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Effects of aging on the electrical resistivity of $La_{1-x}B_xCoO_3$ perovskites (B = Sr, Ca, Ba; $0.20 \leq x \leq 0.30$)

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Abstract

A study of the reliability of the title compounds as a basis for magnetoresistive sensors is presented. For this purpose we have carried out long-term systematic studies of the evolution of the resistive and magnetic properties of samples synthesized by both ceramic and wet chemical routes, allowing them to age during several months. It is observed that, although the magnetic properties remain unaltered, their resistivity does change appreciably. With time, samples that are initially metallic over all the measured temperature range ($T < 300$ K), change to semiconductor-like behaviour at low temperatures and above their ferromagnetic to paramagnetic phase transition temperature, giving rise to a 'reentrant semiconducting behaviour' with associated high electrical noise, relaxation effects of the resistivity and even diodic behaviour.

Keywords: Aging effects; Perovskites; Oxygen stoichiometry; Magnetoresistance

1. Introduction

The topic of magnetic field sensing has experienced a notable activity in the last decade, since the discovery by Baibich et al. of high magnetoresistance in antiferromagnetically coupled multilayers [1]. Later on, the finding of a huge magnetoresistance (or 'colossal magnetoresistance', CMR) in Mn-based perovskites $LaMnO_3$ [2,3] attracted many physicists on the phenomenon and on other related materials with other 3d transition metals than Mn which had been already studied in the fifties [4,5].

Among perovskites $LaCoO_3$ has an unique behaviour which lies on the changing nature of the Co^{3+} spin state [6]. Upon Sr doping the material starts to segregate into hole-rich metallic ferromagnetic clusters and a hole-poor $LaCoO_3$-like matrix that mediates the interactions among the clusters [7]. At $x = 0.20$ a magnetic percolation threshold is reached and the system shows bulk ferromagnetism below $T_c \sim 240$ K [8]. They also show negative MR [9], but it is only as high as $\approx 8\%$ for $La_{0.7}Sr_{0.3}CoO_3$ [10]; however, the MR effect is linear with the applied field for a wide field range and MR does not saturate at least below 70 kOe [11]. This has prompted proposals for the application of $La_{0.7}Sr_{0.3}CoO_3$ as a low temperature linear magnetic field sensor [11]. Here we focus on the reliability of the title compounds for their use as a basis of magnetic field sensors.

2. Results

Polycrystalline single-phase samples were prepared by different routes leading to diverse particle sizes. In Fig. 1 we show the resistivity vs. temperature curves of a large-grain-size $La_{0.80}Sr_{0.20}CoO_3$ sample, measured in the as-prepared material (A), seven months later (B) and ten months later (C). Initially the compound is metallic, and presents the typical change of slope below T_c due to magnon scattering of the carriers in the magnetically ordered phase [12]. But, with time the metallic behaviour is lost at low temperatures and above T_c. Magnetization data taken in the same period do not show significative changes. Also, from a crystallographic point of view the sample did not experience any structural modification (as shown by its X-ray diffraction pattern).

This evolution is faster in samples of smaller grain size, as seen in Fig. 2, for $La_{0.70}Sr_{0.30}CoO_3$. In this case a

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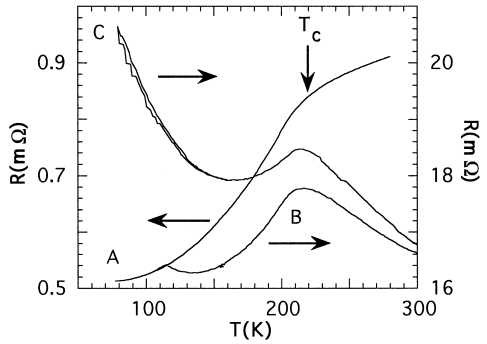

Fig. 1. Electrical resistivity versus temperature curve of large-grain-size $La_{0.8}Sr_{0.2}CoO_3$ measured for the as-prepared sample (A), seven months later (B) and ten months later (C). Horizontal arrows mark the corresponding scales. Note the presence of a change of conduction regime at T_c.

