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Crystal structure and magnetic properties of the intermetallic compounds $\text{La}_2\text{Co}_{17-x}\text{M}_x$ ($\text{M} = \text{Nb}, \text{Mo}, \text{Mn}$)

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Abstract. Novel ternary intermetallic compounds $\text{La}_2\text{Co}_{17-x}\text{M}_x$ ($\text{M} = \text{Nb}, \text{Mo}, \text{Mn}$) with $\text{Th}_2\text{Zn}_{17}$ -type structure were synthesized and their homogeneous ranges were determined: $0.3 \leq x \leq 0.6$ for Nb, $0.6 \leq x \leq 1.2$ for Mo and $1.0 \leq x \leq 4.0$ for Mn. The lattice parameters and the unit-cell volume increase with increasing x in all of the systems. The preferential occupancy of 6c crystallographic positions (dumb-bell sites) and the stabilization of these compounds by M atoms are attributed to the atomic-size and enthalpy effects. These compounds exhibit favourable uniaxial anisotropy with M content $x \geq 0.5$. The Curie temperature decreases monotonically with increasing x for all of the systems. The saturation moment μ_s decreases rapidly with increasing x for $\text{M} = \text{Mo}$ and Nb. In the $\text{La}_2\text{Co}_{17-x}\text{Mn}_x$ system, μ_s increases slightly with x for $x \leq 2.5$ and then decreases for $x > 2.5$.

1. Introduction

Since the discovery of the excellent permanent-magnetic material $\text{Nd}_2\text{Fe}_{14}\text{B}$ [1, 2], a worldwide search for novel rare-earth–transition metal intermetallics has been carried out. It is believed that there exist other compounds in the still unexploited reservoir of ternary compounds in the R–T–M system (R = rare-earth elements, T = transition metals, M = other elements) [3]. Many novel ternary compounds have already been investigated as potential candidates for permanent-magnet applications. These compounds include $\text{RFe}_{12-x}\text{M}_x$ ($\text{M} = \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Nb}, \text{Mo}, \text{W}$ or Si) compounds with ThMn_{12} -type structure [4, 5], interstitial compounds $\text{R}_2\text{Fe}_{17}\text{X}_y$ ($\text{X} = \text{N}$ or C) with $\text{Th}_2\text{Zn}_{17}$ - or $\text{Th}_2\text{Ni}_{17}$ -type structure [6, 7] and $\text{R}_3\text{Fe}_{29-x}\text{M}_x$ ($\text{M} = \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Mo}, \text{Nb}$) with $\text{Nd}_3\text{Fe}_{29-x}\text{Ti}_x$ -type structure [8, 9]. Like the R_2Fe_{17} compounds, $\text{RFe}_{12-x}\text{M}_x$ and $\text{R}_3\text{Fe}_{29-x}\text{M}_x$ are also able to absorb N and C as interstitial atoms, leading to a remarkable improvement in their magnetic properties [10–12].

R_2Co_{17} compounds have been studied extensively because of their high saturation magnetizations and Curie temperatures which lead to permanent-magnet applications. However, it is hard to find practical applications of these compounds individually due to their unfavourable anisotropy. The cobalt sublattice anisotropy in these compounds has been proved to be easy-plane anisotropy, resulting from the presence of short ‘dumb-bell’ pairs of Co atoms [13]. Subsequently, it was found that the anisotropy of R_2Co_{17} compounds can

be improved and the planar anisotropy can be converted to a uniaxial one by replacing Co with appropriate amounts of other 3d or 4d transition metals or Al [14, 15]. The compound $\text{La}_2\text{Co}_{17}$, although it does not exist in the La–Co binary system, is expected to have uniaxial anisotropy, because La, with its larger atomic radius, could increase the Co–Co distance at dumb-bell sites. In our previous work, we found that the isostructural 2:17 compounds of La could be synthesized by adding a third stabilizing element such as Ti or V [16, 17]. These compounds exhibited favourable uniaxial anisotropy. In this work, we have extended our study to other ternary La–Co–M (M = Mo, Nb, Mn, Zr, Cr, Fe, Al, Si and Ga) systems. A series of $\text{La}_2\text{Co}_{17-x}\text{M}_x$ (M = Mo, Nb and Mn) compounds have been synthesized. A systematic investigation of the crystal structure and magnetic properties of these compounds is reported here.

