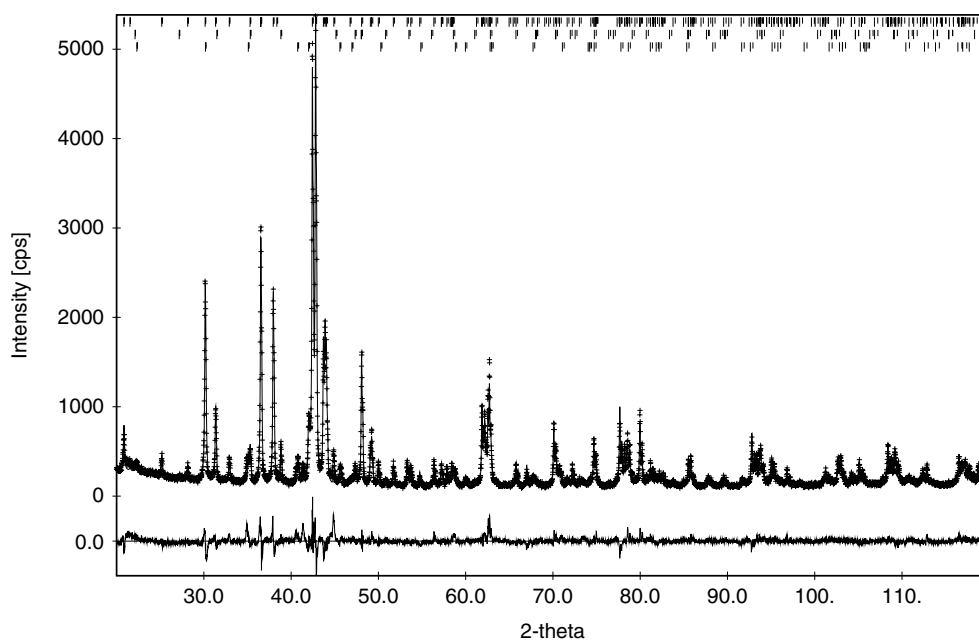
Figure 2. The Rietveld refinement results for the XRD patterns of the $La_2Co_{16.5}Ta_{0.5}$ samples, including the experimental (+) and calculated (full curve) intensities as well as the difference of the intensities between the experimental and calculated data. On top of the plot expected Bragg reflection positions are indicated by vertical bars for 2:17 (top), 1:13 (middle) and 1:5 (bottom) phases.

Table 1. Rietveld refinement results for the $La_2Co_{16.5}Ta_{0.5}$ compound; space group $R\bar{3}m$; ADSN is the average distance of the site to neighbouring Co ($a = 8.5092(1)$ Å, $c = 12.3575(1)$ Å, $V = 774.9(1)$ Å^3, $R_p = 8.74\%$, $R_{wp} = 11.74\%$, $R_{exp} = 6.13\%$).

Atom site	x	y	z	Neighbours	ADSN
La $6c$	0.0	0.0	0.3470	19 Co	3.146
Co $9d$	0.5	0.0	0.5	10Co + 2La	2.476
Co $18f$	0.2860	0.0	0.0	10Co + 2La	2.548
Co $18h$	0.5	0.0	0.1548	9Co + 3La	2.552
[a]Co + Ta $6c$	0.0	0.0	0.0961	13Co + 1La	2.652

[a] The site occupied by 24% Ta atoms and 76% Co atoms.

An estimate for the affinity of one element to another can be done by the semiempirical calculation of the enthalpy of mixing, ΔH, as proposed by Miedema *et al* [7]. ΔH for Ta–La, Ta–Co and La–Co are 48.8 kJ mol^{-1}, -35.7 kJ mol^{-1}, and -23.7 kJ mol^{-1}, respectively. The enthalpy of mixing for Ta–La is large and positive compared with the enthalpy of mixing for Ta–Co. For this reason the number of La neighbours should play a significant role for the site occupation. The chemical affinity drives the Ta atom to occupy the sites which have by far the smallest area of contact with the La atom. It can be seen from table 1 that the $6c$ site has only one neighbouring La atom while other sites have two or more neighbouring La atoms. In view of the large positive enthalpy contribution associated with La and Ta contact, one may expect, therefore, that the $6c$ site should be preferred by Ta atoms.

The temperature dependence of the magnetization (M–T curves) was measured in a low
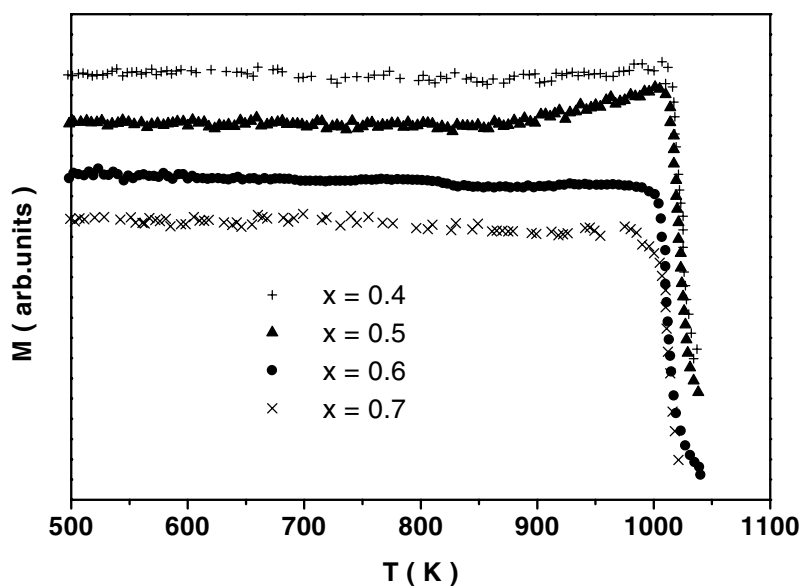
Figure 3. Temperature dependence of the magnetization of the samples ($x = 0.4, 0.5, 0.6, 0.7$) measured by a vibrating sample magnetometer in a low field of 0.1 T.

