

Anomalous Electrical Behavior in Ferromagnetic $\text{La}_{1-x}\text{Ba}_x\text{CoO}_{3-\delta}$ Materials ($0 < x \leq 0.50$)

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Abstract. We prepared in this work $\text{La}_{1-x}\text{Ba}_x\text{CoO}_{3-\delta}$ ($0 < x \leq 0.50$) compounds using the nitrate decomposition method, and focus in the study of the transport properties of the ferromagnetic compounds ($x > 0.15$, $T_c \sim 200$ K) in the temperature range $77 \text{ K} \leq T \leq 300 \text{ K}$.

We find that while for $x < 0.20$ these materials show semiconducting behavior, their electrical conduction being dominated by small-polaron holes, for $x > 0.20$ they show metallic behavior for $T > 100 \text{ K}$, with a transition to semiconducting behavior being observed for $T \leq 100 \text{ K}$. For $x = 0.20$, small changes in the oxygen stoichiometry of the samples - due to slight variations in the thermal treatments - greatly affect the transport properties of the materials that can show either two metal-insulator transitions as the temperature increases or a semiconducting behavior. Very interestingly all these ferromagnetic samples are very sensitive to the polarity of the applied electrical current, and display peculiar "diodic" behaviors.

All these observations are explained on the basis of an inhomogeneous electronic structure in the Ba-doped cobalt perovskites.

1. Introduction

The transition metal oxides with perovskite structure have been extensively studied in the last fifty years because of their unusual and interesting magnetic and electrical properties [1-5] and also due to their high ionic (O^{2-}) conductivity and possible applications in oxygen permeation membranes, fuel cells, etc. [6,7].

In the first of those fields, the cobalt perovskites $\text{La}_{1-x}\text{M}_x\text{CoO}_3$ (M^{2+} = divalent cation) generate special attention in view of how their magnetic and transport properties can be changed and tuned with appropriate doping [8-13]. Even more, the spin transitions at the cobalt ions as a function of temperature and doping introduces additional complexity to the system [9,14-15].

Of all of them, the Sr-doped compounds have been most thoroughly investigated. These studies have shown that while LaCoO_3 shows high resistivity and antiferromagnetic exchange interactions [14], the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$

materials evolve towards a metallic, ferromagnetic behavior as x increases [8], and that this evolution takes place smoothly, a great number of different magnetic and electrical behaviors being present for the different degrees of doping [9,10,14].

On the other hand, less attention has been paid to the Ca- and Ba-doped compounds, although it is also known that their properties show a similar trend as the Sr-doped materials [11-13,16] even if the evolution is affected by the nature of the divalent cation [11].

For example, in the case of the Ba-doped cobaltites although the properties of the end members of the series $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ ($0 < x \leq 0.50$) are well established [17,18], different magnetic and electrical behaviors have been reported for the intermediate degrees of doping [12,16,19].

To get more insight into the behavior of those Ba-doped materials we have synthesized $\text{La}_{1-x}\text{M}_x\text{CoO}_3$

samples with $0 < x \leq 0.50$ and have focused in the transport properties of the ferromagnetic compounds, paying special attention to factors that might affect them: conditions of synthesis, oxygen stoichiometry, etc.

2. Experimental Descriptions

$\text{La}_{1-x}\text{Ba}_x\text{CoO}_{3-\delta}$ materials ($0 \leq x \leq 0.50$) were prepared by decomposition of the corresponding mixture of nitrates following the recommendations given in reference [20]. Stoichiometric amounts of dry La_2O_3 , BaCO_3 and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and SrCO_3 were dissolved in nitric acid 30%. The obtained solution was gently heated so that a slow evaporation of the solvent took place. The resulting mixture of nitrates was decomposed at 600 °C. The so-obtained precursor powders were ground in an agate mortar, pressed into pellets and annealed in air at 1100 °C for periods ranging from 17 to 77 h, the higher the barium content, the longer the annealing time used. After the thermal treatment at high temperature, the samples were slowly cooled to room temperature (rate of cooling < 1 °/min).

