Evolution of Structural and Magnetic Properties in $\text{La}_x\text{Ce}_{2-x}\text{Co}_{16}\text{Ti}$ for $0 \leq x \leq 2$

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Abstract

In the present work we examine the intrinsic magnetic and structural properties of the title alloys, permanent magnet materials based on the abundant rare-earth elements lanthanum and cerium, since these properties (T_C , M_s , $H_a(K_1, K_2)$) will set the upper limits on the quality of permanent magnet that can be fabricated from said alloys. $\text{Ce}_2\text{Co}_{16}\text{Ti}$ has a high magnetic anisotropy ($H_a = 65$ kOe) but a relatively low saturation magnetization ($M_s = 7.3$ kG), and $\text{La}_2\text{Co}_{16}\text{Ti}$ has a high M_s (9.5 kG) but H_a too low for most applications (16 kOe). Though these two end-members have previously well-known properties, changing economic conditions have made re-examination of systems containing cerium and lanthanum necessary as the economic viability of rare earth mining becomes dependent on extraction of products beyond what is currently considered useful and profitable within the rare earth elements. We find that replacing some lanthanum with cerium in $\text{La}_2\text{Co}_{16}\text{Ti}$ increases H_a by a factor of more than two, while decreasing M_s by less than 5%. The measured M_s indicate maximum possible energy products in excess of 20 MG·Oe in these materials, which have Curie temperatures near 600°C. Real energy products are expected to be greatest near $x=1$. These findings identify $\text{La}_x\text{Ce}_{2-x}\text{Co}_{16}\text{Ti}$ as a promising system for development of so-called gap magnets that fill the energy product gap between expensive rare-earth magnets and current non-rare earth alternatives.

Keywords: Permanent Magnet, Magnetic Anisotropy, Critical Materials, $\text{La}_2\text{Co}_{16}\text{Ti}$, $\text{Ce}_2\text{Co}_{16}\text{Ti}$, $\text{Ce}_2\text{Co}_{17}$, $\text{Th}_2\text{Ni}_{17}$, $\text{Th}_2\text{Zn}_{17}$

1. Introduction

The need for reduced rare earth content permanent magnets is on the rise. Also necessary is the use of less “critical” rare earth elements in permanent magnets as they are in greater supply than elements like neodymium and dysprosium whose scarcity and desirability has caused worldwide shortages and price increases. The elements cerium and lanthanum are two such rare earth elements that are in greater relative supply and might be successfully utilized in magnets at reduced cost. However, these elements are seldom used in permanent magnet applications since they generally do not aid in the production of magnetocrystalline anisotropy. For rare earth species, the $4f$ electrons are a major contributor to magnetocrystalline anisotropy, see for example references [1, 2], which originates from spin-orbit coupling and crystal field splitting. This requires a non-zero orbital moment, excluding trivalent lanthanum as an anisotropy increasing ion. Similarly, cerium often appears tetravalent and, thus, as a non-magnetic ion or it appears mixed tetravalent and trivalent which has more complicated consequences, see for example reference [3] and reference [4] and the references therein. The goal of this research is to examine the possibility of making useful “gap magnets” using the most plentiful of the rare earth elements, lanthanum and cerium. For many applications a magnet with an energy product, BH , between the best Alnico ($BH \sim 10$ MG·Oe) and sintered SmCo_x magnets ($BH \sim 22$ MG·Oe) would provide engineers with additional product design options [5]. Currently

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there are no commercial magnets in this energy gap. In most rare earth ores mined around the world (such as the bastnäs site mine in Mountain Pass CA), lanthanum and cerium comprise about 70% of the available rare earths (Ce~40%, La~30%), followed by Nd~15%, Pr~5%, Sm~2%, with small (~1%) amounts of the heavier rare earths such as Dy, Eu, and Tb [6]. A gap magnet that utilizes large amounts of lanthanum and cerium would improve the overall economics of the mine, since at present there are not enough commercial uses for all of the lanthanum and cerium that is currently mined [7].