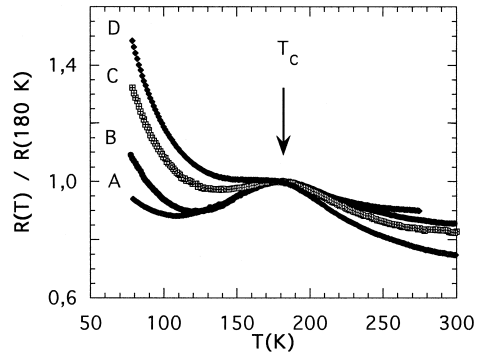

Fig. 3. Normalized electrical resistivity versus temperature curve of $La_{0.8}Ba_{0.2}CoO_3$ at several stages, taken every two months, from the as-prepared stage (A) to the six-month-old one (D). The ferromagnetic transition temperature (T_c) for this sample is marked with an arrow.

metallic regime is found for the as prepared sample, but after five months (curve D) metallic behaviour is lost above T_c; then there is a transition to a metallic regime and again an upturn to semiconductive behaviour at low temperatures. For some compositions, a similar tendency is observed in the as-prepared samples, with a clear semiconductor behaviour above T_c, composing what we have named 'reentrant semiconducting behaviour' (RSB). $La_{0.80}Ba_{0.20}CoO_3$ and $La_{0.70}Ca_{0.30}CoO_3$ belong to this group. In such a case the final evolution is towards a pure semiconductive behaviour over the whole temperature range, as seen in Fig. 3 for $La_{0.80}Ba_{0.20}CoO_3$; A corresponds to the initial measurement, and B, C and D to runs taken after two, four and six months respectively. We have measured the magnetoresistance in steps C and D at the temperatures where differences between $R(H=0)$ and $R(H=5$ kOe) are a maximum. In Fig. 4a we show the magnetoresistance for the C stage; a strong electrical noise is seen. Once the RSB is lost, i.e., the intermediate metallic regime is lost (case D) the MR was measured again and it was seen that the electrical noise is considerably reduced (Fig. 4b). Materials that show RSB also display other unusual properties besides high electrical noise. One of them is a different value of resistivity depending on the sign of the applied measuring electrical intensity. The change of resistivity when inverting the sign of the electrical intensity is not immediate, but presents a time dependent relaxation. In $La_{0.80}Ba_{0.20}CoO_3$ for example, to recover the resistivity measured before the current switch a time of about 600 s is needed. It is worth noting that interface effects between sample and electrical contacts (used for the resistivity measurements) must be discarded. To ensure this point, the silver paint contacts used initially were renewed after detecting changes in resistivity and, in

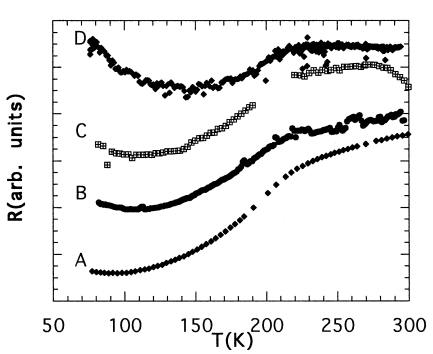

Fig. 2. Electrical resistivity versus temperature curve of small-grain-size $La_{0.7}Sr_{0.3}CoO_3$ at several stages, going from the as-obtained sample (A) to a five-month-old one (D).

