



# Study of $\text{YBaCo}_4\text{O}_{7+\delta}$ thin films grown by sputtering technique on (1012)-oriented sapphire substrates

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## ABSTRACT

We report the growth of thin films of the cobaltite  $\text{YBaCo}_4\text{O}_{7+\delta}$  by means of the dc magnetron sputtering technique at high oxygen pressure onto *r* (1012) sapphire substrates. The films were characterized according to their structural, morphological, electrical, magnetic, and optical properties. An analysis of the X-ray diffraction pattern indicates that the films grown on *r*-sapphire substrates are single phase polycrystalline. Despite the high growth temperature (850 °C), no indication of interface reaction (formation of  $\text{BaAlO}_4$  or  $\text{Y}_2\text{O}_3$ ) is detected. Measurements of resistivity as a function of temperature reveal a semiconductor-like character of the grown films. No indication of possible transitions is observed in the temperature range 50–300 K. The electronic transport mechanism seems to be dominated by Mott variable range hopping (VRH) conduction. Fitting the VRH model to the experimental data allows one to estimate the density of states of the material at the Fermi level  $N(E_F)$ . The resistivity measured in magnetic fields as strong as 5 T increases notably, and positive magnetoresistance values as high as ~60% at 100 K are obtained. Magnetization measurements show well defined hysteresis loops at 300 K and 5 K. Nevertheless, calculated values of the magnetization have ended up being too small for the ferro- or ferrimagnetic states. Raman spectra, in turn, allow one to identify bands associated with vibrating modes of  $\text{CoO}_4$  and  $\text{YO}_6$  in tetrahedral and octahedral configurations, respectively. Additional bands which seem to stem from Co ions in octahedral configuration are also clearly identified. Measurements of transmittance and reflectance show two well defined energy gaps at 3.7 and 2.2 eV.

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## 1. Introduction

Recently, co-based compounds have been researched intensively because of the existence of their intriguing magnetic properties [1,2]. Among these compounds, the double cobaltites  $\text{RBaCo}_4\text{O}_{5+x}$  ( $\text{R} = \text{Y}$  and rare-earth ions,  $0 \leq x \leq 1$ ) have generated great interest among researchers [3]. Their layered structure, diverse phase diagram (including structural and magnetic transitions), giant magnetoresistance, metal-dielectric transitions, and an unusual magnetic behavior, make cobalt-containing compounds extremely attractive from the standpoint of basic sciences [4,5]. Because the crystal field energy differs little from the intra-atomic exchange energies in crystals containing Co ions, these latter may remain in different spin states depending on the actual external conditions (temperature and pressure) [6]. Thus,  $\text{Co}^{3+}$  ions may exist in the low-spin (LS,  $S = 0$   $t_{2g}^6 e_g^0$ ), intermediate-spin (IS,  $S = 1$   $t_{2g}^5 e_g^1$ ), and high-spin (HS,  $S = 2$   $t_{2g}^4 e_g^2$ ) states. It is precisely the different spin states of Co ions and the layered 2D structure of the cobaltites which

account for the rich diversity of properties of this class of compounds [6]. In spite of these basic physical aspects, the technical aspects of these cobaltites should not be overlooked. Certainly, the high ionic and electronic conductivity, the catalytic and electrocatalytic properties of cobalt-containing compounds make them promising material for the development of electrochemical devices such as cathodes in solid-state fuel cells, membranes for oxygen separation, and various sensors [7]. Therefore, the search for Co-based materials and the research of their physical and chemical properties becomes a very important topic in condensed matter physics and material science. Among these materials, the cobaltite family  $\text{RBaCo}_4\text{O}_7$  ( $R-114$ ) with  $\text{R} = \text{Y}$ , Ho, Dy, Tb has caused enormous interest in the last few years [8]. It was found that the  $R-114$  compounds are isostructural with the  $\text{Ba}_2\text{Er}_2\text{Zn}_8\text{O}_{13}$  of hexagonal symmetry [9]. Its space group is  $\text{P}6_3\text{mc}$  with  $a = 6.2982 \text{ \AA}$  and  $c = 10.2467 \text{ \AA}$ , and it displays a layered structure, with layers of three  $\text{CoO}_4$  tetrahedra ( $\text{Co}2$ ,  $d_{\text{Co-O}} = 1.9320 \text{ \AA}$ ) alternating with layers of one  $\text{CoO}_4$  tetrahedron ( $\text{Co}1$ ,  $d_{\text{Co-O}} = 1.8760 \text{ \AA}$ ) and one  $\text{YO}_6$  octahedron. This layer houses, in a large void, a Ba cation surrounded by ten neighbors. All the polyhedra share corners to form a three-dimensional network. Incidentally, materials with sublattices composed of a corner-sharing tetrahedral (such as spinels, pyrochlores, or compounds of the

