On the magnetic behavior of polycrystalline RBaCo$_2$O$_{5+\delta}$ synthesized by solid state and wet chemical routes

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Abstract. In this paper, polycrystalline RBaCo$_2$O$_{5+\delta}$ (R = La, Y, Eu) samples were obtained through solid state reaction and polymeric precursor method. The crystalline quality of the samples was carefully evaluated by means of X-ray diffraction. Depending on the R cation, the main phases were characterized in a tetragonal $P4/mmm$, orthorhombic $Pmmm$ or trigonal $R-3c$ structure. The oxygen content, being a fundamental parameter in the studied system, was determined by iodometric titration. While no stoichiometric oxygen content was determined, the value of $\delta$ ended up being close to 0.5 for all the samples studied. VSM magnetization measurements were taken according to the zero field cooling protocol. The $M(T)$ curves clearly shows the characteristic magnetic behavior of the cobaltate with stoichiometry 112. The temperature at which the paramagnetic-ferromagnetic-antiferromagnetic transition occurs varies with the cation R.

1. Introduction

The RBaCo$_2$O$_{5+\delta}$ cobaltates are transition metal oxides with perovskite-like structure, which exhibit a variety of fascinating physical properties due to the strong interplay between spin, charge, orbital and lattice degrees of freedom[1]. Such cobaltates can content oxygen vacancies, which gives rise to variable ratios of Co$^{2+}$, Co$^{3+}$ and Co$^{4+}$ species. These species possess three possible spin states, namely low-spin (LS) state, intermediate-spin (IS) state and the high-spin (HS) state, which have a strong influence on the electrical and magnetic properties of the system [2]. Such spin states originate from a close competition between the atomic parameter Hund’s exchange energy and the crystal field energy. A small variation in temperature, pressure or magnetic field can produce a drastic change in the physical properties of these complex oxides [3]. The structural degree of freedom of this family of compounds provides a suitable playground to explore the interrelation between electronic, magnetic and structural properties. The crystal structure of these oxides can be described as an ordered sequence of [CoO$_2$]-[BaO]-[CoO$_2$]-[LnO$_x$] layers along the c-axis, where oxygen vacancies exist in the lanthanide layer. The ideal crystallographic description consists of layers of CoO$_6$ octahedra along the (a,c)-planes. These layers are interconnected by two-leg ladders along the $a$-direction of CoO$_2$ pyramids. In between these ladders, the six-sided tunnels are occupied by Ln$^{3+}$ cations [4]. The
structure described above is very flexible i.e. sensitive to variations of the oxygen content and size of the R$^{3+}$ cation so that long range order superstructures or even local distortions may be obtained, leading to dramatic variations of the magnetic properties from one sample to the other. Cobaltates exhibit successive paramagnetic-ferromagnetic-antiferromagnetic (PM-FM-AFM) transitions within a temperature range between 200 K and 300 K. Moreover, these compounds exhibit an insulator-metal transition in the temperature range between 300 K and 400 K [4]. The understanding of magnetic and electrical phases of R$\text{BaCo}_2\text{O}_{5.5}$ is a matter of strong debate. For instance, Taskin et al. [5] studied the Gd compound. They interpreted the successive PM-FM-AFM transitions based on a magnetic structure built up of $S=1$ Co$^{3+}$ cations separated by non-magnetic $S=0$ Co$^{3+}$ cations. The presence of LS Co$^{3+}$ ion ($S=0$) implies that the Co ion should be in an octahedral site. However, an orthorhombic or a tetragonal distortion would destabilize the $S=0$ state due to the gain in crystal field and lowering of the electron-electron repulsion. On the other hand, Plakhty et al. [6] have studied the Tb-based compound and proposed a ferromagnetic structure at 260 K and two antiferromagnetic structures at 230 and 100 K, respectively.

