

Magnetic and Transport Properties of $\text{Ln}_{1-x}\text{Sr}_x\text{CoO}_3$ Perovskite Materials (Ln= La, Nd, Gd) Prepared by Low-Temperature Synthetic Routes

M.P. Breijo¹, C. Rey¹, S. Castro¹, M. Sánchez¹, M.A. Señarís-Rodríguez¹,
J. Mira², A. Fondado² and J. Rivas²

¹Dpt. Química Fundamental e Industrial, Universidad A Coruña, 15071 A Coruña, Spain

²Dpt. Física Aplicada, Universidad Santiago de Compostela, 15706 Santiago de Compostela, Spain

Abstract. We have used three soft-chemistry methods for the efficient preparation of $\text{Ln}_{1-x}\text{Sr}_x\text{CoO}_3$ samples, adapting the combustion and the liquid-mix methods for the synthesis of the Ln = La and Gd compounds, respectively, and the preparation of $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$ by the nitrate decomposition method.

We report the magnetic and electrical properties of these relatively small particle-size materials, specially in the case of the Ln = La and Ln = Nd series ($d \approx 0.2 \mu\text{m}$ and $0.5 \mu\text{m}$, respectively), and we compare them to those displayed by the corresponding compounds prepared at higher temperatures. The compounds here obtained are ferromagnetic for $x \geq 0.15$ when Ln = La and for $x \geq 0.20$ when Ln = Nd and Gd. Their resistivity decreases as the doping degree increases. And, very interestingly, for compositions $0.20 < x \leq 0.45$, when Ln = La, and for $x = 0.40$, when Ln = Nd, they show M-I transitions as the temperature rises. These are very sensitive to the application of electrical current and its polarity and the presence of magnetic fields, displaying peculiar behaviors.

1. Introduction

Strontium-doped rare-earth cobaltite oxides with perovskite structure, $\text{Ln}_{1-x}\text{Sr}_x\text{CoO}_3$ (Ln: La, rare earths), are very attractive materials in view of their interesting magnetic and electrical properties [1, 2], and also because of their high ionic (O^{2-}) conductivity and possible applications in solid oxide fuel cells, oxygen permeation membranes, etc. [3].

In the context of magnetic and electrical properties, these are greatly affected by the spin state of the Co ions - which experience a thermally induced transition to higher spin configurations - by the relative amount of tetravalent and trivalent cobalt ions, by the direct and indirect oxygen-mediated exchange interactions between the cobalt ions, etc. [1].

Of all $\text{Ln}_{1-x}\text{Sr}_x\text{CoO}_3$ series of compounds, the lanthanum $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ perovskites have been most thoroughly investigated. In this system, while the parent compound LaCoO_3 shows high resistivity and anti-ferromagnetic exchange interactions [4], as x increases the

materials tend to show metallic and ferromagnetic behavior [5]. The evolution takes place smoothly, and a number of different magnetic and electrical behaviors have been described for different degrees of doping: superparamagnetism, spin-glass/cluster-glass behavior, etc., semi-conducting/metallic behaviors, and even metal-insulator transitions as a function of temperature [1, 6]. More recently, magnetoresistive effects have also been observed in this system [7].

Other $\text{Ln}_{1-x}\text{Sr}_x\text{CoO}_3$ (Ln: rare earth) systems are also known to show similarly interesting magnetic and electrical properties [2, 8]. Although the general trend is, again, that the materials tend to show ferromagnetic and metallic behavior as x increases. The characteristics of that evolution and the critical doping degree depend on the nature of the lanthanide ion to achieve magnetic and electrical percolation change [2].

To study the influence of particle size on these varying magnetic and electrical properties, it is interesting to prepare fine-particle $\text{Ln}_{1-x}\text{Sr}_x\text{CoO}_3$ materials and compare

their behavior with that exhibited by ceramic samples.

For that purpose, we have adapted two soft-chemistry techniques to prepare efficiently $\text{Ln}_{1-x}\text{Sr}_x\text{CoO}_3$ materials with controlled, homogeneous and comparatively small particle size:

- the "combustion technique", a chemical method that uses the energy liberated in the exothermic decomposition of a redox mixture of the metal nitrates and an organic compound to produce fine particle ashes containing the oxide products or their precursors. These ashes readily convert into the final product when heated for short periods of time at relatively low temperatures [9]. The product characteristics, such as particle size, surface area and porosity are greatly affected by the nature of the combustion, which in turn depend on the nature of the fuels and the proportion oxidizer:fuel;
- the "liquid-mix" or "organometallic precursor" method [10], in which a precursor of the final product is formed by coordination of the metal cations to a polyacid, followed by a polymerization of the solution by condensation with a polyalcohol. The so-obtained resin burns when heated at $\approx 400^\circ\text{C}$, yielding a residue that easily transforms into the perovskite phase when heated at higher, but relatively low temperatures.

Also, we have used the better known nitrate decomposition method, previously used for the synthesis of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ samples [1], to prepare the $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$ series of compounds.

We refer in this paper to the details of such synthesis and to the most outstanding magnetic and electrical properties exhibited by the obtained $\text{Ln}_{1-x}\text{Sr}_x\text{CoO}_3$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Gd}$) materials.