2. Experiments

Alloys were prepared by arc melting the appropriate amounts of the starting materials of purity 99.0–99.95% under a high-purity argon atmosphere. To ensure the homogeneity of the samples, the ingots were turned and melted at least four times. After arc melting, the samples were annealed in vacuum at 1273 K for two weeks. They were then crushed and ground for later measurements.

Phase identification of the samples was carried out by means of x-ray powder diffraction, using a four-layer monochromatic focusing Guinier–de Wolff camera and Co $K\alpha$ radiation. The x-ray diffraction (XRD) data used to determine the lattice parameters were collected on a Philips X'Pert MPD diffractometer with Cu $K\alpha$ radiation and a graphite monochromator. High-purity Si powder was used as an inner standard for correcting the positions of the diffraction peaks.

The 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 65 kOe. The saturation magnetization was derived according to the law of approach to saturation. The temperature dependence of magnetization (M – T) curves in the temperature range 300–1123 K were measured by using a Faraday balance and a vibrating-sample magnetometer, and the Curie temperatures were determined from the M – T curves. The easy-magnetization direction (EMD) was identified from the x-ray diffraction patterns of the 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. From magnetization curves of the aligned samples obtained with the applied field parallel or perpendicular to the alignment direction, the values of the anisotropy field $\mu_0 H_A$ were derived.

3. Results and discussion

3.1. Crystallographic properties

Alloy samples of $\text{La}_2\text{Co}_{17-x}\text{M}_x$ (M = Ti, V, Cr, Mn, Fe, Zr, Nb, Mo, Al, Si and Ga) were prepared. Visual inspection of the XRD patterns indicated that the annealed samples with Ti, V, Mn, Nb and Mo were single-phase samples with the rhombohedral $\text{Th}_2\text{Zn}_{17}$ -type structure (space group $R\bar{3}m$). No trace of 2:17 phase was found in the samples with M = Zr, Cr, Fe, Al, Si and Ga.

The XRD patterns revealed that single-phase samples were obtained in the $\text{La}_2\text{Co}_{17-x}\text{M}_x$ systems with $0.8 \leq x \leq 1.2$ for M = Ti and V [16, 17], $0.3 \leq x \leq 0.6$ for M = Nb, $0.6 \leq x \leq 1.2$ for M = Mo and $1.0 \leq x \leq 4.0$ for M = Mn. The lattice parameters and the

unit-cell volumes of these compounds are listed in table 1. Figure 1 shows the dependence of the unit-cell volume on the concentration of M. Both the lattice parameters and the unit-cell volumes are found to increase monotonically with M content x in all of the systems studied, indicating that the M atoms are substituting for Co in the 2:17 lattice. The crystal structures of $\text{La}_2\text{Co}_{16}\text{M}$ ($M = \text{Ti}, \text{V}$) were refined by the Rietveld powder diffraction profile-fitting technique [16, 17]. The refinement results show that Ti or V preferentially occupies 6c sites (dumb-bell sites).

Since neither $\text{La}_2\text{Co}_{17}$ nor La_2M_{17} are stable, the occurrence of the $\text{La}_2\text{Co}_{17-x}\text{M}_x$ phase with the $\text{Th}_2\text{Zn}_{17}$ -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

Table 1. The lattice parameters and magnetic data for $\text{La}_2\text{Co}_{17-x}\text{M}_x$ compounds. T_c is the Curie temperature (in K), μ_s is the magnetic moment per formula unit (in $\mu_B/\text{f.u.}$), $\mu_0 H_A$ is the anisotropy field (in T).