Despite the aforementioned drawbacks concerning light rare earth utilization in magnets, past efforts to gain anisotropy in cerium and lanthanum containing intermetallic compounds through other substitutions have been successful. The efforts of Fujii *et al.*, reference [8], in 1982 showed that titanium substitution in small amounts was capable of greatly increasing the magnetocrystalline anisotropy of the parent compound $\text{Ce}_2\text{Co}_{17}$. The result of this substitution was shown by Fujii *et al.* to be compounds nearly of the form $\text{Ce}_2\text{Co}_{16}\text{Ti}$ whose crystallographic structure was a hexagonal one very much like that of $\text{Th}_2\text{Ni}_{17}$ (Space Group 194: $P6_3/mmc$), see fig. 1(b). This was only in slight contrast to the parent compound structure of $\text{Ce}_2\text{Co}_{17}$, which happened to mimic the very similar rhombohedral model of $\text{Th}_2\text{Zn}_{17}$ (Space Group 166: $R-3m$) when cooled relatively slowly but shows a preference for the hexagonal $\text{Th}_2\text{Ni}_{17}$ structure when splat-cooled [9]. The aforementioned favorable anisotropy field, H_a , increase was seen in reference [8] to come at the cost of reducing the Curie temperature, T_C , but not to unadaptably low levels for electric motors. The saturation magnetization, $4\pi M_s$, in the $\text{Ce}_2\text{Co}_{16}\text{Ti}$ compound is, however, only ≈ 7.3 kG as measured in this work, significantly less than the value of ≈ 11.4 kG for $\text{Ce}_2\text{Co}_{17}$ [10]. The magnitude of this quantity was not originally reported for $\text{Ce}_2\text{Co}_{16}\text{Ti}$ in reference [8] but the same authors report a similar value (≈ 8.5 kG) instead for zirconium substitution, i.e. $\text{Ce}_2\text{Co}_{16}\text{Zr}$, in reference [11].

A later study by Liu *et al.*, reference [12], related the discovery that small amounts of titanium can stabilize the rhombohedral $\text{Th}_2\text{Zn}_{17}$ structure type with the cerium replaced by lanthanum, namely the compound $\text{La}_2\text{Co}_{16}\text{Ti}$. This revelation is especially interesting as the compound $\text{La}_2\text{Co}_{17}$ is claimed by Liu *et al.* to be unstable. The saturation magnetization in those $\text{La}_2\text{Co}_{16}\text{Ti}$ compounds is seen to be as much as 25% larger than M_s in the aforementioned $\text{Ce}_2\text{Co}_{16}\text{Ti}$ compound. H_a is, however, about 4 times smaller for the $\text{La}_2\text{Co}_{16}\text{Ti}$ compound than for the $\text{Ce}_2\text{Co}_{16}\text{Ti}$ compound. The Curie temperatures for both of these compounds are high enough, >400 °C, for use in electric motors. The goal of the present work is to study the compound $\text{La}_x\text{Ce}_{2-x}\text{Co}_{16}\text{Ti}$ as x is increased from 0 to 2 in an effort to increase H_a while not too severely reducing M_s . The hope here is that somewhere in between $x=0$ and $x=2$ there is permanent magnet with a sufficiently high moment and anisotropy that can meet the needs of industry and, thus, allow the use of lanthanum and cerium in an industrial magnet.

Figure 1: (a) Background subtracted powder x-ray diffraction pattern in arbitrary units compared with refinement. (b) The relationship between the hexagonal $\text{Th}_2\text{Ni}_{17}$ and the rhombohedral $\text{Th}_2\text{Zn}_{17}$ structure types. The shaded boxes highlight structural motifs. The rhombohedral structure is formed by the insertion of an additional (blue) slab between the yellow slabs that make up the hexagonal structure. The transition metal sites that form the “dumbbells” are shown in black.

Figure 2: (a) Experimentally measured values of the Curie temperatures as a function of x . The inset shows two apparent weight vs. temperature curves in a DTA for determination of Curie temperatures. (b) The spin-polarized densities of states for $\text{LaCeCo}_{16}\text{Ti}$ showing contributions from different sites. The positive and negative DOS values correspond to spin-up and spin-down channels respectively and the Fermi level is set to zero.

