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Influence of the grain-size and oxygen stoichiometry on magnetic and transport properties of polycrystalline $La_{0.67}Ca_{0.33}MnO_{3\pm\delta}$ perovskites

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Abstract

Effects of grain size and oxygen stoichiometry in sol-gel and ceramics samples of $La_{0.67}Ca_{0.33}MnO_{3\pm\delta}$ have been studied. Grain size (90 nm versus > 10 µm) does not change either the Curie temperature ($T_{\rm C}$) or the metal-insulator transition temperature ($T_{\rm M-I}$), but great differences in low-field magnetoresistance are observed. These differences have been explained by a spin polarized tunneling model for conduction between grains. Oxygen content (δ) could be changed in La deficient samples via an electrochemical method at room temperature (i.e., without changing grain size). We observe great differences in $T_{\rm M-I}$ when decreasing δ , while $T_{\rm C}$ remains unchanged. Broken ways between Mn ions leads to zones with ferromagnetic behavior, but inhibits conductivity. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Hole doped manganite oxides based on the mother compound $LaMnO_3$ attract renewed attention due to the colossal magnetoresistance (CMR) effects observed close to the metal-insulator

transition temperature (T_{M-I}) [1–4]. The double exchange interaction between pairs of Mn³⁺ and Mn⁴⁺ ions is expected to be responsible for the ferromagnetic and metallic properties in these compounds [5–7]. The eg electron in Mn³⁺ is able to move between neighboring cations with parallel alignment of their spins (Hund's coupling), leading to the characteristic metallic behavior in the ferromagnetic state. From the basis of this double exchange theory, it is easy to understand the close

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coupling between the structural, magnetic and electronic properties of these compounds [8–10]. This mechanism also explains qualitatively why a magnetic field decreases the resistivity near Curie's temperature (T_c) via enhancement of spin ordering [11]. Therefore, it is not surprising that the doping level in the La site, as well as the oxygen content, play an important role in the magnetic and electronic properties of these oxides as the Mn³⁺/Mn⁴⁺ ratio changes [12,13].

Recently, the dependence of magnetic and electrical properties on oxygen stoichiometry [12,13] and grain boundaries [14–17] in polycrystalline $La_{1-x}A_xMnO_3$ (A = Ba,Ca,Sr) have been discussed. These works suggest that the ferromagnetic transition temperature and the resistivity peak shift to lower temperatures with the increase of oxygen deficiency for $La_{0.67}(Ba,Sr)_{0.33}MnO_{3-\delta}$. The metallic resistivity also increases with decreasing oxygen content, suggesting that oxygen deficiency plays an important role in the resistivity behavior.

On the other hand, T_{M-I} is supposed to decrease with decreasing grain size. The total resistivity is assumed to be the sum of the bulk grain resistivity and the intergrain boundaries resistivity [14,17]. The grain boundary resistivity is much larger than the bulk one, and the peak in the grain boundary resistivity occurs well below $T_{\rm C}$. It has been suggested [14–17] that these two effects are responsible for the large differences observed in the magnetic and electric transition temperatures in polycrystalline samples, but there is no general agreement for this explanation. Hwang et al. [18] have found that the negative MR in single crystals is due to the suppression of spin fluctuations, and magnetic domain boundaries do not dominate the scattering process. However, for the polycrystalline samples, the MR is dominated by spin-polarized tunneling between grains.

The main goal of this paper is to test, in a strictly separated way, the concrete role of oxygen stoichiometry and grain size in the magnetotransport of $La_{0.67}Ca_{0.33}MnO_{3\pm\delta}$. Perfect oxygen homogeneity is difficult to achieve, especially in small grain size samples. Otherwise, classical methods to alter oxygen content implies high temperatures that can change grain size. Both effects can be present simultaneously, giving rise to contradictory results.

To clarify the influence of grain size, we have prepared ceramic and sol-gel samples of $La_{0.67}Ca_{0.33}MnO_{3\pm\delta}$ with large differences in their grain size [19,20]. Electrochemical treatments of sol-gel samples alters the oxygen content close to room temperature (50°C). Due to the low temperatures required, this technique is proposed as a useful tool to study the effect of the oxygen stoichiometry in small particles without affecting their grain size.

2. Experiment

 $La_{0.67}Ca_{0.33}MnO_3$ ceramic reference samples were prepared from high purity oxides (CaO, La_2O_3 , MnO and MnO₂, 99.995% of purity at least for all of them) by solid-state reaction. Several heating and griding steps were realized, with a final sintering temperature of 1300°C for 100 h in a static air atmosphere.