2. Experimental Descriptions

The three $\text{Ln}_{1-x}\text{Sr}_x\text{CoO}_3$ series ($\text{Ln} = \text{La}, \text{Nd}, \text{Gd}$) ($0 \leq x \leq 0.50$) were prepared using dry Ln_2O_3 , SrCO_3 and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as starting materials.

$\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ materials were synthesized by the combustion method. Stoichiometric amounts of dry La_2O_3 and SrCO_3 were dissolved in HNO_3 -30% followed by the addition of the stoichiometric amount of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Oxalic acid dihydrazide $\text{C}_2\text{H}_6\text{N}_4\text{O}_2$ (ODH) was used as fuel and added in the appropriate amount to the resulting solution. We first used the theoretical calculated optimum composition of the metal nitrate-ODH mixtures taking

into account the total oxidizing and reducing power of both oxidizer and fuel compounds using concepts of propellant chemistry [11], and taking into account the excess of acid used for the preparation of the La and Sr nitrates with respect to the stoichiometric amounts. Nevertheless, we found experimentally that oxidizing-rich mixtures were needed to obtain the pure phases. In this context, the following relative proportions of oxidant to reducing agent in the mixture were found to yield the optimum conditions for the synthesis of these compounds: [nitrate]: [ODH] (expressed as the nitrate to ODH equivalent mole ratio) = 1:0.5 for $x \leq 0.15$; 1:0.3 for $0.20 \leq x \leq 0.30$; 1:0.1 for $x \leq 0.36$. The obtained solutions containing both the oxidizer and the fuel were evaporated until, at around 300°C , they ignited during 3 sec - 5 min. The so-obtained black and porous ashes were then heated at $500^\circ\text{C}/30$ min. The resulting powders were pressed into pellets and heated at $800^\circ\text{C}/2\text{h}$.

For the preparation of $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_3$ compounds by the liquid-mix method, Gd_2O_3 was first converted into the corresponding nitrate by dissolution in HNO_3 -30%. This product was then added to a 1M citric acid aqueous solution, in which stoichiometric amounts of SrCO_3 and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were also dissolved. After diluting the so-obtained solution, ethylenglycol was carefully added in a proportion 10 % v/v.

After heating and evaporating the resulting solution at 200°C , a brown resin formed and it was then decomposed by heating it at $400^\circ\text{C}/1\text{h}$.

The obtained ashes were given accumulative heating treatments at 600, 700, 800°C followed by intermediate grindings. The pelletized samples were given the following final treatments: $900^\circ\text{C}/60$ h (for samples with $x \leq 0.20$) and $950^\circ\text{C}/24$ h (for samples with $x \leq 0.30$), followed in both cases by a slow cooling to room temperature ($0.7^\circ\text{C}/\text{min}$).

$\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$ materials ($0 \leq x \leq 0.50$) were prepared by the nitrate decomposition method by first dissolving appropriate amounts of the reagents in 30 % nitric acid. Then, the obtained solution was gently evaporating to dryness. The resulting residue was decomposed at 600°C , and the precursor powder pelletized and thermally treated at $970^\circ\text{C}/24$ h followed by slow cool to room temperature ($0.7^\circ\text{C}/\text{min}$).

The three prepared series of compounds were examined by X-ray powder diffraction with a Siemens D-5000