In order to characterize the materials, all samples were examined by X-ray powder diffraction with a Siemens D-5000 diffractometer and $\text{Cu}(\text{K}\alpha) = 1.5418$ Å radiation. The morphology and size of the particles were studied in a Scanning Electron Microscope (SEM) Jeol 6400.

Iodometric titrations under an argon atmosphere were carried out to analyze the oxygen content of the samples: the materials were dissolved in acidified KI solutions, and the so-generated I_2 was titrated against a standardized thio-sulphate solution.

The magnetic properties of sintered pellets were studied in a DMS-1660 Vibrating-Sample Magnetometer. Zero-field-cooled (ZFC) and field cooled (FC) magnetic susceptibility data were obtained in a field of 1000 Oe from 77 to 330 K. ZFC magnetization curves $M(H)$ were obtained at 77 K with fields ± 10 kOe.

The electrical resistivity ρ of pressed pellets was studied in the temperature interval $77 \text{ K} \leq T \leq 300 \text{ K}$ in a dc four-probe homemade device. The electrical contacts between the electrodes (copper wires) and the sample were made with silver paint. To eliminate the thermoelectric effect the resistivity data were obtained, as commonly done, by calculating the averages ρ^+ and ρ^- (+ and – stand for the direction of the current) out of 10 values, respectively, and getting average resistance $\rho = (\rho^+ + \rho^-)/2$. But in some cases only one polarity of the current was used for the experiments, thus measuring either ρ^+ or ρ^- . See-

beck coefficients of pressed pellets were measured in the temperature interval $77 \text{ K} \leq T \leq 450 \text{ K}$ with a home-made device as the one described in [21].

3. Results

3.1. Sample Characterization. According to their room-temperature X-ray diffraction patterns, the obtained $\text{La}_{1-x}\text{Ba}_x\text{CoO}_{3-\delta}$ samples ($0 < x \leq 0.50$) were single-phase materials. Also, a comparative analysis of the X-ray diffraction results shows that as the barium content (x) increases the rhombohedral distortion present in the parent LaCoO_3

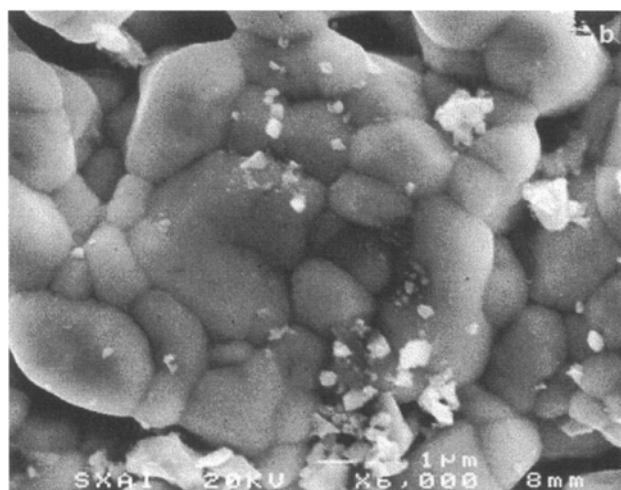
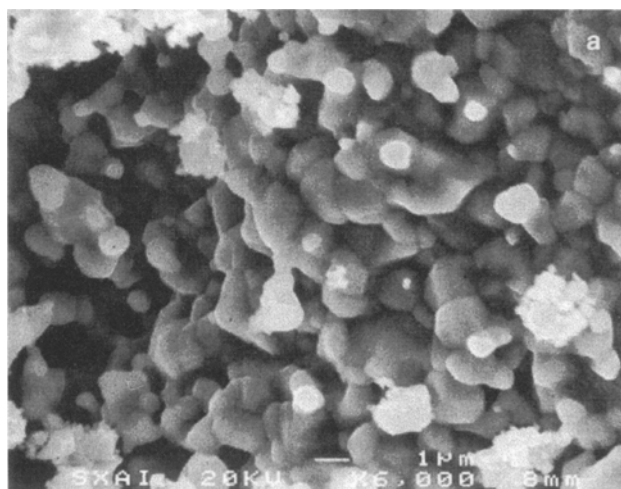


Fig. 1. SEM micrographs showing the particle size of $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ samples: a) $\text{La}_{0.80}\text{Ba}_{0.20}\text{CoO}_3$ sample, prepared at 1100 °C/17h, b) $\text{La}_{0.50}\text{Ba}_{0.50}\text{CoO}_3$ sample, prepared at 1100 °C/77h.