2. Material and Methods

The two pertinent crystal structures are remarkably similar and are illustrated in fig. 1(b). The closest Co-Co distance in both the hexagonal and rhombohedral structures, the so-called “dumbbell” site, is illustrated by a black line between black metal atoms. The claim in reference [8] is that the hexagonal structure, with a smaller unit cell, is favored once titanium is substituted to make $\text{Ce}_2\text{Co}_{16}\text{Ti}$. Those authors used a time consuming, two-step process for their sample synthesis with the last and shortest step being a 10 day anneal at 1000 °C. In an effort to produce samples via a more commercially viable route we used a single-step synthesis at 1000 °C for 200 hours followed by fast quenching in water. Prior to annealing, stoichiometric proportions of high purity (99.95+ %) elemental metals were arc-melted together and sealed in evacuated silica tubes. Nominal starting compositions were determined for $\text{La}_x\text{Ce}_{2-x}\text{Co}_{16}\text{Ti}$ by varying x from 0 to 2 in increments of 0.25 ($x=0.0, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75, 2.0$). Samples created in this way were named “Batch A” and all data in the main portion of this document are on “Batch A” samples. A summary of some results on “Batch A” samples can be found in the appendix in table A.4. Some results on samples created through different annealing schemes are also discussed in the appendix. The ingots that resulted were polished and subjected to compositional analysis after annealing using a Hitachi TM-3000 electron microscope equipped with a Bruker Quantax 70 energy dispersive spectroscopy (EDS) X-ray system. These experiments verified that all samples were single phase with compositions corresponding to the nominal starting values. Powder x-ray diffraction experiments (PXRD) were performed on ground samples. The instrument used for PXRD was a PANalytical XPert Pro diffractometer ($\text{Cu } K_{\alpha 1}, 1.5406 \text{ \AA}$). The background was large due to cobalt fluorescence. Count times had to be long as a result, 10 hours, and the resulting patterns were only good enough to distinguish between the $\text{Th}_2\text{Ni}_{17}$ and $\text{Th}_2\text{Zn}_{17}$ structures and to accurately determine the lattice parameters but not good enough to distinguish between the small intensity differences that would be associated with a titanium site preference. An example of one refinement can be seen in fig. 1(a). Our results show that the rhombohedral structure is preferred for samples manufactured in the way described above, but not completely. A preference for the hexagonal structure for $x=0.25$ is actually observed for these samples but a preference for the rhombohedral structure can also be observed for the same composition if annealing conditions are altered. The lattice parameters as a function of x are displayed in the appendix for the samples associated with the magnetic measurements

here, i.e. the “Batch A” samples. The sensitivity of the lattice parameters and of the preferred structural type on annealing conditions is also discussed in the appendix. The magnetic properties discussed here appear to be relatively insensitive to slight lattice parameter variation or changes in preferred structure type. For consistency’s sake, however, all magnetic data discussed in the main portion of the document are for samples formed under the precise conditions described above for “Batch A” samples.

The saturation magnetization was measured for all “Batch A” samples at 300 K. These measurements were performed in a Quantum Design MPMS in applied external fields, H_{ext} , up to 60 kOe. As the samples were polycrystalline, finely-ground powders aligned in epoxy that cured in an external magnetic field were required for hard-axis measurements. The saturation magnetization, M_s , could be determined from easy axis measurements on these same samples. For lower values of x polycrystalline chunks of material were also used to determine M_s since their anisotropy fields were small enough to completely overcome in the MPMS. The error associated with these points was determined by the spread of M_s measured in multiple powder samples aligned in different applied fields and with polycrystalline chunks when possible. The epoxy aligned samples were also rotated so that H_{ext} was perpendicular to the easy axes and the magnetization was measured. The results are the hard axis $M(H)$ curves. As curvature in a hard axis curve of this type can be associated either with misalignment or with a non-zero K_2 in the expression for the magnetocrystalline anisotropy, namely $E_{mca} = K_1 \sin^2(\theta) + K_2 \sin^4(\theta)$ with θ being the angle of the magnetization with respect to the easy axis [13], the method of alignment becomes important to reduce any curvature due to misalignment. Separate samples of fixed composition in gelcaps with epoxy were allowed to cure at varying magnetic fields in a Quantum Design PPMS to test the dependence of this curvature on alignment field. The field was turned on while the epoxy was still viscous and increased to its final value at a rate of 100 Oe/s. Well separated needle-like structures can form in the epoxy as a result of a large enough applied field. The assumption is, since the epoxy requires 60 min or so to harden, that the particles that form the needle-like structures have had ample time to rotate their easy axes to align with the applied field before being frozen into the solid epoxy. This leaves inter-particle interactions as the main cause of poorly aligned samples, a mechanism that appears to be defeatable by applying higher alignment fields since this is observed to cause the needle like structures to become better separated spatially. Not surprisingly, as the alignment field is increased the curvature in these hard axis measurements decreases and approaches something reproducible for a sample of fixed composition aligned at any field above 30 kOe or so. This corresponds to the largest possible ratio of K_1/K_2 as determined from the fits described below. Perhaps surprising is the fact that fields above a sample’s anisotropy field were just as effective in reducing this curvature as fields just below it, an observation likely made possible by the fact that the alignment field is initially increased from 0 to its final value, making the history of the particle orientations important. As a result, an alignment field well beyond the initial observations of curvature reproducibility for all values of x was chosen for the hard axis measurements; powder samples were aligned in the way described above at 50 kOe. The alignment quality was also checked with x-ray diffraction. XRD measurements in the range of $10^\circ \leq 2\theta \leq 90^\circ$ off the hardened epoxy surface normal to the applied field show only the (006) peak near 44° . Any curvature in the hard axis $M(H)$ curves is assumed to be due, then, to a non-zero K_2 .