Compounds	a (Å)	c (Å)	V (Å ³)	M_S (A m ² kg ⁻¹)	μ_s ($\mu_B/\text{f.u.}$)	T_C (K)	$\mu_0 H_A$ (T)
$\text{La}_2\text{Co}_{17-x}\text{Ti}_x$ (reference [16])							
$x = 0.8$	8.518(1)	12.344(1)	775.6(3)	101.7	23.2	972	Axis
$x = 1.0$	8.525(1)	12.362(1)	778.0(3)	98.4	22.5	914	2.3
$x = 1.2$	8.531(1)	12.379(2)	780.2(4)	94.0	21.3	872	Axis
$\text{La}_2\text{Co}_{17-x}\text{V}_x$ (reference [17])							
$x = 0.8$	8.4971(8)	12.337(1)	771.4(3)	98.5	22.5	926	Axis
$x = 1.0$	8.4986(3)	12.340(1)	771.8(2)	95.0	21.6	880	1.9
$x = 1.2$	8.5003(3)	12.343(1)	772.3(2)	86.1	19.6	827	Axis
$\text{La}_2\text{Co}_{17-x}\text{Mo}_x$ (this work)							
$x = 0.6$	8.5080(6)	12.340(1)	774.5(3)	102.9	24.0	987	Axis
$x = 0.8$	8.5120(4)	12.351(1)	776.0(2)	98.0	23.0	948	Axis
$x = 1.0$	8.5158(5)	12.361(1)	777.2(2)	95.0	22.4	902	1.2
$x = 1.2$	8.5193(5)	12.368(1)	778.3(2)	88.8	21.1	863	Axis
$\text{La}_2\text{Co}_{17-x}\text{Nb}_x$ (this work)							
$x = 0.3$	8.5080(5)	12.340(1)	773.5(2)	109.4	25.3	> 1030	Plane
$x = 0.4$	8.5118(3)	12.351(1)	774.9(2)	106.8	24.7	1025	≈ 0
$x = 0.5$	8.5171(3)	12.361(1)	776.5(2)	106.1	24.6	1001	Axis
$x = 0.6$	8.5220(5)	12.386(1)	777.8(2)	103.3	24.0	973	1.3
$\text{La}_2\text{Co}_{17-x}\text{Mn}_x$ (this work)							
$x = 1.0$	8.5293(9)	12.344(2)	777.7(4)	121.0	27.6	1010	1.6
$x = 1.4$	8.5370(4)	12.363(2)	780.3(2)	121.1	27.6	991	Axis
$x = 2.0$	8.5485(6)	12.378(1)	783.3(2)	121.8	27.7	910	1.9
$x = 2.5$	8.5603(4)	12.403(1)	787.1(2)	123.6	28.1	848	Axis
$x = 3.0$	8.5723(4)	12.429(1)	790.9(2)	116.7	26.5	757	2.1
$x = 3.3$	8.5774(6)	12.442(1)	792.7(2)	111.8	25.4	715	Axis
$x = 3.7$	8.5844(5)	12.454(1)	794.8(2)	103.4	23.4	660	Axis
$x = 4.0$	8.5898(5)	12.466(1)	796.5(2)	97.3	22.0	593	1.4

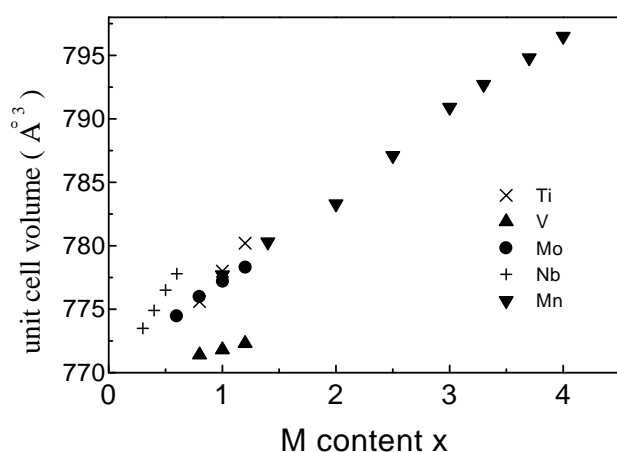


Figure 1. The dependence of the unit-cell volume V of the $\text{La}_2\text{Co}_{17-x}\text{M}_x$ compounds on the M concentration (M = Ti, V, Nb, Mo, Mn).

M atoms preferentially occupy only one type of the available atomic sites (18f, 18h, 9d and 6c). The reasons for the M atoms occupying the dumb-bell sites and stabilizing these ternary compounds can be explained in terms of both atomic-size and enthalpy effects.