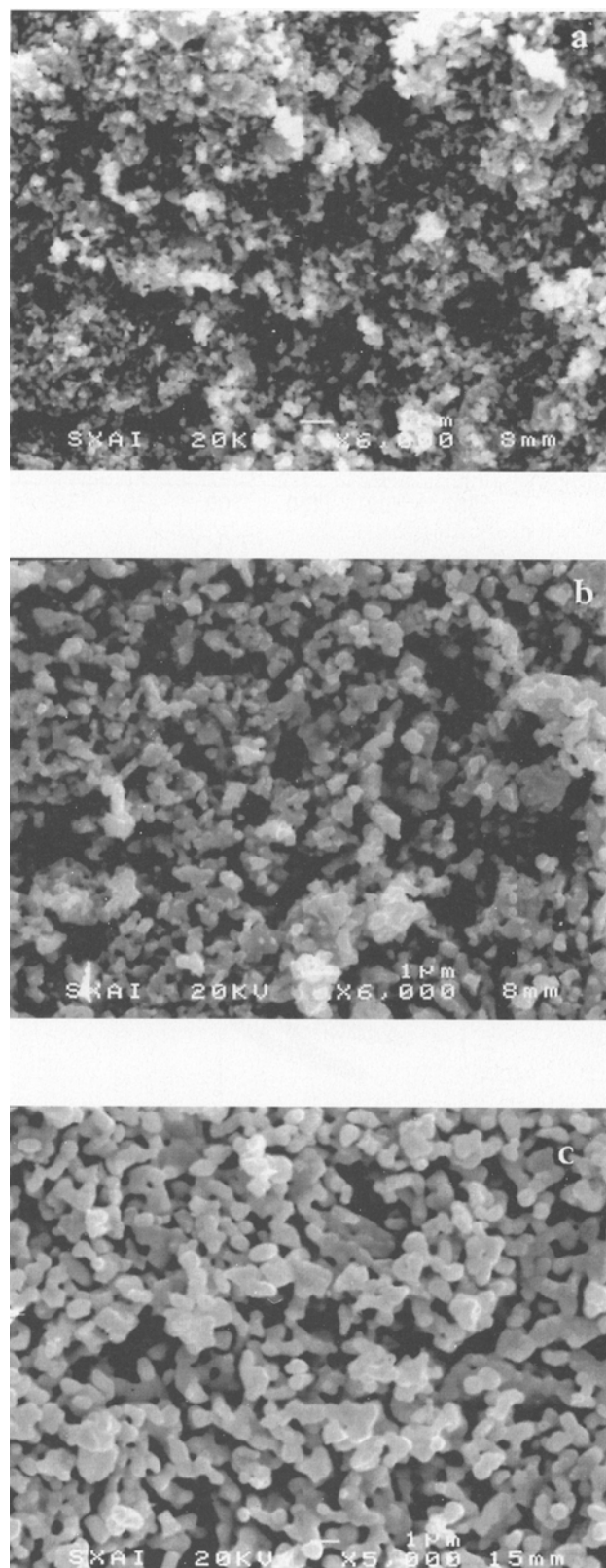


Fig. 1. SEM micrographs showing the particle size of $\text{Ln}_{1-x}\text{Sr}_x\text{CoO}_3$ samples: a) $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ series, prepared by the combustion method, b) $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$ series, prepared by the nitrate decomposition method, c) $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_3$ series, prepared by the liquid-mix method.

diffractometer and $\text{Cu(K}\alpha) = 1.5418 \text{ \AA}$ radiation. The morphology and size of the particles were studied in a scanning electron microscope (SEM) Jeol 6400.

The thermal stability of the samples was checked by differential thermal analysis (DTA) and thermogravimetric analyses (TGA). Iodometric titrations under an argon atmosphere were carried out to analyze the oxygen content of the samples.

Magnetic properties 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 using fields of ± 10 kOe and, in some cases, fields of ± 13 kOe.

The electrical resistance R was measured as a function of temperature in the range $77 \leq T \leq 300$ K in a zero magnetic field ($H=0$) and with a constant field ($H=5$ kOe) using a dc four-probe method employing silver paint contacts. These contacts were renewed or even replaced by 4 new indium contacts or gold sputtered onto the samples, and the measurements repeated when detecting anomalous changes in the resistivity of the samples, in order to discard effects between sample and electrical contacts.

The resistance data were obtained, as commonly done, by calculating the averages R^+ and R^- (+ and - stand for the directions of the current) out of 10 values, respectively, and getting an average resistance $R = (R^+ + R^-)/2$. But in some cases, as it will be shown below, only one polarity of the current was used for the experiments, thus measuring either R^+ or R^- . The magnetoresistance of the samples was measured at a constant temperature between 0 and 10 kOe.

3. Results and Discussion

3.1. Sample Characterization. According to the room-temperature X-ray diffraction results, we have prepared single-phase $\text{Ln}_{1-x}\text{Sr}_x\text{CoO}_3$ compounds with $0 \leq x \leq 0.45$ for $\text{Ln} = \text{La}$, with $0 \leq x \leq 0.50$ for $\text{Ln} = \text{Gd}$ and with $0 \leq x \leq 0.40$ for $\text{Ln} = \text{Nd}$.

These results also show that in the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($0 \leq x \leq 0.45$) samples the introduction of the strontium ion progressively reduces the rhombohedral distortion present in the parent

LaCoO₃ compound (for $x = 0.45$ the crystal symmetry is already almost cubic) and increases the volume of the unit cell, in good agreement with data reported in the literature [12].

In the case of the Gd_{1-x}Sr_xCoO₃ compounds, their X-ray diffraction patterns can all be indexed on the basis of an O-type ($a \leq (c/2) \leq b$) orthorhombic GdFeO₃-like perovskite structure ($\approx \sqrt{2} a_c \times \sqrt{2} a_c \times 2a_c$) ($a_c = 3.8$ Å). Again, the unit cell expands upon doping.

As for the Nd_{1-x}Sr_xCoO₃ system, according to the X-ray diffraction result, this series of compounds have cubic perovskite structures with $a \approx 2a_c$, the a parameter increasing with x .

Therefore, in all these three series the incorporation of the larger size Sr²⁺ ion ($X_{II}r_{Sr^{2+}} = 1.44$ Å) in place of the considerably smaller Ln³⁺ ions ($X_{II}r_{La^{3+}} = 1.36$ Å, $X_{II}r_{Nd^{3+}} = 1.27$ Å, $X_{II}r_{Gd^{3+}} = 1.22$ Å) [13] predominates the influence that upon doping Co³⁺ ($^{VI}r_{Co^{3+}}$ l.s. = 0.55 Å, $^{VI}r_{Co^{3+}}$ h.s. = 0.61 Å) [13] oxidizes to the smaller Co⁴⁺ ions ($^{VI}r_{Co^{4+}} = 0.53$ Å) [13], resulting in the expansion of the unit cell.