The Curie temperatures, T_C , for all samples were measured using a commercial thermo-gravitational analysis instrument with a small external applied field with non-zero spatial gradient. As a sample goes through T_C the apparent weight changes. T_C was determined by the intersection of the steepest tangent line near the transition with the baseline above the transition. The size of the error was determined as the spread of T_C values determined by making measurements on multiple pieces of sample from a batch and said error was generally larger for the smaller moment samples.

3. Theory

The first principles calculations are carried out within density functional theory (DFT). We use the generalized gradient approximation [14] within the projector augmented wave method [15] as implemented in the Vienna *ab initio* simulation package [16, 17]. An energy cutoff of 400 eV and k space sampling on a $8 \times 8 \times 7$ grid are employed. For the sake of expediency, the calculations of T_C and M_s are done in the hexagonal unit cell of $\text{Ce}_2\text{Co}_{17}$ phase, keeping the structure fixed across substitutions. Although most of

System	M_s (μ_B /f.u.)	$4\pi M_s$ (kG)	ΔE (eV/f.u.)	T_C ($^{\circ}\text{C}$)
Ce ₂ Co ₁₇	23.4	11.06	-3.07	425
Ce ₂ Co ₁₆ Ti	19.1	9.03	-2.22	262
LaCeCo ₁₆ Ti	19.9	9.40	-2.34	293
La ₂ Co ₁₆ Ti	20.7	9.78	-2.52	336

Table 1: Calculated magnetic moments, M_s , magnetic energy ($\Delta E = E_{\text{FM}} - E_{\text{NM}}$) and mean-field Curie temperature (T_C) for doped Ce₂Co₁₇ in the hexagonal structure. Lanthanum substitution increases M_s and T_C as expected.

the samples actually crystallize in the rhombohedral unit cell, the hexagonal option was chosen to reduce computation time with the assumption that either choice would yield essentially identical results. The titanium atoms are distributed randomly on the cobalt sites for these calculations.

The electronic densities of states in the LaCeCo₁₆Ti phase are plotted in Fig. 2(b). Spin-orbit coupling is not included for the calculations of electronic structure in Fig. 2(b) and the magnetic data in table 1, and thus the moments correspond to the spin only. The magnetic anisotropy energy is calculated using LAPW [18] including spin-orbit coupling within scalar relativistic approximation. As the projected DOS show, the Ce- f states lie just above the Fermi level with the Ce- $f_{\downarrow}$ states partially occupied. Integrating the DOS upto the Fermi level, we find that Ce is in the electron configuration $4f^{15}5d^1$. However, the exchange splitting is small in the d and f orbitals and leads to the spin moments of $-0.7 \mu_B$ per Ce. The La- f states are about 4 eV above Fermi level and have negligible exchange splitting. The magnetic moments arise from the $5d^1$ electrons. As expected the DOS near Fermi level is dominated by Co- d states with fully occupied spin-up channel and more than half full spin-down channel. The exchange splitting is about 1 eV at the cobalt sites, but becomes negative when replaced with titanium.

The results of the first-principles calculations are summarized in table 1. The parent system Ce₂Co₁₇ has a spin magnetic moment of $23.4 \mu_B$ /f.u. originating mostly from the Co- d states. The cobalt ions contribute on average $1.5 \mu_B$ per atom, while cerium moments are about $-0.7 \mu_B$. Substituting the cerium atoms by lanthanum improves the spin moments slightly by reducing the negative contribution at the Ce sites to $-0.3 \mu_B$. Titanium substitution at the cobalt sites has a larger impact on the total magnetic moments, since titanium is polarized in the opposite direction, with $-0.7 \mu_B$. The Curie temperatures are calculated using the mean field approximation as one third of the magnetic energy, $E_{\text{FM}} - E_{\text{NM}}$, as the antiferromagnetic configurations are found to be unstable in this system. Though the values for T_C in table 1 disagree with experiment, the trend with changing x is consistent.