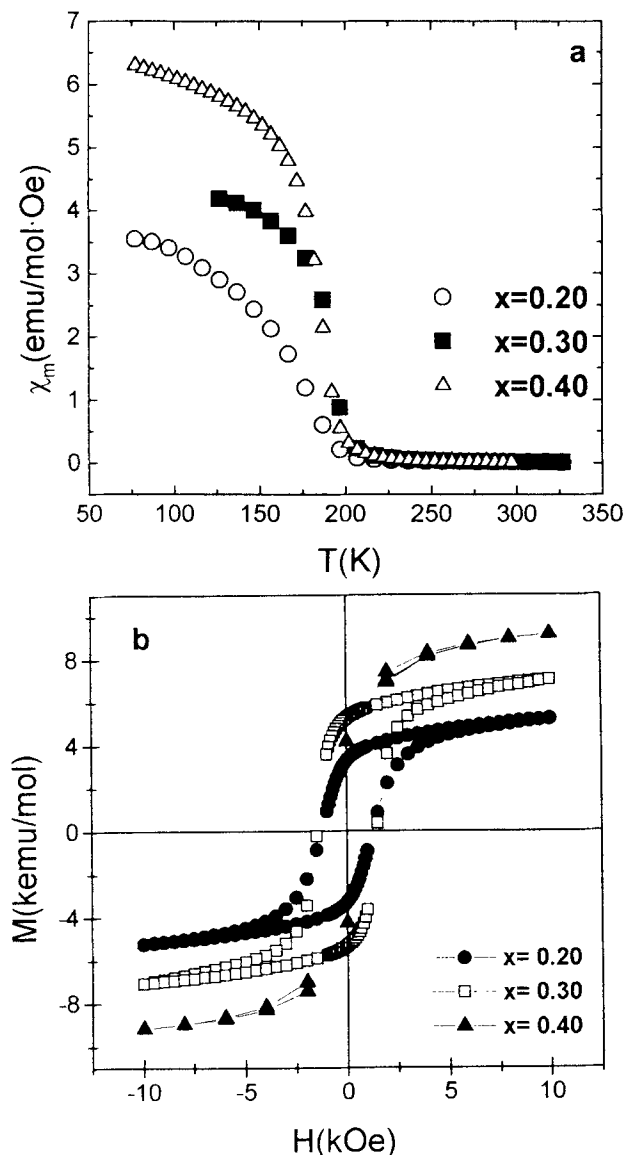


Fig. 2. a) FC molar magnetic susceptibility of $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ samples, $x = 0.20, 0.30, 0.40$, and b) ZFC magnetization versus applied field H , measured at 77 K, of $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ samples, $x = 0.20, 0.30, 0.40$.

decreases, and for $x \geq 0.30$ the crystal symmetry is cubic, in good agreement with data reported in the literature [16].

As for the morphology and particle size of these materials, SEM micrographs show differences between the samples with lower and higher barium doping: while for $x \leq 0.20$ the polycrystalline samples consists of plaquets $\sim 1-2 \mu\text{m}$ long, for $x \geq 0.30$ bigger agglomerates $\sim 10 \mu\text{m}$ long have already formed as a result of a larger degree of sintering (Fig. 1).

As for the oxygen content of the $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ samples, iodometric titrations reveal that while, in general, materials with barium content $x \leq 0.30$ are stoichiometric ($\delta \sim 0$), the samples with higher barium content

are slightly oxygen deficient ($\delta \sim 0.02$). And it is worth noting here than in the case of the $x > 0.20$ materials, and very markedly in the of $x = 0.20$, slight changes in the thermal treatments and/or in the cooling conditions easily result in oxygen variations (for example $\Delta\delta \sim 0.02$ in the case of the here prepared $x = 0.20$ samples, see below).