As for the morphology and particle size of the obtained Ln_{1-x}Sr_xCoO₃ materials, SEM micrographs show that the La_{1-x}Sr_xCoO₃ and Nd_{1-x}Sr_xCoO₃ series of compounds consist of small, homogeneous spherical particles with averaged diameters of ≈ 0.2 μm and ≈ 0.5 μm, respectively (Figs. 1a and 1b).

These relatively small particle size values are the result of the moderate temperatures and relatively short heating treatments used for the synthesis of these materials.

In the case of the Gd_{1-x}Sr_xCoO₃ series, it is observed that sintering between particles is already starting to take place, resulting in plaquets $\approx 1-2$ μm long (Fig. 1c). In this case, repeated longer treatments at temperatures between 600 and 800 °C would have promoted such growth.

The thermogravimetric results show that, in all three series, the samples lose some oxygen on heating above ≈ 923 K. For lower Sr content, $x \leq 0.20$, oxygen is recuperated on slow cooling in air. For $x > 0.25$, the oxygen loss on heating is even more pronounced and only a 98.5 - 99 % of the initial oxygen mole-content is recuperated on slowly cooling in air.

The iodometric titrations indicate that while the as-prepared samples with Sr content $x < 0.25$ are stoichiometric in oxygen, the samples with $x > 0.25$ are oxygen deficient. In this context, preliminary analyses, indicate that in the highest doped Nd and Gd samples, the oxygen

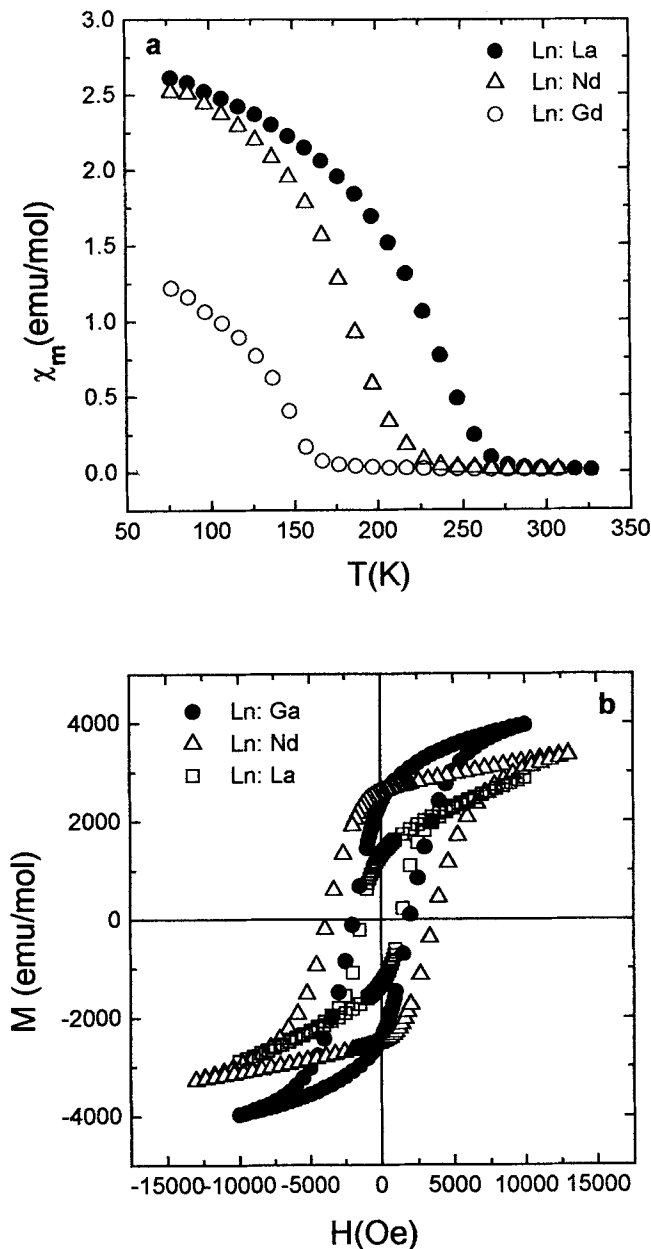


Fig. 2 (a) FC molar magnetic susceptibility of $x = 0.30$ Ln_{1-x}Sr_xCoO₃ (Ln: La, Nd, Gd) samples. (b) ZFC magnetization versus applied field H , measured at 77 K, of $x = 0.30$ Ln_{1-x}Sr_xCoO₃ samples (Ln: La, Nd, Gd).

content is 2 and 4 % smaller, respectively, than in the lower-doped samples.

3.2. Magnetic Properties. In these so-prepared Ln_{1-x}Sr_xCoO₃ series, ferromagnetism is found for $x \geq 0.15$ in the case of La_{1-x}Sr_xCoO₃, for $x \geq 0.20$ in the Nd_{1-x}Sr_xCoO₃ and Gd_{1-x}Sr_xCoO₃ series.

It is worth noting that in all three series, Curie temperatures are seen to increase only very slowly with x ,

and to decrease as the size of Ln gets smaller, so that $T_c(\text{La}_{1-x}\text{Sr}_x\text{CoO}_3) \approx 255$ K, $T_c(\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3) \approx 230$ K, $T_c(\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_3) \approx 160$ K (Fig. 2a).