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SrCr<sub>9x</sub>Ga<sub>12-9x</sub>O<sub>19</sub> type) are geometrically frustrated magnets [10,11]. This structural pattern of the corner-sharing 2D CoO<sub>4</sub> tetrahedra in R-114 (the Kagomé lattice), linked by triangular CoO<sub>4</sub> layers along the *c* axis produces a structure similar to that of the pyrochlore. The only difference is that the triangular layers in the pyrochlores are arranged along the [111] direction of the cubic lattice, while in R-114 they are [001]-oriented in the hexagonal lattice [10–13]. On the other hand, it is known that exchange interactions between spins in geometrically frustrated systems are such that (depending on the actual rare-earth species), a rich spectrum of ground states (namely: spin glass, spin liquid, and spin ice) may be observed. This is the case of titanium- or thin-based rare-earth pyrochlores [11]. As to the R-114 compounds, there are some authors whose publications explore the structure and certain electrical and magnetic properties of samples in single crystal and powder forms [8,13–15]. Nevertheless, there are no reports on R-114 compounds in thin film form.

The aim of this work is to present some results concerning the structural, morphological, electrical, magnetic, and optical properties of thin films of the cobaltite YBaCo<sub>4</sub>O<sub>7+δ</sub>. The samples were grown by high-oxygen pressure dc magnetron sputtering on *r* sapphire (Al<sub>2</sub>O<sub>3</sub>) substrates.

## 2. Experiment

The YBaCo<sub>4</sub>O<sub>7+δ</sub> sputter targets were fabricated from stoichiometric mixtures of Y<sub>2</sub>O<sub>3</sub>, Ba(CH<sub>3</sub>COO)<sub>2</sub> and Co<sub>2</sub>O<sub>3</sub> powders. After mixing the constituents thoroughly in an agate mortar, the metal oxide mixture was slowly heated in air (~5 °C/min) up to 1200 °C and calcined for 48 h. The sample was then cooled inside the furnace at an ambient rate. The black single phase YBaCo<sub>4</sub>O<sub>7+δ</sub> powder was grounded and then pressed into pellets (~3 cm in diameter and thickness ~5 mm) which were finally sintered at ~1300 °C for 11 h. The planar targets were mounted on a Cooper holder and the set was then assembled into the sputtering cannon. From these targets, YBaCo<sub>4</sub>O<sub>7+δ</sub> thin films were deposited by dc-sputtering at high oxygen pressure (3.5 × 10<sup>2</sup> Pa) onto (1012)-oriented sapphire substrates at a voltage of 300 V and a current of 100 mA (~30 W). The substrate block temperature was maintained at 850 °C during the deposition. After film deposition, the chamber was flooded with oxygen at a pressure of ~8 × 10<sup>4</sup> Pa and then the samples were cooled down to room temperature. The as-grown YBaCo<sub>4</sub>O<sub>7+δ</sub> layers were characterized after their structural properties using X-ray diffraction (XRD). The X-ray diffraction patterns of the films were registered using a two-circle diffractometer (Panalytical X'Pert Pro) with CuK<sub>α</sub> radiation (λ = 0.15418 nm) for standard θ–2θ scans on symmetric reflections. The microstructure of the films was analyzed by a scanning electron microscope (SEM) operated at 7 kV. An elemental analysis was carried out by means of energy-dispersive X-ray spectroscopy (EDS). Electronic transport measurements were carried out in a four-terminal configuration using an integrated Physical Properties Measurement System (Quantum Design) equipped with a 14 T superconducting magnet. Sensible measurements of magnetization as a function of temperature and field were performed using a Superconducting Quantum Interference Device (Quantum Design) magnetometer. Here, the magnetic field was applied parallel to the film surface (in-plane configuration). The Raman microprobe spectra of YBaCo<sub>4</sub>O<sub>7+δ</sub> films were recorded by employing a JY instrument with 623 nm laser excitation. A UV–Vis spectrophotometer (Perkin–Elmer) equipped with an integrating sphere was employed to measure the optical properties of the films.