Although the physical method known as solid state reaction has been extensively used in the synthesis of transitions metal oxides, the ordering of the cations in the form of alternating layers is rather difficult to achieve using this route. In order to favors the ordering of the R$^{3+}$ and Ba$^{2+}$ cations, the synthesis temperature must be as low as possible, and consequently a soft-chemistry synthesis route should be used instead since it allows a high reactivity at relatively low temperature [7]. Chemicals methods such as the polymeric precursor method or Pechini [8] route, are suitable for obtaining high-quality ceramics oxides at low cost and in a highly controlled way. The synthesis of R$\text{BaCo}_2\text{O}_{5+\delta}$ compounds with layered structures containing trivalent R$^{3+}$ and Ba$^{2+}$ cations distributions is complicated due to the differences in their ion sizes that can promote statistical distribution in the lattice [7]. In the present work, results of the structural and magnetic characterizations of R$\text{BaCo}_2\text{O}_{5+\delta}$ (R= Eu, La, Y) cobaltates are reported. Special attention is devoted to the discussion of the synthesis of these compounds via soft chemistry methods as reports on these alternative synthesis methods are rather scarce.

2. Experiment.

A first set of polycrystalline R$\text{BaCo}_2\text{O}_{5+\delta}$ (R= Eu, La, Y) samples was obtained by standard solid state reaction. Stoichiometric quantities of Y$_2$O$_3$, La$_2$O$_3$, BaCO$_3$, Eu$_2$O$_3$ and Co$_2$O$_3$ reactants were mixed together and calcined at 1170 K for 12 h to achieve decarbonisation. The resulting powder was slowly heated in air ($\sim$ 5°C/min) up to a temperature of 1270 K and maintained there for 24 h. A second set of powders was prepared based on the classic Pechini method using Y(NO$_3$)$_3$·6H$_2$O, Co(NO$_3$)$_2$·6H$_2$O, Ba(NO$_3$)$_2$·4H$_2$O, Eu$_2$O$_3$, La$_2$O$_3$ and Eu$_2$O$_3$ as starting precursors. First, precursors of lanthanum or europium were dissolved in nitric acid. Then the other precursors were added and combined with citric acid (CA) or ethylenediaminetetraacetic acid (EDTA). The final solution was heated to 350 K under strong stirring until a homogeneous, translucent (violet colour) solution was obtained. Then, ethylene glycol (EG) was added, and the polymerization process was carried out at 383-393 K under constant stirring until a resin was formed. This resin was heated at 390 K for 5 hours in order to eliminate the H$_2$O traces. Next, the resin was heated in a stepwise process to 520 K, 620 K and 770 K for 5 h, respectively. The solid obtained was ground and annealed in air at 1270 K for 15 hours and then slowly cooled to room temperature. X-ray powder diffraction patterns of the compounds were registered with a Panalytical X’Pert Pro MPD diffractometer using CuKα radiation ($\lambda=0.15418$ nm). Crystallographic parameters were obtained through Rietveld refinement using the FULLPROF package [9]. The oxygen content of the samples was determined by standard iodometric titration. In turn, the magnetic measurements were performed using a vibrating sample magnetometer (VSM) coupled to a PPMS system (Quantum Design). The $ZFC M(T)$ data were recorded in a 100 Oe magnetic field over the temperature range 5-400 K.
3. Results and discussion

