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Phase segregation as origin of magnetoresistance in $La_{0.85}Sr_{0.15}CoO_3$

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Abstract

The $La_{0.85}Sr_{0.15}CoO_3$ compound has been synthesized under different annealing temperatures. It has been observed that the transport properties and magnetoresistance of this compound depend on such temperatures. This response is discussed in the framework of a model of electronic phase segregation.

Keywords: Cobalt oxides; Perovskites; Magnetoresistance; Phase segregation

1. Introduction

In recent years, the physical properties of the manganese perovskites $Ln_{1-x}A_xMnO_3$ have been intensively investigated due to the discovery of colossal magnetoresistance (CMR) in some members of this family [1]. Numerous efforts have been done to characterize and understand this CMR effect. A wide variety of experimental results and theoretical investigations have demonstrated that these materials are electronically inhomogeneous and that phase segregation plays an import role in CMR [2].

$La_{1-x}Sr_xCoO_3$ cobalt perovskites, related to these materials, have similar properties. But changes in their cobalt spin configuration with temperature and Sr doping add a new source

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of variation of their magnetic and transport properties that has attracted considerable interest over the last four decades [3,4]. At low temperature, the parent compound $LaCoO_3$ is a diamagnetic insulator, the Co^{3+} cations are in a low-spin (LS) configuration t^6. Increments of temperature give rise to a progressive conversion from low-spin to higher-spin configurations at around ≈ 35 K [5,6]. Substitution of Sr^{2+} for La^{3+} in $LaCoO_3$ brings about remarkable changes in the system: the $La_{1-x}Sr_xCoO_3$ materials evolve towards a ferromagnetic (FM) and metallic behaviour as x increases. Also, the material segregates into hole-rich, metallic ferromagnetic regions and a hole-poor matrix similar to $LaCoO_3$ [7]. The Co^{3+} ions of the FM phase are in intermediate-spin configurations; the hole-poor matrix experiences a thermally induced spin transition similar to $LaCoO_3$. For low Sr doping ($x < 0.2$), the hole-rich regions are isolated from one another, but for $x \geq 0.2$ the metallic ferromagnetic clusters reach magnetic percolation and the compounds become ferromagnetic cluster-glasses [8]. From the electrical point of view, the $x < 0.2$ compounds are semiconducting, with the electrical conduction modulated by the matrix, and for $x \geq 0.3$ electrical percolation is achieved and the samples are metallic and ferromagnetic.

For intermediate composition $0.2 \leq x \leq 0.3$ insulator–metal–insulator transitions were observed as a function of temperature. In any case, it should be mentioned that in the compositional range $0.1 < x < 0.3$ different behaviours in the magnetic and resistivity properties were obtained by different authors. The origin of these discrepancies has been attributed to the annealing temperature used to prepare these samples and the oxygen content of the sample [9,10].

$La_{1-x}Sr_xCoO_3$ compounds also show magnetoresistive effects (MR), but not as pronounced as in manganese perovskites. Here, again, the phenomenology differs with doping: for the semiconducting $x \leq 0.15$ compounds a large MR is found at low temperature [11,12] whereas for the more conducting samples ($x \geq 0.2$) the magnitude of the MR is typically small [13].

In recent years, the phase segregation (PS) model of the cobalt perovskites has been corroborated by different experimental evidences like transmission electron microscopy [10,14], nuclear magnetic resonance [15] and small-angle neutron scattering [16,17].

In this work, we have focused on the influence of the annealing synthesis temperature on the transport properties and MR of $La_{0.85}Sr_{0.15}CoO_3$. This compound is in the region of isolated clusters and we have found important changes in the PS state and magneto-transport properties as a function of the annealing temperature.

2. Experimental details

$La_{0.85}Sr_{0.15}CoO_3$ samples were prepared by a co-precipitation method using La_2O_3, $Co(NO_3)_2\,6H_2O$ and $SrCO_3$ as starting materials. Dry amounts of La_2O_3 and $SrCO_3$ were dissolved in nitric acid and the cobalt nitrate was dissolved in water. Known volumes of the cobalt solution were then mixed with corresponding lanthanum and strontium nitrate solutions and co-precipitation at $pH = 11$ was achieved by adding aqueous solutions of KOH and K_2CO_3 as precipitating agents. The precipitates were carefully washed, dried, and decomposed at 873 K. The obtained precursor powders were finally heated in air at different temperatures ($T_{ann} = 1273$, 1373 and 1573 K) and then cooled very slowly to room temperature (at 0.3 K min^{-1} down to 973 K and at 0.7 K min^{-1} thereafter).