The crystal structure of the R_2Co_{17} compounds can be considered to be derived from that of RCO_5 compounds by substituting a dumb-bell pair of Co atoms (at a 6c crystallographic position) for a rare-earth atom in every third unit cell. R_2Co_{17} is stable for all rare-earth metals except La, with the larger radius; this might be attributable to the fact that the La site in LaCo_5 is too large for a Co–Co pair. Therefore, substitution for some of the Co atoms at dumb-bell sites with larger M atoms is necessary to stabilize the $\text{La}_2\text{Co}_{17-x}\text{M}_x$ phases. It is indeed found from the metallic radii (listed in table 2) that the M atoms which can stabilize the $\text{La}_2\text{Co}_{17-x}\text{M}_x$ phases are much larger than Co—such as Ti, V, Mn, Mo or Nb—while the other atoms with smaller radii—such as Cr, Fe and Si—cannot stabilize the 2:17 compounds. Zr atoms, however, might be too large to insert into the dumb-bell sites, and $\text{La}_2\text{Co}_{17-x}\text{Zr}_x$ phases cannot form. The bond lengths and number of coordinating atoms in the structure of the $\text{La}_2\text{Co}_{16}\text{Ti}$ compound are listed in table 3. The average T–T bond length for the T positioned at dumb-bell sites is largest, indicating that the largest space is around that site. So the dumb-bell site is expected to be preferred over the 18f, 18h and 9d sites for large M atoms (M = Ti, V, Nb, Mo, Mn).

Table 2. The calculated enthalpies of solution of liquid metals in solution in liquid La [18], ΔH in kJ mol^{-1} and the metallic radii for the coordination number 12, in Å.

Element	Zr	Ti	V	Mn	Nb	Mo	Cr	Fe	Co	Al	Si	Ga
ΔH	+45	+64	+69	+8	+120	+102	+52	+14	−51	−127	−178	−142
Radius	1.60	1.47	1.34	1.35	1.46	1.39	1.30	1.26	1.25	1.43	1.32	1.41

The enthalpies of formation of alloys can be used as a guide in explaining the site occupancy in the systems under study. Table 2 lists the enthalpies of solution of liquid metals in solution in liquid La [18]. These enthalpies are strongly positive for La–Ti, La–V, La–Nb and La–Mo, slightly positive for La–Mn and strongly negative for La–Co, La–Al, La–Ga and La–Si. It follows from this that the formation of an R–M bond is energetically unfavourable in the case with M = Ti, V, Nb, Mo, Mn. In fact, a large number of compounds are found in the La–Co, La–Al, La–Ga and La–Si, while no intermetallic compound exists in the La–M binary system. It can be seen from table 3 that the dumb-bell site has only one La neighbour while other sites

Table 3. The bond lengths (in Å) and numbers of coordinating atoms ($\times N$) of the compound $\text{La}_2\text{Co}_{16}\text{Ti}$; ABLTT = average T-T bond length; T = transition elements.

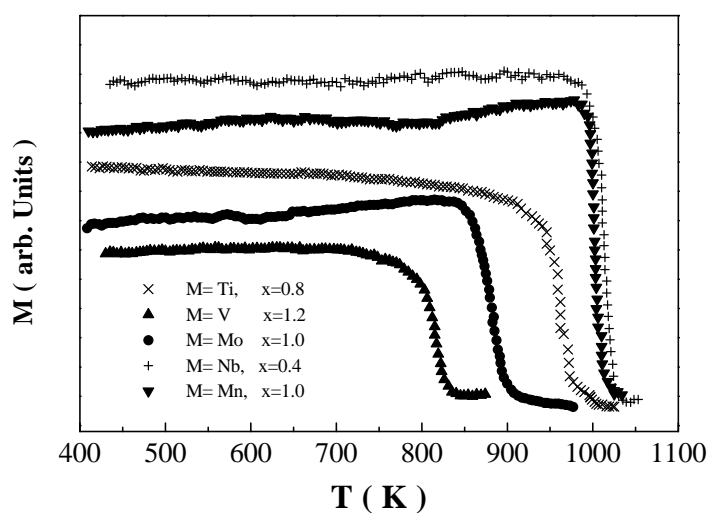
Site	La, 6c	T, 9d	T, 18h	T, 18f	T, 6c	ABLTT
La, 6c		3.321×3	3.145×9	3.052×6	3.104×1	
T, 9d	3.321×2		2.465×4	2.423×4	2.611×2	2.477
T, 18h	3.145×3	2.465×2	2.478×2	2.587×4	2.664×1	2.544
T, 18f	3.052×2	2.423×2	2.587×4	2.508×3	2.737×2	2.563
T, 6c	3.104×1	2.611×3	2.664×3	2.737×6	2.376×1	2.663