We have also conducted calculations of the magnetocrystalline anisotropy energy for the parent compound Ce₂Co₁₇ as well as the substituted compound LaCeCo₁₆Ti, using the all-electron density functional theory code WIEN2K. The calculations of K_1 are done in the rhombohedral unit cell for Ce₂Co₁₇ and the hexagonal unit cell for LaCeCo₁₆Ti. Consistent with experiment, we find a substantially higher anisotropy for the substituted compound, with the calculated first anisotropy constant K_1 increasing from 2.2×10^6 erg/cm³ for the parent compound to 5.6×10^6 erg/cm³ for the substituted compound. This latter result is in good agreement with the experiments here.

4. Results and Discussion

Representative apparent weight vs. temperature curves are plotted in the inset of fig. 2(a) normalized by their respective maximum values between 300 $^{\circ}\text{C}$ and 700 $^{\circ}\text{C}$. The x dependence of T_C as measured here is plotted in fig. 2(a). All the values of T_C measured are high enough for use in electric motor applications, the lowest being the $x=0$ sample which has a T_C of 450 $^{\circ}\text{C}$ as measured in this work. This value is in contrast to the value of 650 $^{\circ}\text{C}$ reported for the $x=0$ samples of Fujii *et al.* in reference [8]. One possible explanation for this discrepancy is that T_C may be sensitive to the types of slight structural differences that result from different annealing conditions, a subject that is further addressed but not fully resolved in the appendix. It is worth noting here, however, that we were unable to observe such a difference between samples of batches

Figure 3: (a) The leftmost axis shows saturation magnetization as a function of x at 300 K in units of kilogauss. The rightmost axis displays the anisotropy field determined from the equation $H_a = (2K_1 + 4K_2)/M_s$. (b) Fits of the magnetization perpendicular to the crystalline c axis vs. the external applied magnetic field in polycrystalline samples field-aligned as described in the text for determination of K_1 and K_2 at 300 K.

with $x=0$ annealed in different ways. For $x=2$, the value reported here agrees well with that reported by Liu *et al.* in reference [12]. It is also worth noting here that a differential scanning calorimetry (DSC) measurement is simultaneously performed during these TGA measurements and any sign of unusual entropy changes, for example that due to an order-disorder transition, unassociated with the ferromagnetic transition happened to be unobservable for all samples.

The results of magnetization measurements are displayed in fig. 3. The leftmost axis of fig. 3(a) shows the saturation magnetization determined from easy axis field sweeps (not shown). The general trend is an increasing one with increasing x . Figure 3(b) shows hard axis field sweeps. The open symbols represent the actual data points and the solid lines represent fits. A strictly linear fit of $M(H)$ was unacceptable, especially as x approaches 0, in contrast to the claims of references [8, 12]; as a result we required both K_1 and K_2 for our curve fitting. Our hard axis $M(H)$ curve fitting also made use of a demagnetization factor. Since the demagnetization factor in the easy direction is apparently small, an approximation useful for fitting the hard axis curves is that these needle like structures contain well isolated, spheroidal particles; then the relevant demagnetization factor for the hard direction will be $1/2$. Then, the hard axis curves could be fit to eq. (1) with the dependent and independent axes inverted, in the vane of reference [19], using the M_s values determined from fig. 3(a). The magnetization was fit from 0 to $9M_s/10$. The region close to M_s was avoided as the magnetization there is not smooth in this simple model, see reference [20] for more details.

$$H_{\text{ext}} = \left(\frac{2K_1}{M_s} + \frac{4\pi M_s}{2} \right) \cdot \left(\frac{M}{M_s} \right) + \frac{4K_2}{M_s} \cdot \left(\frac{M}{M_s} \right)^3 \quad (1)$$

The anisotropy field, understood as the field required to saturate a hard axis isothermal magnetization curve, is plotted on the rightmost axis of fig. 3(a) and was calculated using the equation $H_a = (2K_1 + 4K_2)/M_s$. The general trend with x is opposite that of M_s . Our theoretical calculations support these observations. According to the calculations, the cerium and lanthanum spin moments are found to be antiparallel to the cobalt moments, but the lanthanum moments are weaker on account of the empty La- f orbitals. This leads to the increase in overall magnetic moment upon lanthanum substitution. However, this also reduces the magnetic anisotropy energy of the system as the contribution from the La- f states are absent, which explains the trends observed in fig. 3.