If we compare these results with those reported in the literature for samples prepared at higher temperatures [1, 2, 14], we find differences in the case of the $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$ and the $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_3$ series. While in our samples the Curie temperatures are higher and remain almost constant with x , they are smaller and clearly increase with x in the ceramic samples [2]. For example, for the $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$ system, the Curie temperatures reported for the ceramic sample with $x = 0.40$ is only 90 ± 10 K and increases to 190 ± 15 K for $x = 0.50$ [2], a higher value that nevertheless is still smaller than the $T_c = 240$ K displayed by our samples.

In this context, variations in the oxygen content of the compared samples could be the origin of such observed differences.

As for the $M(H)$ curves corresponding to the ferromagnetic samples, they show that at 77 K none of them reaches saturation under the maximum field used (Fig. 2b) and that in all three series, as x increases, the values of maximum magnetization get higher.

From the comparison of the $M(H)$ loops corresponding to the different $\text{Ln}_{1-x}\text{M}_x\text{CoO}_3$ series (Fig. 2b), especially remarkable is the much higher coercive field displayed by the ferromagnetic $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$ samples. This coercive field achieves a maximum value of ≈ 3800 Oe for $x = 0.30$, then decreases to ≈ 3200 and 2400 Oe for $x = 0.40$ and for $x = 0.20$, respectively.

These high coercive fields could be related to the fact that Nd^{3+} ions have a big orbital angular momentum ($L = 3$), different from La^{3+} and Gd^{3+} for which L is zero [15].

In the case of the ferromagnetic $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ compounds, if we compare our magnetic results with those displayed by the corresponding compounds prepared by the ceramic, coprecipitation and nitrate decomposition methods [1,14], we find that the samples prepared here are magnetically much harder. That hardening comes mainly from two effects [16]: the reduction in particle size, with the concomitant diminution in the number of magnetic domains and a greater difficulty to magnetize and demagnetize the materials; and also from the fact that the characteristics of the combustion method favor the formation of a larger concentration of defects in the samples, defects that would pin and obstruct the movement of the domain walls.

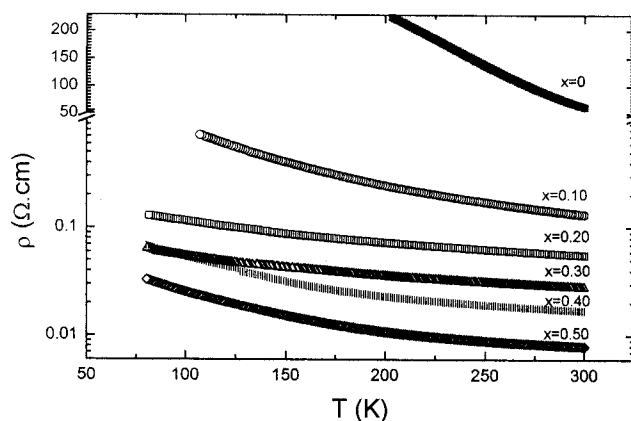


Fig. 3. Plot of resistivity versus temperature of $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_3$ samples ($0 \leq x \leq 0.50$).

3.3. Electrical Properties. When measuring the resistivity as a function of temperature $R(T)$, the first general observation is that the sample resistivity decreases as the doping degree increases (Fig. 3), in good agreement with data reported in the literature [1,2].

In the case of the $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_3$ series, despite that diminution, the temperature dependence of the resistivity remains semiconducting in the whole $0 \leq x < 0.50$ interval.

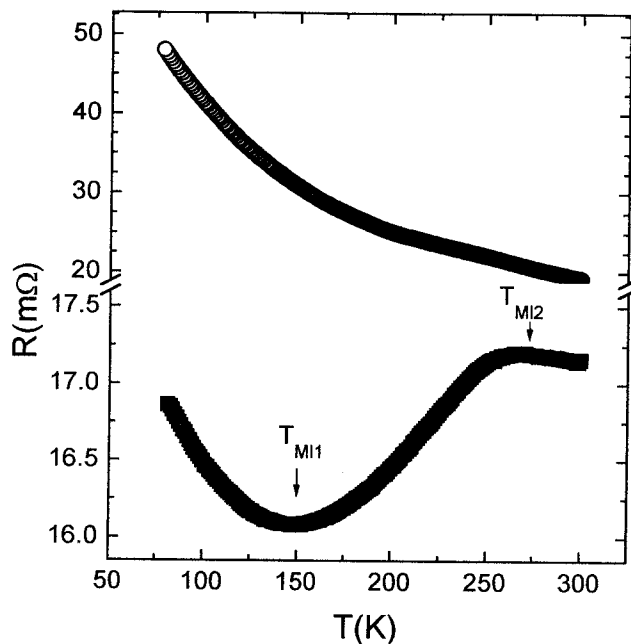


Fig. 4. Typical "reentrant semiconducting behavior" found in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ samples ($0.20 < x \leq 0.45$) prepared by the combustion method (■). Evolution of the electrical behavior of those samples after having made several $R(T)$ runs (O).