have more than two La neighbours. In other words, the dumb-bell site has by far the smallest area of contact with the La atom. In view of the positive enthalpy contribution associated with R and M contact, one may expect therefore that the dumb-bell site will be preferred by M elements. Similar effects are observed in $\text{RFe}_{12-x}\text{M}_x$ and $\text{R}_3\text{Fe}_{29-x}\text{M}_x$ systems [4]. Although the radii of Al, Si and Ga atoms seem suitable, the enthalpies of La with Al, Si and Ga are negative and much less than that of La with Co. So they fail to preferentially occupy the dumb-bell sites and stabilize the $\text{La}_2\text{Co}_{17-x}\text{M}_x$ ($M = \text{Al}, \text{Si}, \text{Ga}$) phase.

There are three pairs of the dumb-bell atoms and three formula units of $\text{La}_2\text{Co}_{17-x}\text{M}_x$ in a unit cell. If the M occupy exclusively dumb-bell sites, the homogeneous range in the $\text{La}_2\text{Co}_{17-x}\text{M}_x$ series should be limited to $x \leq 2.0$, which is consistent with the results for Ti, V, Nb and Mo systems. The wide range of solid solubility of $\text{La}_2\text{Co}_{17-x}\text{Mn}_x$ from $x = 1.0$ to $x = 4.0$ implies that Mn atoms occupy not only the dumb-bell sites but also 18f, 18h or 9d sites. This can be attributed to the fact that the Mn atom is smaller than those of Ti, Mo and Nb, which implies that more Mn atoms are required, and the alloying enthalpy of Mn with La is close to zero, allowing Mn to occupy sites other than 6c and to contact with more La atoms.

3.2. Magnetic properties

The temperature dependence of the magnetization was measured in a low field, and some typical $M-T$ curves are shown in figure 2. The Curie temperature T_c was determined from the $M-T$ curves and is plotted as a function of x in figure 3 (also listed in table 1). As can be

**Figure 2.** The temperature dependence of the magnetization of the $\text{La}_2\text{Co}_{17-x}\text{M}_x$ compounds measured by a vibrating-sample magnetometer in a low field.

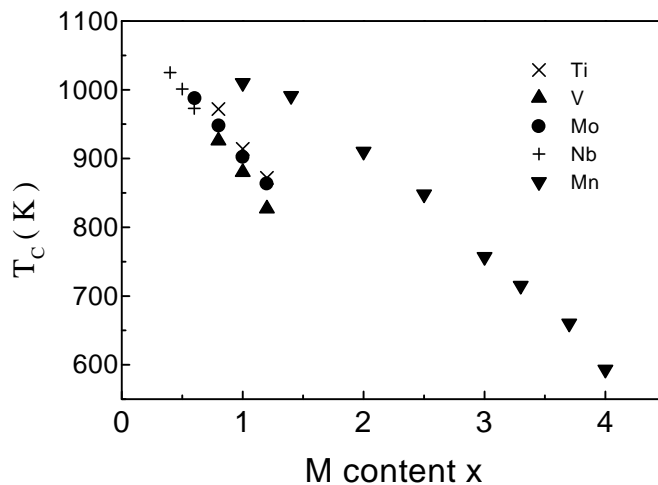


Figure 3. The dependence of the Curie temperature T_c of the $\text{La}_2\text{Co}_{17-x}\text{M}_x$ compounds on the M concentration ($M = \text{Ti}, \text{V}, \text{Nb}, \text{Mo}, \text{Mn}$).

seen from table 1 and figure 3, the Curie temperature decreases monotonically with increasing x for all of the systems, indicating a weakening of the Co–Co magnetic interaction.