3.2. Magnetic Properties. Substitution of the trivalent La^{3+} by the divalent Ba^{2+} results in a marked increase in the magnetic susceptibility of these materials, and an evolution towards ferromagnetic behavior, that is achieved for $x > 0.15$ (Fig. 2a). The Curie temperature of the ferromagnetic samples hardly changes with x , so that they all have $T_C \sim 200 \text{ K}$ (Fig. 2a). As the $\chi(T)$ data follow the Curie-Weiss law for $\sim 250 \text{ K} < T < 330 \text{ K}$ from the corresponding fittings we can obtain information about the effective magnetic moment per cobalt ion (μ_{eff}) and the Weiss constant (θ). In this context, μ_{eff} is seen to decrease from $4.6 \mu_B$ (an anomalous very high value) to $3.5 \mu_B$ as x increases. Meanwhile θ increases with x from 120 K for $x = 0.20$ to 210 K for $x = 0.40$.

As for the $M(H)$ curves corresponding to the ferromagnetic samples, they show that the maximum magnetization increases with x , even if none of them achieves full saturation under the highest field used. Also, the coercive field gets the highest value for $x = 0.30$ ($H_{C(\text{max})} = -1475 \text{ Oe}$) and then decrease for higher doping degrees.

3.3. Transport Properties.

a) Resistivity Measurements

Upon Ba-doping the resistivity of the samples decreases so that the higher x the lower is their resistivity (Fig. 3). As for their temperature dependence, it is observed that the $x < 0.20$ samples show semiconducting behavior for $77 \text{ K} \leq T \leq 300 \text{ K}$; meanwhile, the samples $0.20 < x \leq 0.50$ are metallic for $T > 100 \text{ K}$, a change in their positive slope takes place at T_C , and they show a smooth transition to a semiconducting behavior for $T < 100 \text{ K}$.

The $x = 0.20$ composition deserves special attention. Its electrical behavior is greatly affected by small changes in the oxygen content due to slight variations in the thermal treatment used to prepare it. For example, samples annealed at the same final temperature but for different periods of time and/or cooled to room temperature at different rates can exhibit different temperature dependencies, see Fig. 4. Although in all of them the doping degree is $x = 0.20$, sample A is semiconducting below a metal-insulating transition temperature T_{MI1} and above a T_{MI2} , and metallic for $T_{\text{MI1}} < T < T_{\text{MI2}}$ (the so-called "reentrant semiconducting behavior" (RSB)[9]); meanwhile sample

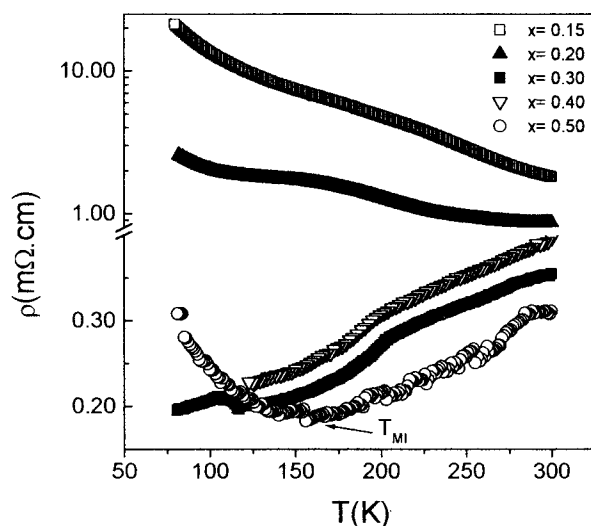


Fig. 3. Plot of resistivity versus temperature of $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ samples ($0 < x \leq 0.50$).

B is semiconducting in the whole temperature range, and sample C shows a much less pronounced RSB in which the semiconducting branch has markedly increased.