field of 0.1 T as shown in figure 3. The Curie temperatures are 1032 K for $x = 0.5$, and 1020 K for $x = 0.6$ derived from $M–T$ curves. The decrease of T_C with increasing x may be due to the magnetic dilution by Ta substitution for Co. There is a very small difference of Curie temperatures for samples between $x = 0.4$ and $x = 0.5$, and also a very small difference between $x = 0.6$ and $x = 0.7$, indicating that the homogenous range of the La$_2$Co$_{17-x}$Ta$_x$ phase is probably $0.5 \leqslant x \leqslant 0.6$, which agrees well with the above results of XRD. Figure 4 show the magnetization curves ($M–H$ curves) at 1.5 K measured by an extraction sample magnetometer in a field of 6.5 T, from which the saturation moments M_S of La$_2$Co$_{17-x}$Ta$_x$ were derived and are 104.3 A m^2 kg^{-1} for $x = 0.5$ and 98.5 A m^2 kg^{-1} for $x = 0.6$.

The x-ray diffraction patterns for magnetically oriented polycrystalline powder indicate
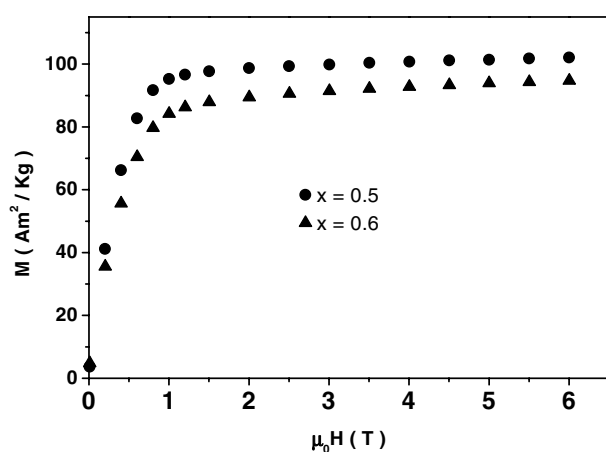

Figure 4. The magnetization curves of the bulk samples ($x = 0.5, 0.6$) measured by an extraction sample magnetometer at 1.5 K.

that the compounds $La_2Co_{17-x}Ta_x$ ($x = 0.5$ and 0.6) exhibit a uniaxial magnetocrystalline anisotropy and that the easy magnetization direction (EMD) is along the c-axis. In order to evaluate the uniaxial anisotropy, the powder sample of $La_2Co_{16.5}Ta_{0.5}$ was made to align in a magnetic field of 1 T and fixed by epoxy resin. Figure 5 shows the magnetization measured with the applied field parallel or perpendicular to the EMD of the aligned powder sample, respectively. The anisotropy fields H_A of 0.85 T was derived by linearly extrapolating ΔM to the zero of the ΔM ($= M_\parallel - M_\perp$)–H curve. The value of H_A is very low because the contribution of La without magnetic moment to the magnetocrystalline anisotropy is negligible.
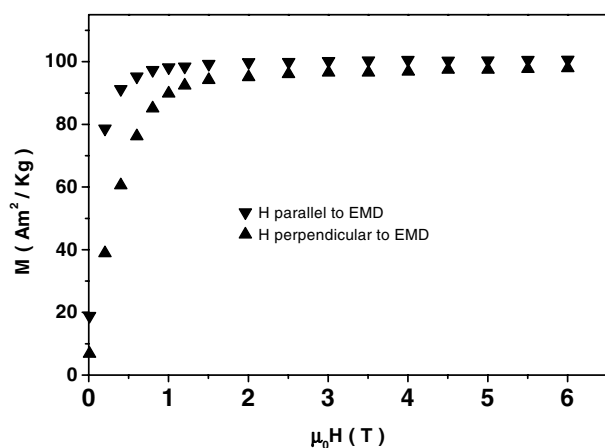

Figure 5. The magnetization curves of magnetically aligned powder samples $La_2Co_{16.5}Ta_{0.5}$ at 1.5 K with the field parallel or perpendicular to the EMD.

In conclusion, novel ternary intermetallic compounds $La_2Co_{17-x}Ta_x$ ($x = 0.5$ and 0.6) with the Th_2Zn_{17}-type structure were synthesized with Ta as a stabilizing element. The lattice parameters are $a = 8.5092$, $c = 12.3575$ Å for $x = 0.5$, and $a = 8.5104$, $c = 12.3591$ Å for $x = 0.6$. Rietveld refinement of the crystal structure reveals that Ta atoms occupy exclusively the $6c$ crystallographic position. The preferential occupation of Ta atoms can be understood in terms of the site volume and enthalpy of mixing. These compounds exhibit favourable uniaxial magnetocrystalline anisotropy parallel to c-axis. The Curie temperature T_C and saturation moment M_S are 1032 K and 104.3 A m^2 kg^{-1} for $x = 0.5$, and 1020 K and 98.5 A m^2 kg^{-1} for $x = 0.6$, respectively.

Acknowledgments

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