5. Conclusions

We have studied the structure and magnetism in $\text{La}_x\text{Ce}_{2-x}\text{Co}_{16}\text{Ti}$ as x is varied from 0 to 2. For certain x , the lattice parameters and structure type are seen to be dependent on thermal processing, but with little associated change in the magnetic behavior. We find that replacing one half of the lanthanum in $\text{La}_2\text{Co}_{16}\text{Ti}$ with cerium increases the anisotropy field by a factor of 2 with only a 5% decrease in saturation magnetization. The theoretical maximum energy products can be calculated from $(B \cdot H)_{\max} = (4\pi M_s)^2/4$ [19] and are in the range of the so-called “gap magnets” [5]. This term refers to magnets with energy products greater than that of alnico and less than that of samarium-cobalt magnets. There is a great economic need for these magnets for some applications where the cost and performance of samarium-cobalt magnets is excessive. As lanthanum and cerium are rare earth elements with a current need for monetization, the $\text{La}_x\text{Ce}_{2-x}\text{Co}_{16}\text{Ti}$ system may prove more useful and cost effective for the manufacture of processed, multi-domain magnets than samarium-cobalt magnets in some cases and perhaps help improve the economics of US rare earth mining. In fact, the small decrease in M_s with decreasing x and sharply increasing H_a with decreasing x observed in this work is a promising observation when one considers what the energy products might look like as a function of x at elevated temperatures in multi-domain magnets made from $\text{La}_x\text{Ce}_{2-x}\text{Co}_{16}\text{Ti}$. One might expect the new compounds synthesized here, those with intermediate x , to out-perform the $x=2$ end-member in electric motor applications where the total magnetic moment for an $x=2$ magnet might decrease more drastically at elevated temperature than it would in the case of the intermediate values of x which have larger anisotropy energy and, thus, may be more resilient at elevated temperatures. The extremely high anisotropy field for $x=0$ may prove unnecessarily large and the intermediate compounds could outperform that end-member as well, assuming the aforementioned $x=0$ anisotropy turns out to be needlessly excessive, since they have larger saturation magnetizations. This is a highly speculative line of thought, however, and experiments on multi-domain samples to determine coercivities as a function of x is a promising future line of research.

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Appendix A. Lattice Parameters and Additional Annealing

The samples whose magnetic data is reported in the main sections of this document were synthesized via a one-step annealing process. After arc-melting, ingots were sealed in silica tubes, annealed at 1000 °C for 200 hours and quenched in water. These samples are referred to as “Batch A”. The lattice parameters as a function of x for “Batch A” samples are displayed in fig. A.4(a,b). The green and black data points correspond to Rietveld refinements in the hexagonal and rhombohedral models, respectively. All refinements were performed with the FullProf software package [21]. Results of refinements from both structures are displayed together to emphasize the insignificance of the structure model choice on the lattice parameters that result from Rietveld refinements. For the hexagonal model, the c lattice parameter is multiplied by 3/2 so the result may be plotted with its rhombohedral counterpart. The lattice parameters reported for the samples of Liu *et al.* [12] and Fujii *et al.* [8] are also displayed. Agreement with Liu *et al.* is excellent for the $x=2$ case. There is disagreement with Fujii *et al.* for the $x=0$ case, however. Both the a and c lattice parameters are seen to differ quite significantly and the choice of structure model disagrees as well. We get a preference for the rhombohedral structure for our “Batch A” samples as opposed to the hexagonal preference reported in reference [8]. The structural model preference is easy to determine. The background subtracted PXRD data along with fits in both models for small x is shown in fig. A.4(c). Clearly, for “Batch A” samples the rhombohedral (0 2 4) peak at $2\theta=38.15^\circ$ is prominent in the $x=0$ and $x=0.5$ samples while

Figure A.4: (a) a lattice parameter and (b) c lattice parameter as a function of x for “Batch A” samples. These are the samples used for the magnetic measurements in the main sections of the document that refers here as supplemental material. The green and black solid data symbols refer to fits in the hexagonal and rhombohedral structures referred to in the main sections of the document respectively. The open data symbols represent the values reported by reference [12] and reference [8]. (c) Actual fits of background subtracted PXRD data for $x=0$, $x=0.25$ and $x=0.5$ samples from “Batch A”. The preference, with the sole exception of the $x=0.25$ case, for the rhombohedral structure model is apparent for this sample batch.