The samples were characterized by X-ray powder diffraction with a Siemens D-5000 diffractometer using Cu $K\alpha = 1.5418$ Å radiation. According to room temperature powder X-ray diffraction measurements, all compounds are single-phase polycrystalline materials.

Iodometric titrations were carried out to analyze the oxygen content of the materials: the samples were dissolved in acidified KI solutions and the I_2 generated was titrated against a thiosulphate solution; the whole process was carried out under a nitrogen atmosphere.

The electrical resistivity of pressed pellets was measured by a standard four-probe technique using silver paint as contact between the electrode and the sample. The resistivity was measured as a function of temperature in the range $4 \leq T$ (K) ≤ 300 and the magnetoresistance was measured at a constant temperature ($T = 5$, 50 and 100 K) using a magnetic field ranging between 0 and 70 kOe.

Seebeck coefficients were measured in the temperature interval $77 \leq T$ (K) ≤ 300 using a homemade device similar to the one described in Ref. [18].

3. Results

The resistivity of the $x = 0.15$ samples annealed at $T_{ann} = 1273$, 1373 and 1573 K is shown as a function of temperature in Fig. 1. The three samples show a semiconducting behaviour, with a marked increase of resistivity below ≈ 50 K.

In addition, whereas at the lowest temperatures the resistivity of the three samples shows no significant differences, for $T \geq 50$ K the sample annealed at 1573 K shows the highest resistivity, while the sample annealed at 1373 K shows the lowest resistivity.

Measurements of thermoelectric power versus temperature $\alpha(T)$ are shown in Fig. 2. The different α values obtained for the three samples reveal a different number of positive charge carriers that are mobile at long range: highest in the case of the sample annealed at 1273 K and lowest for $T_{ann} = 1573$ K.

We have also studied the influence of the magnetic field on the resistivity of these samples, and we have observed that it is the physical property that is more affected by the annealing temperature.

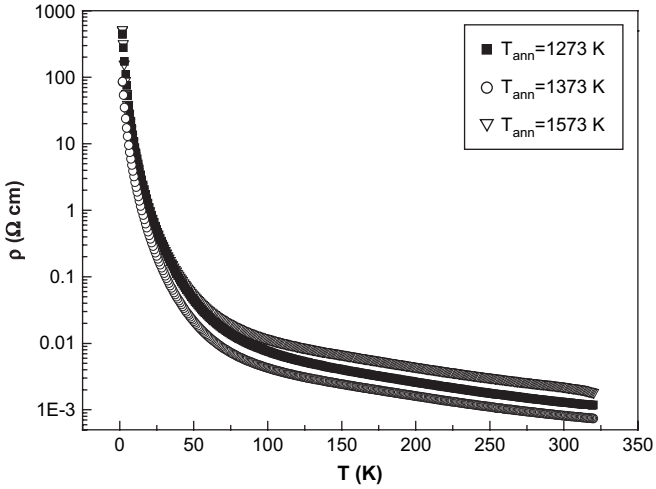

Fig. 1. Electrical resistivity versus temperature curves of the $La_{0.85}Sr_{0.15}CoO_3$ compound treated at different annealing temperatures $T_{ann} = 1273$, 1373 and 1573 K.