Figure 1 shows the XRD pattern of two YBaCo₂O₅₊δ samples obtained by solid state reaction and Pechini method, respectively. The results show that the two methods are able to synthesize high quality YBaCo₂O₅₊δ cobaltate. The Rietveld refinement of the XRD pattern confirm the formation of a single-phase material with tetragonal symmetry and $P4/mmm$ space group. The lattice parameters ended up being $a=3.85$ Å and $c=7.45$ Å at room temperature which are very close to those reported by Akahoshi et al [10]. For the LaBaCo₂O₅₊δ system, the analysis of the XRD results and the definition of a type of structure or superstructure are much more complex. The first structural study of an ordered oxygen deficient perovskite of type LnBaCo₂O₅₊δ was presented for the series Ln = Pr to Ho [11]. Although, the series has been investigated in details for almost all lanthanide elements of the periodic table, interestingly there was no such report on the first member of this series, i.e. for LaBaCo₂O₅. Recently, LaBaCo₂O₅.₅ was reported and characterized by neutron diffraction, electron microscopy and magnetic studies, showing that at room temperature the structure is 112- layered orthorhombic $a_p \times 2a_p \times 2a_p$ supercell with $Pmmm$ space group [12]. In turn, XRD measurements on EuBaCo₂O₅₊δ samples (not shown) show that the compound is characterized in an orthorhombic structure with lattice parameters (obtained by Rietveld analysis) $a=3.92$ Å, $b=3.88$ Å and $c=7.53$ Å ($Pmmm$ space group). This result is very similar to that reported for M.M. Seikh et al. [12]. Indeed, according to E. L. Rautana, et al. [7], the system La-Ba-Co-O can exists in three phases, namely disordered LaₐₓBa₁₋ₓCoO₃, ordered LaBaCo₂O₅₊δ and nanoscale ordered LaBaCo₂O₆. The disordered phase LaₐₓBa₁₋ₓCoO₃, as well as the ordered phase LaBaCo₂O₆ could be defined considering the structural data from the literature with the cubic $Pm-3m$ or rhombohedral $R-3c$ and orthorhombic $Pmmm$ space groups, respectively. The XRD pattern of the nanoscale-ordered LaBaCo₂O₅₊δ is very similar to that observed for the disordered phase and it is indexed as a simple perovskite using the same space group and the same structural parameters. According to XRD measurements and Rietveld refinements, the LaBaCo₂O₅₊δ samples obtained by Pechini method with citric acid (La-PC) and EDTA (La-PE) have rhombohedral structure and space group $R-3c$, with the lattice parameters $a=5.44$ Å and $c=13.10$ Å. In turn, measurements on samples obtained by solid state reaction (La-SS) show a cubic structure (space group $Pm-3m$). This result excludes the possibility of obtaining a cation ordering between LaO/BaO layers for samples synthesized by this route because the La/Ba ordering involves a slight deformation of the perovskite sublattice with a dilatation of the $a_p$ parameter within the LaO/BaO layers and a compression along the LaO/BaO layers stacking direction. [7]. The main difficulty here is the possibility of obtaining random distribution of the cations Ba²⁺ and La³⁺ because the ionic radii are very close (considering an octahedral environment $r_{Ba}=1.49$ Å, $r_{La}=1.17$ Å and $\Delta r = 0.32$ Å) [15]. However, a better definition of these structures requires the use of more powerful characterization techniques such as neutron diffraction or transmission electron microscopy.

![Fig. 1. XRD patterns of YBaCo₂O₅₊δ samples synthesized by standard solid state reaction (a) and Pechini’s method (b). The Rietveld refinement profiles of the samples are also included and marked by symbols. The solid lines correspond to the experimental data.](image-url)
The lattice parameters of the polycrystalline RBarCo2O5+δ (R= Eu, La, Y) samples synthesized by the two mentioned routes are listed in Table 1. The results allow one to appreciate the effect of the size of the R cations on the structure of the cobaltates. The increasing in the size of the R3+ cation leads to increased lattice parameters and loss of symmetry. This is consistent with the fact that replacement of the cation in the R position by a larger cation provokes an increase in the dimensions of the unit cell. The ionic radii of Y3+, Eu3+, and La3+ cations are 101.9, 106.6 and 116, 0 Å, respectively.

Table 1. Lattice parameters of polycrystalline RBarCo2O5+δ (R= Eu, La, Y) samples obtained by Rietveld refinements. The oxygen content has also been included.

| Sample   | space group | a(Å)   | c(Å)   | χ²  | Rwp | Oxygen (5+δ) |
|----------|-------------|--------|--------|-----|-----|--------------|
| Y-PC     | P4/m       | 3.8443(3) | 7.43974(1) | 3.08 | 15,8 | 5.57         |
| Y-PE     | P4/m       | 3.85593(6) | 7.46365(7) | 2.46 | 13,55 | 5.52       |
| Y-SS     | P4/m       | 3.86549(5) | 7.48284(7) | 2.37 | 12,03 | 5.55       |
| Eu-SS    | Pmmm       | 3.91103(6) | 7.55374(1) | 1.76 | 13,88 | 5.54       |
| Eu-PE    | Pmmm       | 3.92085(8) | 7.57030(3) | 2.54 | 12,73 | 5.52       |
| Eu-PC    | Pmmm       | 3.92101(5) | 7.55558(6) | 2.19 | 12,69 | 5.51       |
| La-PE    | R-3c       | 5.44671(0) | 13.11153(7) | 2.05 | 5.16  | -           |
| La-PC    | R-3c       | 5.44460(7) | 13.09548(0) | 2.27 | 8.55  | -           |