Also, very surprisingly, the value and even the temperature dependence of the resistivity of samples $x \geq 0.20$ are greatly affected by the polarity of the applied electrical current (Figs. 5a and 5b). For example, for the $x = 0.20$ sample which exhibits RSB when measuring ρ inverting the direction of the current at every temperature (sample A in Fig. 4), the application of only one polarity of the current leads to a $\rho^+(T)$ that not only exhibits higher values but also a semiconducting behavior. On the other

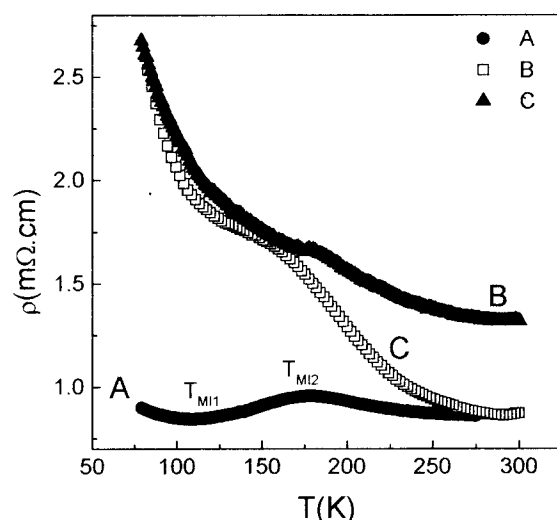


Fig. 4: Resistivity versus temperature curves of three samples $\text{La}_{0.80}\text{Ba}_{0.20}\text{CoO}_3$ prepared under slightly different conditions: sample A (1100 °C/17h, slow cool), sample B (1100 °C/17h, fast cool), sample C (1100 °C/36h, slow cool).

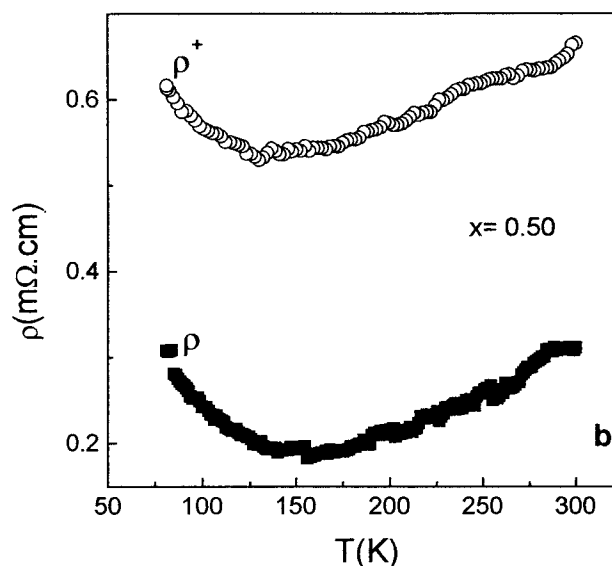
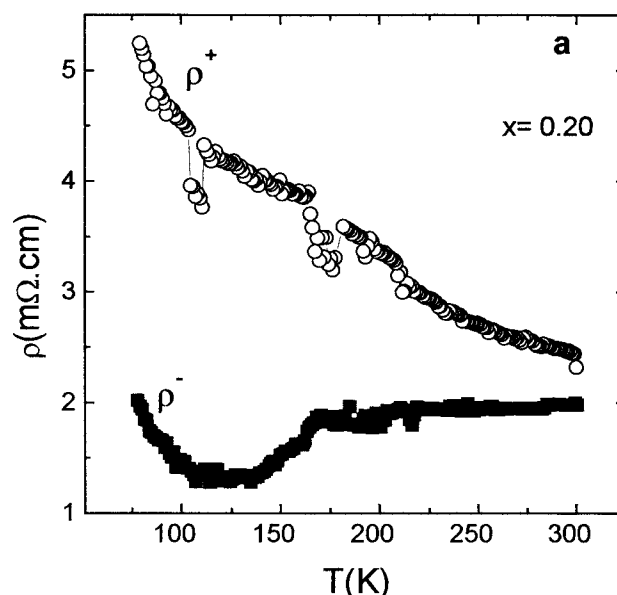


Fig. 5. Temperature variation of the electrical resistivity of the $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ samples, measured using only one polarity of the current ρ^+ and ρ^- : a) $x = 0.20$, b) $x = 0.50$.

hand the values of $\rho^-(T)$ are smaller and show a M-I transition (Fig. 5a). As for the samples with $x \geq 0.30$, the $\rho^+(T)$ and $\rho^-(T)$ curves show the same temperature dependence, although their values can differ as much as by a factor of two (Fig. 5b).

b) Seebeck Results.