the hexagonal (203) peak at $2\theta=41.22^\circ$ is prominent in the $x=0.25$ case. The Co-Co distances between the atoms of the dumbbell site are also more reasonable after refinement of the atom positions in the preferred model in all cases. In fact, for larger x only the rhombohedral model appears to be appropriate as the Co-Co distances in the dumbbell site quickly become unreasonably small after refinements of the atomic positions in the hexagonal $\text{Th}_2\text{Ni}_{17}$ model. For example, we get a distance of $2.28 \text{ \AA}$ in the rhombohedral model for the $x=0.75$ sample in “Batch A” and only $1.32 \text{ \AA}$ for the same sample refined in the hexagonal model. These numbers can be compared to the value of $2.35 \text{ \AA}$ for the dumbbell site distance in $\text{Sm}_2\text{Co}_{17}$ given in reference [22]. The R values associated with the fits are displayed in table A.2 for comparison purposes.

It may strike the reader as interesting that the lattice parameter data points in fig. A.4 corresponding to the sample of Fujii *et al.* appear to lie nicely on a line formed by our “Batch A” samples for $x \geq 0.75$. This observation spurred further investigation of annealing effects on the structure. There is one notable difference between the $x=0$ samples of Fujii *et al.* and ours from “Batch A”; Fujii *et al.* annealed samples for at least a month. To see what the general effect of further annealing on the lattice parameters might be, two more batches were synthesized, “Batch B” and “Batch C”. These were subjected to the same first treatment as the “Batch A” samples and subsequently subjected to one additional step. The details are displayed in table A.3. All values reported in the main sections of this document are also listed for convenience in table A.4. The “Batch B” samples were small x value samples. For the “Batch B” $x=0$ sample it became impossible from the refinements to determine which structural model was preferred. The a lattice parameter also nearly matches that of Fujii *et al.* for this twice annealed “Batch B” sample, making a plot like fig. A.4(a) much more Vegard-like. There is not much change for the c lattice parameter. The other two “Batch B” samples appear to prefer the hexagonal model. It is worth mentioning here that the characteristic PXRD peak width is comparable to that shown in fig. A.4 for all samples of all batches and is narrow enough to assume that the results represent either one phase or two very similar phases with nearly identical lattice parameters. The “Batch C” samples were chosen to cover the whole range of x . Again, as in the “Batch B” case, it is impossible for refinements of the $x=0$, “Batch C” data to determine a structure type

x	R _p ; R _{wp} in $R-3m$	R _p ; R _{wp} in $P6_3/mmc$
0	4.33; 5.47	5.84; 8.03
0.25	7.17; 9.40	6.85; 8.82
0.5	4.18; 5.37	4.67; 6.11
0.75	5.69; 7.13	8.22; 11.1
1	4.32; 5.46	5.60; 7.72
1.25	4.03; 5.09	5.55; 8.01
1.5	5.64; 7.14	8.35; 11.7
1.75	2.20; 2.81	2.49; 3.38
2	4.31; 5.45	5.95; 8.19

Table A.2: Agreement factors associated with PXRD refinements in both model crystal structures for each sample of “Batch A”

preference. The change in the a lattice parameter here is similar to the “Batch B” case. There is essentially no observed change for the $x=1$ and $x=2$ “Batch C” samples when compared to the “Batch A” case. It becomes apparent from these preliminary observations that the lattice parameters and preferred structure type are extremely sensitive to formation conditions. There is, however, an overall increasing trend in unit cell volume with increasing x , a fact attributable to the size difference of lanthanum and cerium. However, for our samples this trend is not monotonic. Whether extremely long annealing times might produce more Vegard-like results for fig. A.4(b) is unknown to us at this time but seems possible upon consideration of the general trend towards volume contraction for “Batch B” and when also considering the data of Fujii *et al.*