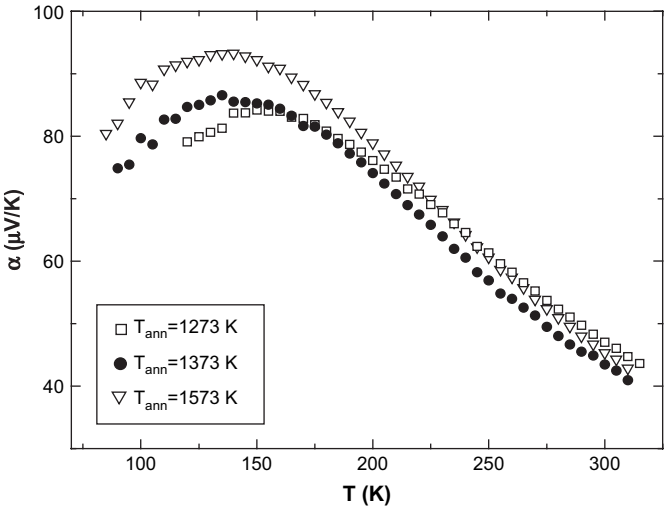

Fig. 2. Temperature dependence of the Seebeck coefficient (α) of the $La_{0.85}Sr_{0.15}CoO_3$ treated at different annealing temperatures.

In general, we observe that the magnetoresistance MR ($(\rho_{H\neq 0} - \rho_{H=0})/\rho_{H=0}$) of these samples increases as temperature decreases so that the highest MR $\approx$ 60% is found at $T = 5$ K under a field of 70 kOe, see Fig. 3.

As for the influence of the annealing temperature on the MR of the samples, it is particularly important for $T \geq 50$ K, see Fig. 3. The sample annealed at 1573 K always shows the highest MR, which is up to 30% higher than that of the sample with $T_{ann} = 1273$ K.

4. Discussion

As we have indicated previously, the $La_{0.85}Sr_{0.15}CoO_3$ sample segregates into hole-rich clusters (metallic ferromagnetic regions) and a hole-poor matrix similar to $LaCaO_3$ [6]. Inside the hole-rich regions, ferromagnetic coupling through Co^{4+}–O–Co^{3+} superexchange interactions or by double-exchange interactions, gives rise to the superparamagnetic behaviour observed below $T_c \approx 240$ K. Furthermore, the hole-rich clusters stabilize high-spin (HS) $t^4\ e^2$ or intermediate-spin (IS) $t^5\ e^1\ Co^{3+}$ at the interface of the hole-poor matrix, and the magnetic coupling between superparamagnetic regions is antiferromagnetic via superexchange interactions between the Co^{3+} cations in HS or IS. Since the superparamagnetic clusters are distributed randomly, frustration in the intercluster exchange interactions leads to noncollinear orientations of the cluster moments and a huge anisotropy below a magnetic blocking temperature $T_g \approx 70$ K. From the electrical point of view, this compound is semiconductive and the electrical conduction is modulated by the matrix, which experiences a spin state transition with temperature.

In this work, the key point is to identify what is changing with the annealing temperature and what gives rise to such interesting variation in the transport properties, especially in the magnetoresistance of these samples.

We have previously studied the evolution of the magnetic properties of $La_{0.85}Sr_{0.15}CoO_3$ as a function of annealing temperature (T_{ann}) [10,14]. From those studies we concluded that the

