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Comparison between magnetic and electrical properties of La$_{1-x}$Sr$_x$CoO$_3$ $(0 < x \leqslant 0.50)$ particles obtained by different synthesis methods

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Abstract

We have prepared polycrystalline La$_{1-x}$Sr$_x$CoO$_3$ $(0 < x \leqslant 0.50)$ particles using the ceramic method and other alternative soft-chemistry techniques that yield materials with smaller particle size. The study of their magnetic and electrical properties shows differences between these series of samples, among them: changes in the compositional range for ferromagnetic behaviour, magnetic hardening as the particles get smaller; different composition for the metal–insulator transition, and changes in the conduction regime in the semiconducting interval. We try to interpret these differences taking into account the inhomogeneous electronic structure of these doped cobaltates. © 1998 Elsevier Science B.V. All rights reserved.

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LaCoO$_3$ is a semiconductor with perovskite structure which presents additional complexities with respect to other transition metal oxides. These complexities are due to the variation of the spin state of the Co ions [1]. Partial substitution of La^{3+} with Sr^{2+} introduces very important changes in the system: although LaCoO$_3$ presents high electrical resistivity and antiferromagnetic exchange interactions, La$_{1-x}$Sr$_x$CoO$_3$ with $0 < x \leqslant 0.50$ evolves to a ferromagnetic and metallic behaviour. Recent studies have shown the complexity of such evolution [2]. Therefore, although from a crystallographic point of view the samples contain a unique phase, from an electronic point of view they are inhomogeneous: upon Sr^{2+} doping, the materials segregate into hole-rich regions, which are ferromagnetic and metallic, and a hole-poor matrix similar to the undoped compound [2]. The higher the degree of doping, the stronger the interactions between the hole-rich regions, and several magnetic

(superparamagnetism, spin-glass, spin-cluster, etc.) and electrical behaviours (semiconductor, metal–insulator transitions, metallic) are shown by the material [2]. As the degree of interaction between such regions depends not only on the total number of holes in the sample (doping degree) but also on the size and distribution of clusters within the material, the electrical and magnetic behaviour of these materials should be very much influenced by factors affecting those, among them the particle size of the samples. In order to analyze this problem we have prepared the series La$_{1-x}$Sr$_x$CoO$_3$ with $0 < x \leqslant 0.50$ using the ceramic method (CER), and the combustion (COMB), coprecipitation (COP) and nitrate decomposition (NIT) methods (COP for samples with $0 < x \leqslant 0.36$ and NIT for doping values $0.36 < x \leqslant 0.50$). These latter methods allow a synthesis at lower temperatures, producing materials of smaller particle size. From X-ray diffraction, the four methods yield crystalline and single-phase materials. Depending on the synthetic method, we obtain materials with different particle size and morphology: CER samples: $1 < d$ (μm) < 5; COP and NIT samples: $0.7 < d$ (μm) < 0.9 and COMB samples $0.2 < d$ (μm) < 0.3. According to the magnetic

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behaviour we can distinguish two regimes in the $La_{1-x}Sr_xCoO_3$ series: (a) For CER and COP samples with $0 < x \leqslant 0.15$ and COMB with $0 < x \leqslant 0.10$, magnetic ordering within the hole-rich regions takes place at a temperature $T_c = 240$ K; at a temperature $T_g < T_c$ blocking of clusters occurs and for $T < T_g$ an independent field cooled magnetization typical of a spin-glass behaviour is observed [2, 3] (Fig. 1). Also, for COP and COMB samples a shoulder at temperatures $T_g < T < T_c$ is observed (Fig. 1). (b) For CER, COP and NIT samples with $0.20 \leqslant x \leqslant 0.50$, and COMB ones with $0.15 \leqslant x \leqslant 0.50$ long range ferromagnetic ordering is established below T_c. This temperature essentially remains constant. From M vs. H measurements the COMB samples show larger values of remanence and coercivity than the CER, COP and NIT ones, indicating a magnetic hardening with respect to those. Also, for a same doping value, the differences between zero-field-cooled (ZFC) and field-cooled (FC) DC magnetizations increase when going from CER to COP and NIT to COMB samples, as show in Fig. 1. From the electrical point of view a transition from a semiconducting to a metallic regime is observed upon doping (Fig. 2). The composition at which this transition takes place depends on the synthetic method used. For example, while for CER materials $x \leqslant 0.15$ samples are semiconducting and $x \geqslant 0.20$ are metallic, for the COP ones with $0.20 \leqslant x < 0.30$ samples show a reentrant metallic behaviour (Fig. 3) and are only metallic for $x \geqslant 0.36$.

We have synthesized samples with the same nominal composition but different particle size. As particles get smaller magnetic processes become more irreversible, as it can be seen from the difference between FC and ZFC curves. It seems that particle size reduction enhances interactions between the ferromagnetic clusters embedded in the $LaCoO_3$ matrix. It is worth noting that, for low doping and in samples with smaller particle size, clusters seem to interact appreciably between T_g and T_c, as deduced from the shoulder observed in Fig. 1. Also, in
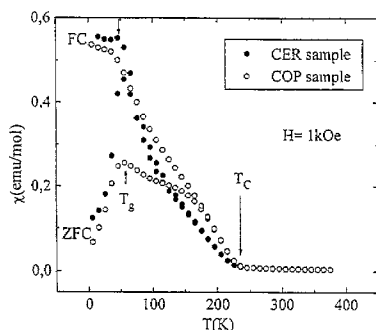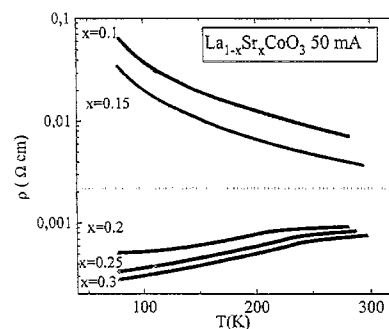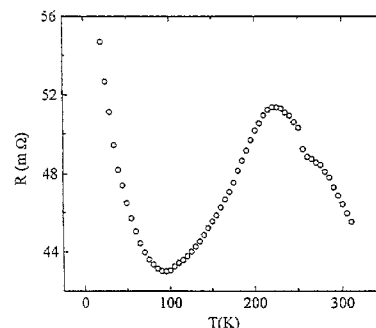
Fig. 2. R vs. T for $La_{1-x}Sr_xCoO_3$ CER samples.

Fig. 3. Semiconducting–metallic behaviour of the COP $La_{0.75}Sr_{0.25}CoO_3$ sample.

the COMB samples magnetic percolation is already achieved at $x = 0.15$ while for the others is not until $x = 0.20$. Once the magnetic percolation has taken place in all the samples ($x \geqslant 0.20$) magnetic hardening is detected due to reduction of magnetic domains caused by a smaller particle size. As for the electrical behaviour, different particle size (differences in grain boundaries) together with differences in size and distribution of the clusters within the matrix can account for the observed differences.

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Fig. 1. FC and ZFC DC susceptibilities of $La_{0.90}Sr_{0.10}CoO_3$ CER and COP samples.