Cursory measurements of M_s , H_a , and T_C were also performed on the “Batch B” and “Batch C” samples. For “Batch B” and “Batch C” samples the alignment process used to determine H_a was not nearly as time consuming or careful as the 50 kOe method described above. Samples were aligned in epoxy on top of strong permanent magnets rather than inside a QD PPMS at high field. The resulting hard axis $M(H)$ curves for these samples had some curvature due to poor alignment, evidenced directly by XRD patterns that show less relative enhancement of the (006) peak when compared to the “Batch A” samples. However, fits of hard axis $M(H)$ curves on “Batch B” and “Batch C” samples aligned on top of permanent magnets give values of H_a within 10% of the “Batch A” counterparts, despite giving smaller K_1/K_2 ratios that result presumably because of poorer alignment. The M_s values determined from easy axis curves of “Batch B” and “Batch C” samples aligned on top of permanent magnets is within 5% of the “Batch A” counterparts. These observations, along with the inability to observe a trend in T_C differences between batches using the method described in the main sections of this document, is reasonable evidence that though the structure seems sensitive to annealing conditions the magnetic properties are, in contrast, relatively insensitive. Due to preliminary observations of this nature only the “Batch A” samples were studied carefully.

Sample Name	Heat Treatment; Step 1	Heat Treatment; Step 2	Best Model	a (Å)	c (Å)
Ce ₂ Co ₁₆ Ti→B	1000 °C for 200 hours	1100 °C for 100 hours	H/R	8.3943(3)/8.3937(3)	8.2100(5)/12.3159(7)
La _{0.25} Ce _{1.75} Co ₁₆ Ti→B	1000 °C for 200 hours	1100 °C for 100 hours	H	8.3944(4)	8.2221(6)
La _{0.5} Ce _{1.5} Co ₁₆ Ti→B	1000 °C for 200 hours	1100 °C for 100 hours	H	8.4069(5)	8.2270(6)
Ce ₂ Co ₁₆ Ti→C	1000 °C for 200 hours	1100 °C for 200 hours	H/R	8.3973(7)/8.3972(6)	8.1985(9)/12.2999(11)
LaCeCo ₁₆ Ti→C	1000 °C for 200 hours	1100 °C for 200 hours	R	8.4567(4)	12.3190(7)
La ₂ Co ₁₆ Ti→C	1000 °C for 200 hours	1100 °C for 200 hours	R	8.5198(3)	12.3582(6)

Table A.3: Effects of further annealing, i.e. “Step 2”, showing the sensitivity for small x of the lattice parameters in La _{x} Ce_{2- x} Co₁₆Ti to heat treatment conditions. The magnetic properties for these further annealed samples were not observably changed. The letters to the right of the chemical formula in the “sample name” column indicate arbitrary batch labels.

x	T_C (°C)	Best Model	a (Å)	c (Å)	$4\pi M_s$ (kG)	K_1 (10^6 erg/cm ³)	K_2 (10^6 erg/cm ³)	H_a (kOe)
0	445(50)	R	8.4566(4)	12.3159(6)	7.35(25)	12.98(22)	2.99(19)	64.8
0.25	585(30)	H	8.3986(5)	8.2184(6)	8.75(30)	7.79(28)	3.48(24)	42.4
0.5	660(20)	R	8.4268(4)	12.3201(8)	9.00(25)	8.21(35)	3.38(30)	41.8
0.75	640(20)	R	8.4462(4)	12.3114(6)	9.20(40)	5.17(34)	4.15(28)	36.8
1	630(30)	R	8.4566(4)	12.3159(6)	9.20(30)	5.74(24)	2.64(19)	30.1
1.25	610(20)	R	8.4897(3)	12.3281(6)	8.95(20)	5.15(23)	2.73(18)	29.8
1.5	645(20)	R	8.4916(3)	12.3427(6)	9.50(20)	4.41(25)	2.20(19)	23.3
1.75	655(20)	R	8.5109(5)	12.3503(9)	9.80(30)	4.87(17)	1.65(14)	20.9
2	650(25)	R	8.5212(3)	12.3593(5)	9.50(20)	2.60(21)	1.77(16)	16.2

Table A.4: Summary of magnetic and structural properties of $\text{La}_x\text{Ce}_{2-x}\text{Co}_{16}\text{Ti}$ created by reaction in evacuated quartz tubes for 200 hours at 1000 °C (“Batch A” samples). The “R” structural model corresponds to the $\text{Th}_2\text{Zn}_{17}$ rhombohedral structure type. The “H” structural model corresponds to the $\text{Th}_2\text{Ni}_{17}$ hexagonal structure type. H_a is calculated from the equation $(2K_1 + 4K_2)/M_s$ and is understood as the maximum external applied field required to saturate the magnetization.

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