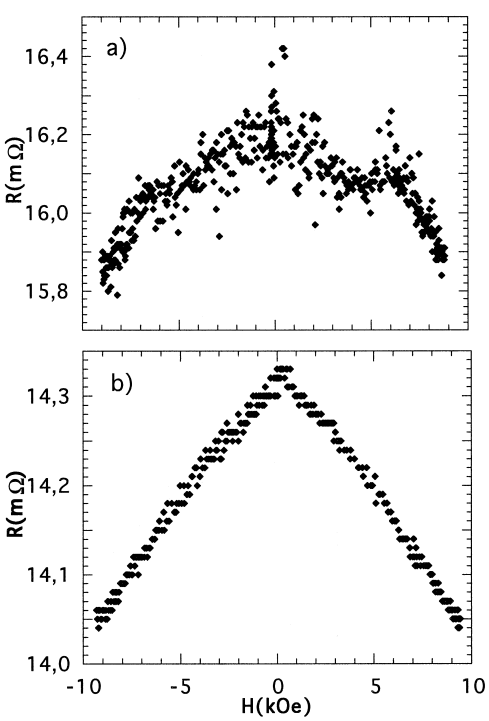

Fig. 4. Magnetoresistance of the $La_{0.8}Ba_{0.2}CoO_3$ sample, when it presented RSB (a) and after becoming completely semiconductive (b). In both cases MR is measured where $R(H)$ vs. T curves at $H=0$ and $H=5$ kOe display the maximum difference.

some cases they were replaced by four new contacts, pressing metallic indium or sputtering gold onto the sample. In all the cases new thermal treatments followed by slow cooling in air to room temperature made the samples return to the initial conditions.

3. Discussion

The main requirement for a practical magnetic field sensor is reproducibility. In this work a long term storage test evidences important variations in the electrical properties of Co-based perovskites. It must be noted the recovering of initial properties of the material after new thermal treatments at high temperature followed by a slow-cooling to room temperature so as to ensure the right oxygen stoichiometry. This suggests that oxygen content plays a crucial role on the electrical properties of these cobaltites. This dependence has already been detected in electrodes made with the parent compound $La_{0.5}Sr_{0.5}CoO_3$ [13], for which a slow cooling in an oxygen deficient atmosphere led to pure semiconducting phases. Here in addition, we see RSB in some stages of the samples. This peculiarity had already been reported by Señarís Rodríguez and Goodenough in Sr-doped cobaltites [8] and attributed to the changing spin state of the $LaCoO_3$-like hole-poor phase segregated in it. The small energy gap between low spin (t^6e^0, $S = 0$) and high-spin (t^4e^2, $S = 2$) configurations (in the order of 0.03 eV) allows a thermally activated increase of the population of the latter one, taking place gradually in the temperature range 35–100 K, until a 50:50 ratio is achieved. This rate is maintained up to 300 K; in between a dynamic fluctuating equilibrium between high-spin and low-spin Co^{3+} ions is established [6]. Just below T_c the ferromagnetic metallic regions percolate magnetically, but they are embedded in the $LaCoO_3$-like matrix, that contains a certain proportion of high-spin Co^{3+} ions, i.e., with carriers in the conducting e-bands, enabling conduction. But below 100 K the decreasing population of high-spin ions reestablishes a semiconducting dependence. Oxygen deficiencies would have the effect of decreasing hole carriers (two holes lost per oxygen vacancy) and therefore would decrease conductivity. Oxygen losses are favoured by smaller particle sizes. It is reasonable to think that a higher surface/volume ratio for smaller particle sizes enables a faster reducing process.

In summary, we conclude that possible users of Co-based perovskites as magnetic field sensors or other applications should be aware of the variable conduction character of these materials, tending to reentrant semiconducting behaviours that, among other features, present a very noisy magnetoresistive effect. Probably a protective coating should be provided for the use of these perovskites to guarantee long-term storage stability.

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Biographies

J. Mira was born in Baio, Spain, in 1968. He received the B.S. and M.S. degrees in physics from the University of Santiago de Compostela in 1991 and 1992, respectively, and the PhD and European PhD degrees in physics from the same university in 1995. He is currently Assistant Professor at the Faculty of Physics at the University of Santiago de Compostela. His topic of research involves the study of magnetic materials and magnetism in solids. He published more than 40 scientific papers.

J. Rivas was born in Lugo, Spain, in 1947. He received the PhD degree in physics from the University of Valladolid, Spain, in 1973. He has been a research worker at the Max-Planck-Institut, Stuttgart, Germany (1974–1975), and Assistant Professor at the Universities of Valladolid and Murcia, Spain (1975–1981). Since 1981, he has been Professor of Physics at the University of Santiago de Compostela. His topic of research involves the study of magnetic materials, on which he has published more than 100 scientific papers.

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