The saturation moments μ_s of the $\text{La}_2\text{Co}_{17-x}\text{M}_x$ compounds are listed in table 1 and are plotted as a function of x in figure 4. For the Mn system with $x \geq 2.5$ and the Ti, V, Mo and Nb systems, μ_s decrease rapidly with increasing x . The rate of the decrease is larger than that expected for a simple dilution. A similar effect has been observed in $\text{Ce}_2\text{Co}_{17-x}\text{M}_x$ [14]. This phenomenon can be explained by the filling up of the 3d vacancies by the outer electrons of Ti, V, Mn, Mo or Nb. The rigid-band model appears to be appropriate for the small- x regions for the $\text{La}_2\text{Co}_{17-x}\text{Mn}_x$ system, in which μ_s increases with x , and the onset of the decrease of μ_s which occurs at $x \approx 2.5$ corresponds to the situation in which the majority band is completely filled [19].

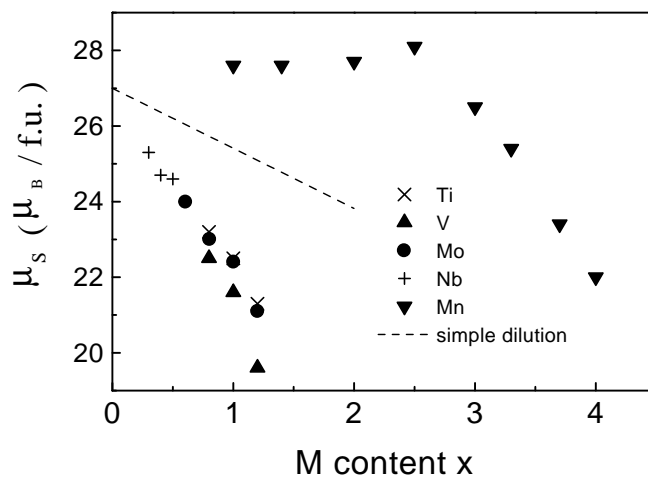


Figure 4. The dependence of the saturation magnetization μ_s of the $\text{La}_2\text{Co}_{17-x}\text{M}_x$ compounds on the M concentration ($M = \text{Ti}, \text{V}, \text{Nb}, \text{Mo}, \text{Mn}$).

We present XRD patterns for magnetically oriented polycrystalline powder in figure 5. The XRD patterns indicate that for $M = \text{Mo}$ and Mn samples the easy-magnetization direction (EMD) is parallel to the c -axis, and for $\text{La}_2\text{Co}_{17-x}\text{Nb}_x$ samples the EMD changes from the basal-plane direction ($x = 0.3$) to the c -axis direction ($x \geq 0.5$) with increase of the Nb content, while the $\text{La}_2\text{Co}_{16.6}\text{Nb}_{0.4}$ compound is almost isotropic. Figure 6 shows the magnetization curves of magnetically aligned powder samples with the field applied parallel to the alignment direction (EMD) and perpendicular to the alignment direction (HMD). By extrapolating ΔM to zero in the curve for $\Delta M (=M_{EMD} - M_{HMD})$ against H , the anisotropy fields $\mu_0 H_A$ of some samples are determined and these are listed in table 1.

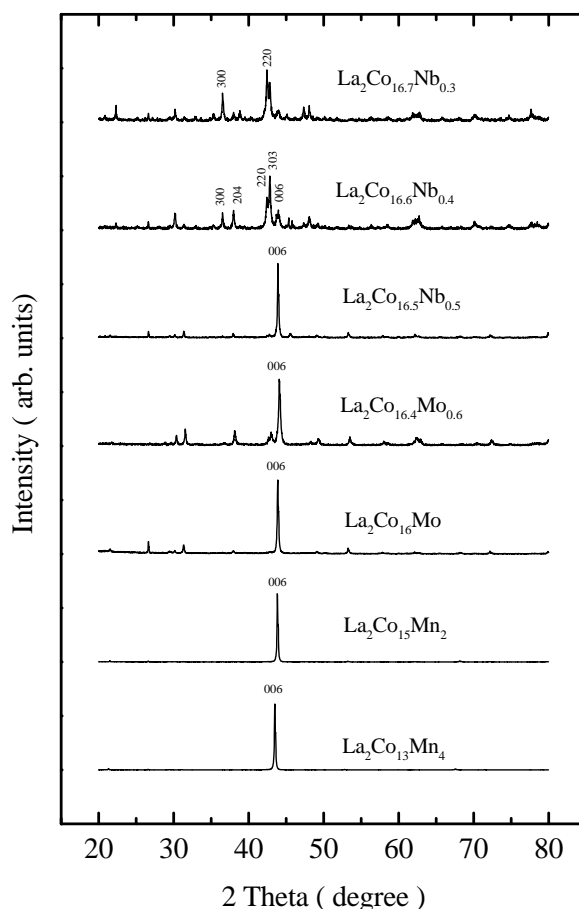


Figure 5. The XRD patterns of magnetically aligned $\text{La}_2\text{Co}_{17-x}\text{M}_x$ powders ($M = \text{Nb}, \text{Mo}, \text{Mn}$).