## 3. Results and discussion

Results of thermal analysis and coulometric titration, and also the *p*(O<sub>2</sub>)-dependencies of total conductivity and the Seebeck coefficient of single-phase powders of YBaCo<sub>4</sub>O<sub>7+δ</sub> were reported by Tsipis et al. [16]. Here, it was found that heating above 1070–1110 K in air and/or

decreasing oxygen partial pressure resulted in a phase transition accompanied by substantial oxygen losses from the lattice, forming essentially stoichiometric YBaCo<sub>4</sub>O<sub>7</sub>. Additionally, the great affinity between YBaCo<sub>4</sub>O<sub>7</sub> and oxygen has also been firmly established by several research groups [4,16] demonstrating the material large oxidation–reduction capabilities at temperatures near 350 °C. As much as 1 to ~1.5 extra oxygen atoms per unit formula had been added to the material at ambient and high oxygen pressures, respectively. Hence, it was established that transport properties and oxygen content are almost *p*(O<sub>2</sub>)-independent down to a pressure of 1 Pa. In the present work, the YBaCo<sub>4</sub>O<sub>7+δ</sub> films were grown in an oxygen-rich atmosphere (3.5 × 10<sup>2</sup> Pa). This certainly would allow for one to incorporate additional oxygen atoms into the structure. On the other hand, it was mentioned above that the cobaltite films were deposited on *r* (1012) sapphire substrates. The most usual substrate is *c* (0001) sapphire, but it frequently induces the growth of polar layers in functional oxide films with würtzite-like crystal structures [17]. Certainly, polarity surfaces may spontaneously get charged [18]. The subsequent electric field may then affect the growth process and produces the emergence of a higher concentration of defects. The growth polarity has been shown to have a dramatic effect on the ingrown point defects in GaN [19,20]. In *c*-plane GaN, the incorporation of impurities and the formation of native defects are significantly enhanced when the growth is accomplished in the N Polar (as opposed to the Ga polar) direction. Additionally, the distribution of impurities and native defects is highly non-uniform as a function of the distance from the GaN/sapphire interface. On the other hand, on the non-polar *a*-plane GaN, defect distributions are flat and concentrations are similar to the N polar GaN. Thus, in order to overcome the problem, non-polar layers are grown on *r* sapphire, which does not have polar surfaces.

Shown in Fig. 1 is an XRD pattern of a YBaCo<sub>4</sub>O<sub>7+δ</sub> film grown on an *r* (1012) sapphire substrate by high-oxygen pressure dc sputtering. All diffraction peaks in the XRD pattern could be indexed with hexagonal symmetry belonging to the space group P6<sub>3</sub>mc. The results are consistent with the ones reported in Ref. [21] and no phase impurities were found. The appearance of several narrow reflections in the θ–2θ scan without preferred orientation such as (001), (100), etc. suggests that the films grown on *r* (1012) sapphire substrates are single phase polycrystalline. All reflection peaks corresponding to the film on the sapphire substrate were fitted using Gaussian and Lorentzian functions. From the fits of the peak positions, the lattice constants of the unit cell for the grown films were calculated as being *a* = 6.22 Å and *c* = 10.18 Å. The determined values are smaller than those of the bulk material (*a* = 6.2982 Å and *c* = 10.2467 Å), suggesting an amount of excess oxygen incorporated into the YBaCo<sub>4</sub>O<sub>7+δ</sub> lattice. Even though oxygen stoichiometry is beyond our direct

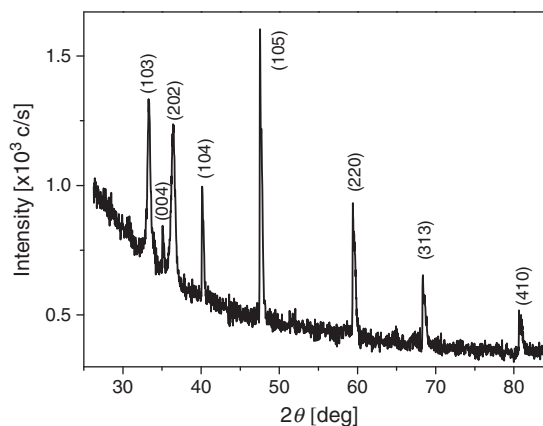


Fig. 1. X-ray diffraction pattern of a YBaCo<sub>4</sub>O<sub>7+δ</sub> film grown on *r* (1012) sapphire substrate by dc magnetron sputtering at 850 °C.

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