In the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ series of compounds, while the lower doped samples $0 \leq x \leq 0.20$ are semiconducting, samples with $0.20 < x \leq 0.45$ show I-M-I transitions, also known as "reentrant semiconducting behavior" (RSB) [1]: i.e. the samples are semiconducting below a T_{MI1} and above a T_{MI2} , and metallic for $T_{\text{MI1}} < T < T_{\text{MI2}}$ (Fig. 4).

This behavior was reported earlier for samples $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ prepared by the coprecipitation method [1], but only in the interval $0.20 \leq x < 0.30$. Outside that interval, the samples were semiconducting for $x < 0.20$ and metallic for $x \geq 0.30$.

In our case, the extension of the compositional interval for RSB could be due to changes in the intergranular conduction provoked by the smaller size of the particles, differences in the characteristics and oxygen content and microstructure of the grain boundaries, etc.

But changes in the intragranular conduction can also be an important factor. In this context, according to [1] this reentrant semiconducting behavior of some $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ samples would be a manifestation of the coexistence of two distinguishable electronic phases within the same crystallographic phase in this system: one would be hole-rich, metallic, ferromagnetic and would grow with x ; the other, the matrix, would be very similar to the undoped LaCoO_3 [17] and would be hole-poor, semiconducting, and with AF exchange interactions, and with Co ions in a spin state that changes with temperature.

For x slightly lower than the electrical percolation threshold, the electrical conduction in the ferromagnetic regions is modulated by the mediating matrix. Changes in the spin state of the cobalt ions in this matrix would either allow the metallic regions to percolate or, on the contrary, would disconnect those hole-rich regions, giving rise to the observed M-I transitions as temperature rises.

Within that model, changes in the characteristics and size of the particles could greatly affect the size, number and distribution of such ferromagnetic and metallic clusters embebbed in the semiconducting LaCoO_3 matrix, therefore modifying their electrical behavior.

In the case of the $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$ system, we find that while samples with $x < 0.40$ are semiconducting, the sample with $x = 0.40$ shows a M-I transition as a function of temperature: the $\text{Nd}_{0.60}\text{Sr}_{0.40}\text{CoO}_3$ compound is semiconducting for $T < T_{\text{MI1}} = 160$ K and metallic above it (Fig. 5a). This case is very similar to the RSB reported above, but at difference with the previous case,

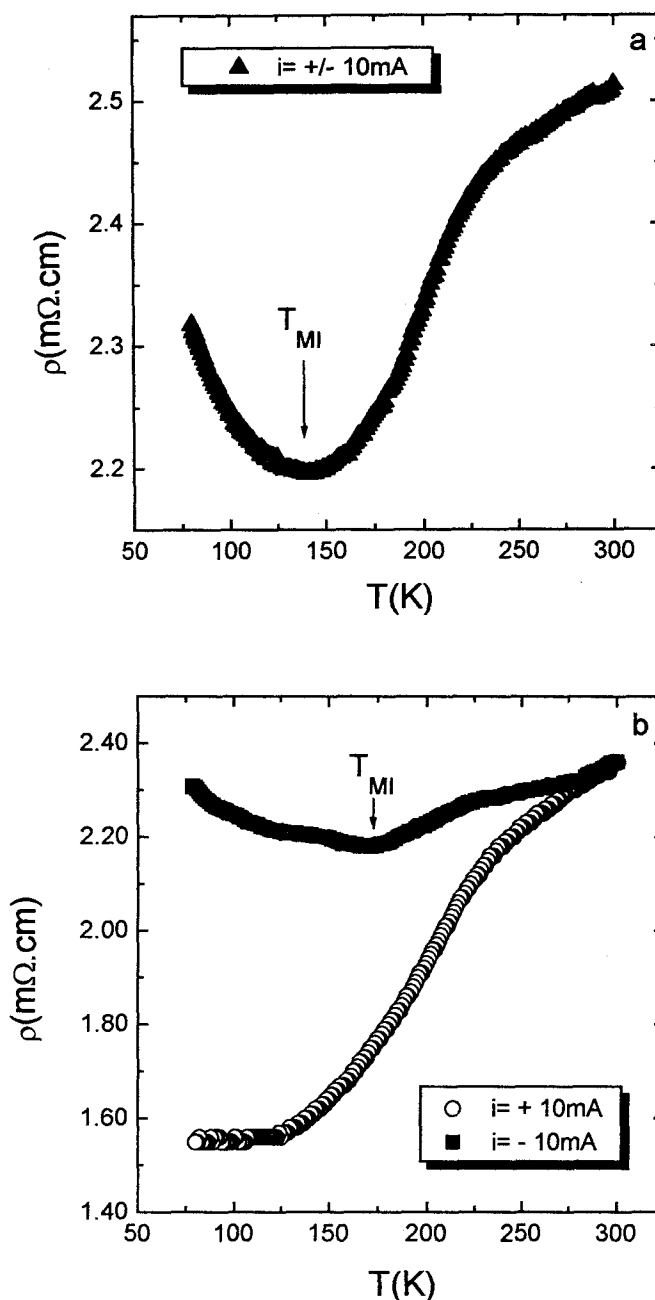


Fig. 5. a) Temperature variation of the electrical resistivity of the $\text{Nd}_{0.60}\text{Sr}_{0.40}\text{CoO}_3$ sample measured by inverting the polarity of the electrical current, $R(T)$ and b) $R^+(T)$, $R^-(T)$ curves measured using only one polarity of the current.

only a small change in the positive slope of the $R(T)$ curve takes place at T_c and the sample remains metallic up to room temperature.