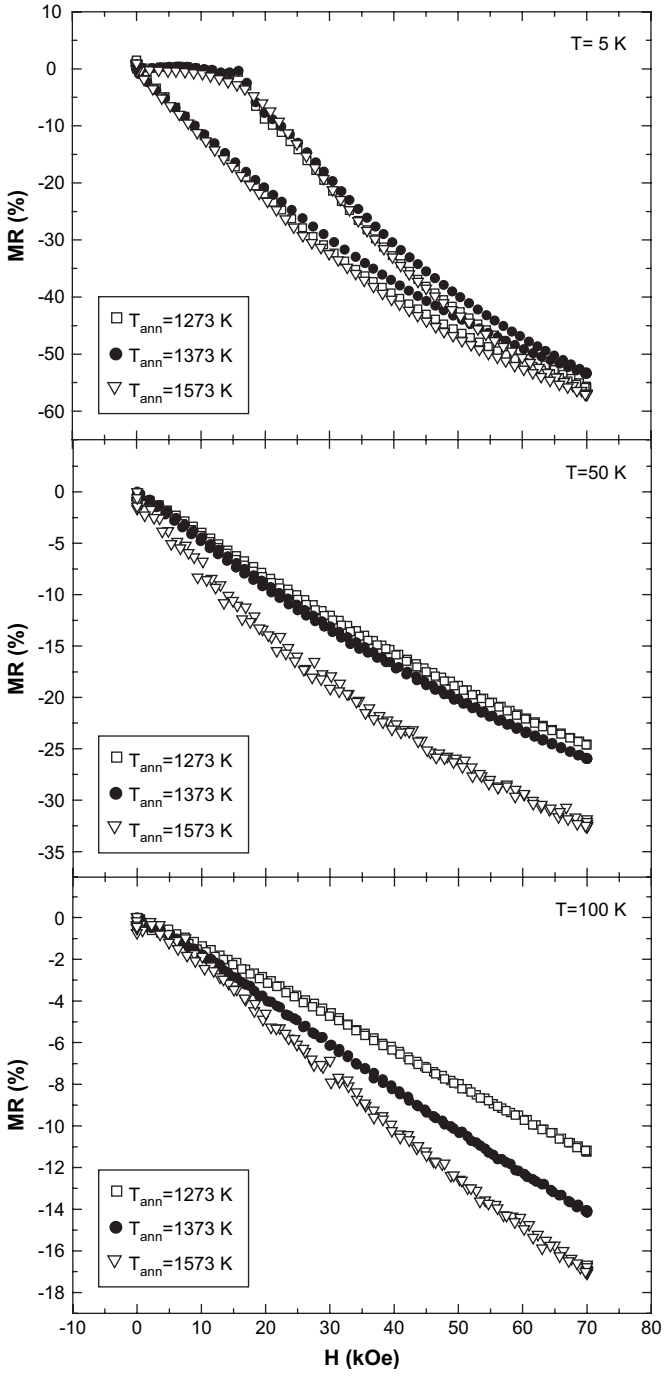

Fig. 3. Magnetoresistance versus magnetic field of these samples measured at several temperatures: 5, 50 and 100 K.

annealing temperature influences the intrinsically inhomogeneous electronic structure of this compound and that charge-carrier redistribution takes place as T_{ann} increases.

Concomitantly, from the magnetic point of view, for low T_{ann} the ferromagnetic hole-rich regions are of heterogeneous size and some even form interconnected magnetic clusters, see Fig. 4(a). Meanwhile those annealed at highest temperatures comprise isolated clusters of homogeneous size within a paramagnetic hole-poor matrix, see Fig. 4(b).

Now we see that important changes take place also from the electrical point of view, both in the intragranular and in the intergranular conduction. In this context, the Seebeck results reveal that the number of charge carriers decreases as the annealing temperature increases. This is most probably related to the increasing tendency of the samples to lose oxygen as T_{ann} increases, even if the differences are small as inferred from the variation of the Seebeck coefficient. It should also be mentioned that, according to iodometric titrations carried out in these samples, they are all oxygen stoichiometric. Nevertheless, as the samples annealed at higher temperature only dissolve in more acidic conditions, in which the experimental error increases, there can be a slight oxygen-deficiency in these samples with respect to those annealed at lower temperature.

It must be noted that physical properties like resistivity and Seebeck coefficient are very sensitive to slight variations in the oxygen stoichiometry.

On the other hand, in the case of the electrical conductivity, higher annealing temperatures imply larger particle size, better sintering and more homogenous distribution of metallic FM clusters giving rise to better (inter/intra)granular conductivity for the sample annealed at 1573 K, followed by the one at 1373 K.

The observed variation of the conductivity data as a function of T_{ann} is the result of a balance between the previous factor and the charge carrier concentration in the sample, that combined, gives the lowest resistivity for the sample annealed at 1373 K and the highest for the sample annealed at 1573 K, where the smaller number of charge carriers predominates.

Concerning MR, we have observed two different responses: one at $T = 5$ K and another at $T = 50$ and 100 K.