The oxygen content of the different samples is indicated in Table 1. The iodometric tritration analysis shows that the Y and Eu samples have oxygen contents very close to 5.5. This means that practically all the cobalt ions are Co3+. However, for La samples the oxygen determination by iodometric tritration did not yield consistent results. By repeating the iodometric tritration analyzes, the reproducibility of the results ended up being ±0.02, demonstrating that chemical methods (except for La) can be used confidently to determine the oxygen content in the studied cobaltates [16].

Figure 2 shows the dependence of the magnetization on the temperature for RBarCo2O5+δ (R= Eu, La, Y) polycrystalline samples. The Eu-SS sample shows a paramagnetic-antiferromagnetic transition in a narrow temperature window (~40 K) around ~250 K which is typical for this compound. The observed transitions are associated with magnetic ordering of the Co3+ ions. The additional transition observed at ~77 K has been attributed to the presence of ferromagnetism reentrant due to ordering of the ions Eu3+ [17]. Certainly, Eu as well as Gd possess intrinsic magnetic properties which should be separated from those displayed for the cobaltates. In turn, the Y-PC sample features the para-ferro-antiferromagnetic transition on a wider temperature window starting at ~300 K. A similar trend has been observed for Y-cobaltates with δ<0.5 [1]. Hence, the wide para-ferro-antiferromagnetic transition observed for the Y-sample can be associated with oxygen variations. Finally, the La-PE sample exhibits a para-ferro-antiferromagnetic transition in a narrow temperature window around ~200 K (probably associated with a high oxygen content). Interestingly, this sample shows a diamagnetic component at low temperatures which could be assigned to the presence of impurities.

The results achieved are consistent with those reported in the literature for the studied system. Thus, it is concluded that for an oxygen content δ=0.5, the cobalt ions are purely trivalent, with half of cobalt ions in charge ordering). However, δ may vary between 0 and 1, which leads to the mixed valence configurations Co2+/Co3+ and Co3+/Co4+, respectively. Hence, the magnetic response of these cobaltates seems to be dominated mainly by three different ferromagnetic states, depending on the cobalt valence. Thus, for δ<0.5 (Co3+) the ferromagnetic state could be called FM1, for δ<0.5 (Co2+/Co3+) FM3, and for δ >0.5 (Co3+/Co4+) FM3. It has been demonstrated that the FM state of YBaCo2O5+δ has a Curie temperature, TC, of ~300 K and a transition width of less than 40 K when the oxygen content δ = 0.50 [12]. Nevertheless, when the oxygen deviates from the optimal doping, i.e., when the system is electron-doped (δ < 0.5) or hole-doped (δ > 0.5), the FM phase becomes more stable and the FM-AF transition shifts to lower temperatures [14].
4. Conclusions

Polycrystalline R$\text{BaCo}_2\text{O}_{5+\delta}$ (R=Eu, La, Y) cobaltate were synthesized both by solid state reaction and soft chemistry method. The polymeric precursor route, using citric acid or EDTA as a complexing agent was chosen as chemical method to the synthesis. The XRD analysis showed that the compounds obtained by the two routes were single-phase with no appreciable affectation by foreign phases or impurities. The oxygen content as determined by iodometric titration resulted to be close to the nominal value of 0.5 although deviations were observed for some samples. The non-stoichiometric oxygen content seemed to be related to the size of the cation $\text{R}^{3+}$. The lower oxygen content was obtained for the La-cobaltates. The size of the La ion is larger than the other ones (Y and Eu). The $M(T)$ curves showed para-ferro-antiferromagnetic transitions with Curie temperatures varying according the cation R. In addition, it seemed that the presence of Co$^{3+}$ ions in the lattice affected considerably the ferromagnetic response of the studied cobaltates.

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