This result differs from those reported in ceramic samples [2], where metallic behavior was found for $x \geq 0.30$. This discrepancy could again be due to not only to the intergranular but also to the intragranular effects referred to above, as the previously explained electronic

model for $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ can also be extended to this system [18].

The so-obtained samples with M-I transitions are particularly peculiar: different from the other compounds with semiconducting behavior, these samples seem to be in a "metastable" state from the electrical point of view as their resistivity is very sensitive to external influences, in particular to the electrical current and application of a magnetic field.

In this context, the resistivity value and in some cases even the temperature dependence of the resistivity are greatly affected by the polarity of the applied electrical current. For example, in the case of $\text{Nd}_{0.60}\text{Sr}_{0.40}\text{CoO}_3$ (Fig. 5b): when we measure its resistivity as a function of temperature using the current I^+ in one direction, the obtained $R^+(T)$ shows a M-I transition; if we invert the direction of the current and measure $R^-(T)$ the curve now shows a metallic temperature dependence, and the resistivity of the sample is smaller. On the other hand, the averaged $R(T)$ curve, obtained when inverting the polarity of the current to take each measurement, shows again the M-I transition and in this case the resistivity values are closer to the $R^+(T)$ results (Fig. 5a).

Interestingly, similar effects have also been recently found in other RSB $\text{La}_{1-x}\text{M}_x\text{CoO}_3$ ($M = \text{Ca}, \text{Sr}, \text{Ba}$) samples consisting of polycrystalline materials with bigger particle size [19].

Such diodic behavior can be understood if the materials are thought, as explained before, as an electrically inhomogeneous medium, where some metallic clusters are covered with a semiconducting and dielectric material. Then, the changes in the polarity of the electrodes would affect the charge distribution in the dielectric medium and this, in turn, would change the density of charge carriers and therefore R , as found in other perovskite materials [20].

Another interesting observation is that, after making several runs of $R(T)$ measurements the resistivity of the samples increases, specially if the electrical current is applied in only one direction, until the M-I transitions finally disappears leading to a purely semiconducting behavior (Fig. 4). In the case of the RSB samples, the magnetic field is also seen to help that evolution. But once the samples have evolved, their resistivity remains stable.

Such "aging" effects have also been found to occur in RSB $\text{La}_{1-x}\text{M}_x\text{CoO}_3$ ($M = \text{Ca}, \text{Sr}, \text{Ba}$) compounds as a function of time and they have been related to small va-

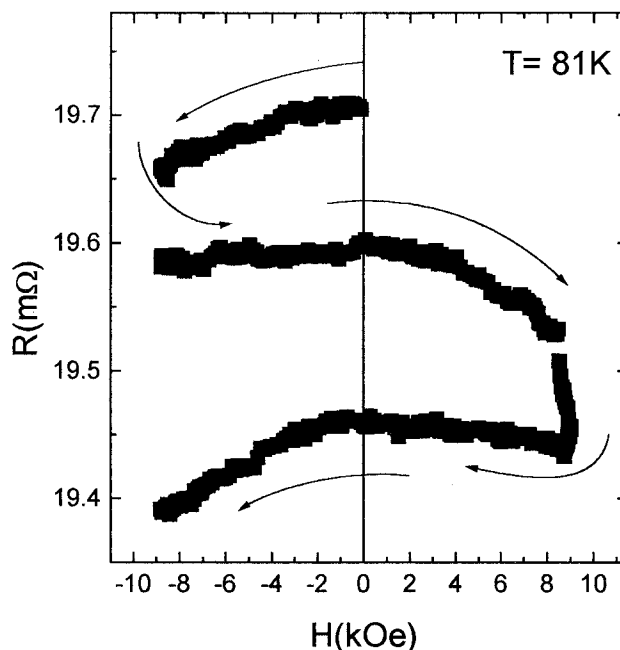


Fig. 6. Evolution of the electrical resistance of the $\text{Nd}_{0.60}\text{Sr}_{0.40}\text{CoO}_3$ sample under the influence of the magnetic field ($T = 81 \text{ K}$).

riations in the oxygen stoichiometry of the samples [21,22].

If these samples are in an unstable situation, as it seems to be the case, the applied electrical current could help reorganizing, even subtly, that metastable state in these smaller particles resulting in the observed changes in their electrical behavior.

Finally, the particular case of the $\text{Nd}_{0.60}\text{Sr}_{0.40}\text{CoO}_3$ sample also deserves attention. Its resistivity shows a very peculiar behavior when applying a small magnetic field ($H \leq 10 \text{ kOe}$) as it keeps decreasing while sweeping the field (Fig. 6). Such $R_T(H)$ curves suggest the existence of important relaxation processes in this sample. The high magnetocrystalline anisotropy and high coercive fields induced by the Nd^{3+} ions are probably involved in such effects, and this rich dynamics is now being studied.