One of the characteristic structural features of the R_2Co_{17} compounds is the presence of so-called dumb-bell pairs of Co atoms. They are usually considered to be responsible for the easy-plane anisotropy of the Co sublattice in the R_2Co_{17} compounds, as compared to the easy-axis anisotropy in the parent RCo_5 compounds, where the Co dumb-bell atoms are absent [13]. M atoms preferentially occupy the dumb-bell sites in the structure of $\text{La}_2\text{Co}_{17-x}\text{M}_x$ compounds. Thus, the substitution of M for Co at the dumb-bell sites weakens the easy-plane anisotropy and results in a favourable uniaxial anisotropy when $x \geq 0.5$.

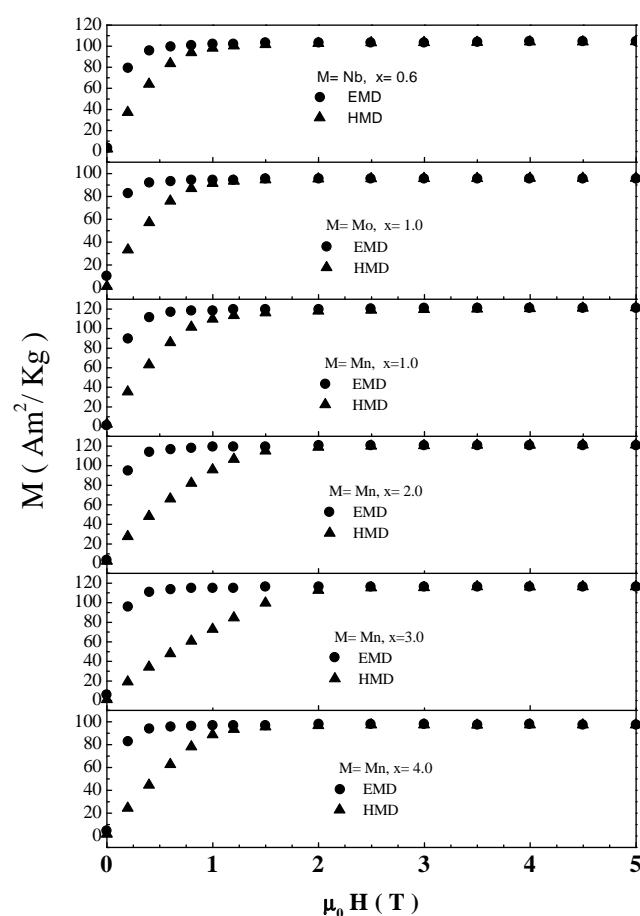


Figure 6. The magnetization curves of magnetically aligned powder samples with the field applied parallel to the alignment direction (EMD) and perpendicular to the alignment direction (HMD).

4. Conclusions

$\text{La}_2\text{Co}_{17-x}\text{M}_x$ ($M = \text{Mn}, \text{Nb}, \text{Mo}$) compounds with $\text{Th}_2\text{Zn}_{17}$ -type structure were synthesized and their homogeneous ranges, lattice parameters and unit-cell volumes are determined. The reasons for the M atoms occupying the dumb-bell sites and stabilizing these ternary compounds are elucidated in terms of atomic-size and enthalpy effects. As a stabilizing element, M must simultaneously satisfy the geometric and thermodynamic requirements. These compounds exhibit favourable uniaxial anisotropy when the M content $x \geq 0.5$. The Curie temperature decreases monotonically with increasing x for all of the systems. The saturation moment μ_s decreases sharply with increasing x for the Mo and Nb systems. In the $\text{La}_2\text{Co}_{17-x}\text{Mn}_x$ system, μ_s increases slightly with x for $x \leq 2.5$ and then decreases sharply for $x > 2.5$.

Acknowledgments

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