While the thermoelectric power of undoped LaCoO_3 is positive and has very large values for $T < 400$ K [15], upon Ba-doping those positive α values start to decrease as x increases (Fig. 6a).

In view of the different values and temperature dependencies of the Seebeck coefficients, we can distinguish

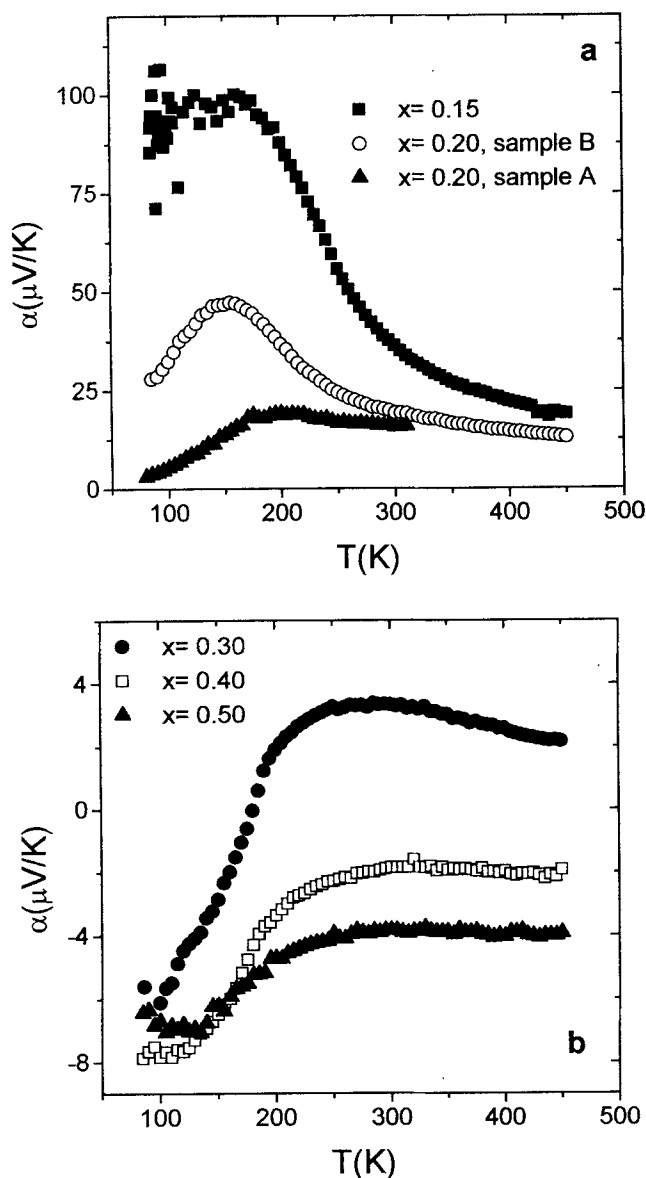


Fig. 6. Thermoelectric power, α , of samples $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ as a function of temperature: a) $x = 0.15, 0.20$ (samples A and B), b) $x = 0.30, 0.40, 0.50$.

two groups of samples: a) samples with $x < 0.20$, b) samples with $x > 0.20$.

In the first case (a), the Seebeck coefficient at low temperature ($T < 200 \text{ K}$) is positive, relatively high, and remains nearly temperature independent (Fig. 6a). This behavior signals a temperature range in which electronic conduction is dominated by small-polaron holes of nearly constant concentration. As this concentration increases with x , lower positive α values are found on increasing x . Then, for $T > 200 \text{ K}$, the $\alpha(T)$ curves decrease rapidly with temperature reaching much smaller values of $\alpha \sim 20 \mu\text{V/K}$ at room temperature.