4. Conclusions

We have adapted the combustion and liquid-mix methods for the efficient preparation of $\text{Ln}_{1-x}\text{Sr}_x\text{CoO}_3$ ($\text{Ln} = \text{La}, \text{Gd}$) samples. We have also used the nitrate decomposition method for the synthesis of $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$ series of compounds.

The magnetic and electrical properties of these materials change upon doping: as x increases the samples tend to ferromagnetic behavior and their resistivity di-

minishes. The characteristics of that evolution depends on the $\text{Ln}_{1-x}\text{Sr}_x\text{CoO}_3$ system.

The magnetic and electrical properties of these systems are greatly affected by the characteristics of the preparation method, that can vary properties such as the doping degree, the oxygen content and their distribution in the sample, the particle size of the polycrystalline materials and their microstructure.

In this context, by using soft-chemistry methods that yield relatively small particle-size materials, we have enhanced for larger compositional intervals the appearance of M-I transitions as a function of temperature in the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ and $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$ systems.

Samples with such transitions are very sensitive to the application of electrical current and the presence of magnetic fields, displaying peculiar behaviors.

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

5. Acknowledgements

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

6. References

- [1] M. A. Señarís-Rodríguez and J. B. Goodenough, *J. Solid State Chem.* **118**, 323 (1995).
- [2] C.N.R. Rao, O.M. Parkash, D. Bahadur, P. Ganguly, A. Nagabhu Share, *J. Solid State Chem.* **22**, 353 (1977).
- [3] Y. Kaga, J. Ohno, K. Tsukamoto, F. Uchiyama, M.J. Lain, T. Nakajima, *Solid State Ionics* **40-41**, 1000 (1990).
- [4] P.M. Raccach, J.B. Goodenough, *Phys. Rev.* **155**, 932 (1967).
- [5] P.M. Raccach, J.B. Goodenough, *J. Appl. Phys.* **39**, 1209 (1968).
- [6] M. Itoh, I. Natori, S. Kubota, K. Matoya, *J. Phys. Soc. Jpn.* **63**, 1486 (1994).
- [7] V. Golovanov, L. Mihaly and A. R. Moodenbaugh, *Phys. Rev. B* **53**, 8207 (1996).
- [8] C.N.R. Rao, O.M. Parkash, *Philosophical Magazine* **35**, 1111 (1977).
- [9] S. Sundar Manoharam, K.C. Patil, *J. Solid State Chem.* **102**, 267 (1993).
- [10] F. Licci and T. Besagni, *I.E.E.E. Trans. on Magn. MAG.* **20**, 1639 (1984); F. Licci and T. Besagni, European Patent Application. n° 85830253.2.
- [11] S.R. Jain, K.C. Adiga, V.R. Verneker, *Combust. and Flame* **40**, 71 (1981).
- [12] A. Mineshige, M. Inamba, T. Yao, Z. Ogumi, K. Kikuchi, M. Kawase, *J. Solid State Chem.* **121**, 423 (1996).
- [13] R.D. Shannon and C.T. Prewitt, *Acta Crystallogr. Sect B* **25**, 925 (1969).
- [14] M.A. Señarís-Rodríguez, M.P. Breijo, S. Castro, R. D. Sánchez, J. Mira, J. Rivas, *Boletín de la Sociedad Española de Cerámica y Vidrio* **37**, 25 (1998).
- [15] S. Chikazumi, *Physics of Magnetism*, Chapters. 7 and 10, Krieger Publ. Co., Malabar (Florida) (1986).
- [16] B.D. Cullity in: *Introduction to Magnetic Materials*, Chapter 11, Addison-Wesley Publish. Co. (1972).
- [17] M.A. Señarís-Rodríguez and J.B. Goodenough, *J. Solid State Chem.* **116**, 224 (1995).
- [18] M.A. Señarís-Rodríguez, M.P. Breijo, S. Castro, C. Rey, M. Sánchez, R.D. Sánchez, J. Mira, A. Fondado, J. Rivas, *Proceed. International Conference on Inorganic Materials, Versailles (France) 15-19 September 1998* (to be published).
- [19] R.D. Sánchez, J. Mira, J. Rivas, M.P. Breijo, M.A. Señarís-Rodríguez, *J. Mater. Res.* (1998) (to be published).
- [20] C.H. Ahn, R.H. Hammond, T.H. Geballe, M.R. Beasley, J.M. Triscone, M. Decroux, Fisher, L. Antognazza and K. Char, *Appl. Phys. Lett.* **70**, 206 (1997).
- [21] J. Mira, J. Rivas, M.P. Breijo, M.A. Señarís-Rodríguez, R.D. Sánchez, *Sensors and Actuators A: Physics* (1998) (to be published).
- [22] R. Ramesh, A. Krishnan, D. Keeble, E. Poindexter, *J. Appl. Phys.* **81**, 3543 (1997).

Paper presented at the 5th Euroconference on Solid State Ionics, Benalmádena, Spain, Sept. 13-20, 1998.

Manuscript rec. Sept. 1, 1998; acc. Oct. 19, 1998.