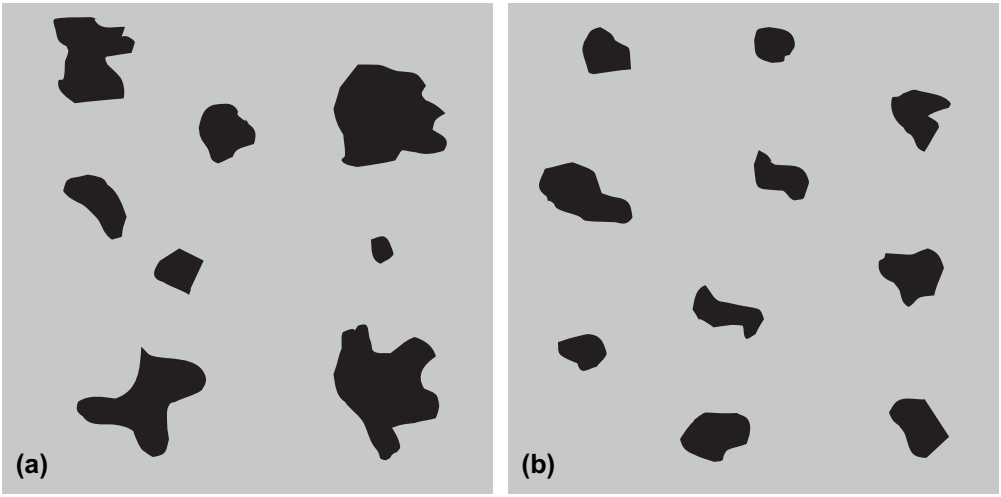

Fig. 4. Schematic representation of the phase segregation present in this compound: (a) in samples annealed at lower temperatures ($T_{ann} = 1273$ and 1373 K) and (b) in the sample annealed at higher temperature ($T_{ann} = 1573$ K). Dark grey: hole-rich metallic ferromagnetic regions; light grey: hole-poor paramagnetic and semiconducting regions.

At 5 K we have observed that the MR value is the highest and almost the same for the three samples. Below 35 K, the holes are trapped in the superparamagnetic clusters and there are few charge carriers mobile at long range. The matrix, where all Co^{3+} cations are in low-spin configuration, is insulating and does not allow electrical connection among the clusters. The application of magnetic field increases the size of the hole-rich regions and the hopping probability of the charge carriers, which implies a decrease in the resistance.

In a recent work Wu et al. [17] have found that, in $La_{0.85}Sr_{0.15}CoO_3$ single crystals, there is a good correlation between MR and cluster size as a function of temperature; the MR increases as the cluster size increases. This does not happen below 35 K, where the cluster size decreases and the MR increases sharply. Wu et al. [17] did not explain this result, but we suppose that the cluster size decreases because, at this temperature and without applied magnetic field, the LS–Co^{3+} is more stable than the IS–Co^{3+}. In such a case, a large magnetic field can induce a spin transition in the Co^{3+} cation from LS to IS [19,20], so that the magnetic field has greater influence on the resistance at these temperatures.

Another important feature of this low temperature region is that the FM clusters are isolated and the intercluster interaction is not possible. Wu et al. [17] argued that this system is a natural analogue of the artificial structures fabricated by depositing nanoscale FM particles in a metallic or insulating matrix, as the MR of these composites shows the same features of the low-doped cobaltites, such as hysteretic MR.

At higher temperatures, 50 and 100 K, the MR is very sensitive to the annealing temperature of the sample and it increases when the system presents a homogenous distribution of FM clusters. At these temperatures, intercluster interactions are possible because, as temperature raises, the concentration of IS/HS–Co^{3+} cations in the matrix increases, and this allows the movement of holes through the matrix. Also, as the annealing temperature increases and the samples present a more homogenous electronic structure, the intercluster interactions increase due to the fact that the hole-rich regions are closer to each other. These facts seem to indicate that this interaction plays an important role in the MR of this compound at temperatures higher than 35 K.

The application of a magnetic field induces an alignment of the magnetic clusters in the direction of the magnetic field. We suppose that intercluster interactions would collaborate with the external magnetic field in the alignment of the FM regions. Consequently, the spin-dependent transport between FM clusters is reduced and a higher MR is observed.

In summary, we have induced without any compositional modification important changes in the magneto-transport properties of the $La_{0.85}Sr_{0.15}CoO_3$ compound. In this work we have shown the strong influence of the phase segregation state in the physical properties of the $La_{1-x}Sr_xCoO_3$ perovskite.

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