The $\alpha(T)$ curves for the highly doped samples, $x \geq$

0.30, look quite different. α is negative within the ferromagnetic temperature domain, and rises towards more positive values as the temperature increases, but only becomes $\alpha > 0$ in the sample with $x = 0.30$ (Fig. 6b). At room temperature the $|\alpha|$ values increase monotonically with x and their small values are typical of a metal.

The case of $x = 0.20$ samples deserves again special mentioning. While the sample that shows RSB in Fig. 4, (sample A), has an $\alpha(T)$ very similar to that shown by the highly doped samples, in the case of the sample that shows semiconducting behavior in Fig. 4 (sample B) both the values of its Seebeck coefficient and its temperature dependence are intermediate between those displayed by the low- and high-doped materials (c.f. Figs. 6a and b).

4. Discussion

Substitution of trivalent La^{3+} by divalent Ba^{2+} ions in $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ introduces holes in the system and gives rise to mixed valency (+3, +4) in the cobalt ions. Stabilization of relatively small amounts of tetravalent cobalt in the structure is quite easy, but it becomes more and more difficult to achieve higher degrees of oxidation. Thus as we try to force the system to oxidize more by increasing the barium doping level the system tends to reduce the amount of Co^{4+} ions by losing oxygen, and so unless special strategies are used to increase the amount of oxygen content (treatments under O_2 , slow cooling from high temperature, etc. [9,17]) the $x \geq 0.20$ samples will be oxygen deficient. And this difference in the oxygen stoichiometry is one of the main sources of the disparity of results found by the different authors, not only on the $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ samples, but very often in the better studied $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ system [9-10,13,22]. And as it will be discussed below, the samples with compositions near the critical percolation threshold will be specially sensitive to those changes, even if they are very small.

This mixed-valency in the cobalt ions brings about important changes in the crystallographic and electronic structure of the system, and therefore in its magnetic and transport properties.

From the crystallographic point of view, it is found that single-phase perovskite materials are formed for barium doping levels $x \leq 0.50$. Also, the introduction of barium diminishes the rhombohedral distortion present in the LaCoO_3 compound [1]. As that distortion is due to the cooperative rotation of the $[\text{CoO}_6]$ octahedrons about the threefold axis of the ideal cubic perovskite structure [14], and makes the Co-O-Co angle different from 180° ,

its gradual disappearance will bring it closer to the ideal value. This crystallographic change will also modulate the strength of the Co-O-Co interaction and therefore the magnetic and transport properties of the materials.

As for the magnetic and transport properties of the $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ system, we find that the paramagnetic, highly resistive LaCoO_3 compound becomes ferromagnetic for doping levels $x > 0.15$ and tends towards metallic behavior for $x > 0.20$, although this behavior is not completely achieved as a smooth transition to semiconducting behavior is observed for $T < 100$ K. In the case of the $x = 0.20$ composition, semiconducting or RSB behavior have been observed depending on the thermal treatment conditions used for their synthesis.

These electrical results are different from the ones reported by other authors who find that for $T < 300$ K the samples $0 < x \leq 0.40$ are all semiconducting [12,16]. These differences probably arise from changes in the oxygen stoichiometry of the studied samples, as explained before.

In any case, the observed general evolution in the properties of $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ compounds upon doping is similar to that shown by the closely related $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ materials, for which a phase diagram has recently been established [9]. In that context, it has been proposed that upon Sr-doping the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ materials segregate into two distinguishable electronic phases that coexist within the same crystallographic phase [9]: one would be hole-rich, metallic and ferromagnetic (clusters) while the other would be hole-poor, semiconducting and with AF exchange interactions, in which the spin state of the cobalt ions changes with the temperature.

For low doping degrees those clusters are isolated from one another and thus the materials are semiconducting. When the ferromagnetic phase reaches the magnetic percolation threshold, bulk ferromagnetism is observed below T_C . For higher x the ferromagnetic hole-rich regions also percolate from the electrical point of view, but for a compositional interval with x slightly lower than the electrical percolation threshold, the electrical conduction in the ferromagnetic regions is modulated by the mediating matrix.

The introduction of Ba^{2+} instead of Sr^{2+} will, of course, slightly change factors such as the width of the Co-O bands, the strength of the superexchange interaction, and the spin state of the cobalt ions [23]. But, in view of the obtained magnetic and transport results for the $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ samples ($0 < x \leq 0.50$) this two-phase electronic

model can be basically extended to them, since for example:

The magnetic results show that the Curie temperature of the ferromagnetic samples changes very little with x , as in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ [9], and it is worth noting that a constant T_C would indicate a phase segregation.

Also, for compositions near the percolation threshold a $\theta < T_C$ is found suggesting the presence of AF interactions within the ferromagnetic materials.

Evenmore, the analysis of the Seebeck results allow to distinguish the contributions of two phases: a) of the Ba-poor matrix, that manifests itself in the low-doped samples ($x < 0.20$): in these materials without large ferromagnetic clusters, $\alpha(T)$ has an important positive value in the temperature range $110 \text{ K} < T < 450 \text{ K}$. b) of the hole-rich regions, that manifest themselves in the higher doped samples ($x > 0.20$). In this case, the domains of interconnected ferromagnetic clusters give a negative contribution to $\alpha(T)$ that increases with x relative to the positive contribution to $\alpha(T)$ from the matrix.

In the case of the $x = 0.20$ composition, slight changes in the oxygen content of the samples and therefore in the number of charge carriers have the result that either the contribution from the matrix or the contribution from the hole-rich regions dominate the obtained $\alpha(T)$ curves.

The electrical behavior of samples near the percolation threshold ($x \geq 0.20$) is also very revealing: if there were two electrically conducting phases in the system the predominant phase would control the observed electrical behavior.

Within this model, the semiconducting behavior observed at low temperatures is due to the fact that the metallic regions are disconnected so that the semiconducting behavior of the other phase is observed. Between T_{M1} and T_{M2} (or above T_{M1} , in the $x \geq 0.30$ samples) spin-state-changes in that semiconducting matrix allow the metallic, ferromagnetic clusters to percolate and the spin-disorder scattering is the dominant mechanism. Above T_{M2} (or T_C in the $x \geq 0.30$ samples) the ferromagnetic phase becomes paramagnetic and spin-disorder scattering reduces its volume. In the case of $x \geq 0.30$ samples, this effect gives rise to a change in the slope of the $\rho(T)$ curve, while in the case of $x = 0.20$ sample the percolation pathways then break and what dominates the electrical conduction is the movement of charge carriers through the semiconducting phase with an activated mobility.

In the case of $x = 0.20$, a decrease in the number of charge carriers in the sample that has not the full oxygen

stoichiometry leads the hole-poor matrix to dominate the electrical conduction throughout the whole temperature range studied, and a semiconducting behavior is therefore observed in this case.

Other support for the model of two-electrically different phases coexisting in the system comes from the "di-dic" effects observed in samples $x \geq 0.20$. If the materials are thought of being an electrically inhomogeneous medium, where some metallic clusters are covered with a semiconducting and dielectric material, changes in the polarity of the electrodes will affect the charge distribution in the dielectric medium. This, in turn, will change the density of charge carriers and therefore the resistivity of these materials as found in other perovskite compounds [24].

Finally it is worth mentioning here that although intergranular as well as intragranular effects could be playing a role in all these electrical effects, the relatively large particle size of some of the materials ($x \geq 0.30$) exhibiting such peculiar behaviors suggest the importance of the intragranular ones.

More work is in progress to fully characterize these samples and to clarify all these interesting results.

5. Acknowledgments

We thank the Spanish DGICYT for financial support under project code MAT98-0416-C03-02 and we acknowledge SXIAIN of the University of A Coruña for their technical support.

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Paper presented at the 6th Euroconference on Solid State Ionics, Cetraro, Calabria, Italy, Sept. 12-19, 1999.

Manuscript rec. Sept. 18, 1999; acc. Oct. 17, 1999.