Small particles were prepared via sol–gel method by dissolving a stoichiometric mixture of nitrates of the cations and using urea as the geling agent [20]. This method has been optimized to obtain best homogeneity and a faster crystallization. The gel was decomposed during a period of 3 h at 250° C in a static air atmosphere. This precursor was calcined at 800° C for 3 h. X-ray analysis reveals the formation of La_{0.67}Ca_{0.33}MnO₃ after this step, and only small amounts of spurious phases. This powder was ground, pelletized and reheated for another 5 h. Final step temperatures were changed from 450 to 800° C in order to obtain a series of increasing particle sizes (Fig. 1).

Structure was checked in all the cases by X-ray diffraction and no secondary phases were detected at the final stage of the reactions. The oxygen content (δ) was determined by iodimetric titrations [21]. Ceramic and sol-gel samples show the same oxygen stoichiometry in all cases ($\delta = 0.00$).

Particle and crystallite size in the different steps for the samples were determined by scanning electron microscopy (SEM) (Fig. 2) and by means of Scherrer formula by measuring the half-peak width



Fig. 1. Sintering temperature dependence of crystalline size for sol-gel samples of $La_{0.67}Ca_{0.33}MnO_3$.

of the line in X-ray diffraction patterns:

$$D = \frac{0.9\lambda}{\beta\cos\theta},\tag{1}$$

where *D* is the diameter of the crystallite in Å, β is the difference of the width of the half-maximum of the peaks between the standard of KCl used to calibrate the intrinsic width associated to the equipment, and λ is the wavelength of the X-rays.

Particle size shows great differences between 50 nm for the smallest sol-gel samples and $>10 \ \mu$ m in the case of ceramics.

To carry out the electrochemical treatment, cyclic voltametries were performed in order to obtain the oxidation/reduction potentials of Mn³⁺/Mn⁴⁺ giving values of 0.570 and -0.189 V, respectively. For the electrochemical potentiostatic experiments the working electrode was a disk of 13 mm diameter $\times 1$ mm thickness. A platinum wire and an Ag/AgCl were used as the counterelectrode and reference electrode, respectively. The electrolytic solution, in continuous stirring, was 1 M NaOH. Working electrodes were attached to a platinum wire using silver paint fully covered with epoxy resin and teflon files. The exposed area was the same for all the pellets studied (1.5 cm^2) . A potentiostat was used to keep the potential between working and reference electrodes constant.

Magnetic measurements were performed in a vibrating sample magnetometer (VSM) in zero field



Fig. 2. SEM photograph for samples of $La_{0.67}Ca_{0.33}MnO_3$ with different grain sizes. (a) Sol–gel sample sintered at 800°C with grain size around 90 nm. (b) Ceramic sample with all their grains bigger than 10 μ m.

cooling (ZFC) conditions, from 77 to 400 K, (H = 5 kOe). Electrical DC resistivity and magnetoresistance were measured in the range 77–300 K using the standard four-probe method in fields up to 5 kOe.

3. Results and discussion

3.1. Grain size dependence

To study the dependence of magnetic properties with grain size, we have measured magnetization as a function of temperature in sol-gel and ceramic samples. Both samples show the same Curie temperature (~ 265 K), defined as the peak in the derivative of the magnetization curve (Fig. 3). However, the magnetization is larger in the ceramic sample, where the theoretical value of saturation is reached at 77 K, due to its much larger crystalline size.

Both ceramic and sol-gel samples with exactly the same oxygen stoichiometry show the same $T_{\text{M-I}}$, which is close to the T_{C} value, in spite of the large grain differences (Fig. 4). This result is against previous works done by other authors [14–17]. The reason for this discrepancy is probably the fact that, as we said, oxygen stoichiometry is difficult to obtain in small grain samples, and both effects (size and oxygen stoichiometry) could be mixed. So, from our results, it seems that the grain size is not the key parameter determining $T_{\text{M-I}}$.

However, as it is clearly seen, differences in grain size play an important role in the resistivity



Fig. 3. Temperature dependence of magnetization for sol-gel samples sintered at 800°C (open circles) and ceramic samples (open squares) of La_{0.67}Ca_{0.33}MnO₃. Inset: derivative of magnetization versus temperature for the two samples. From the derivative of the magnetization it is clear that the Curie temperature is the same for the two samples, $T_{\rm C} = 265$ K.



Fig. 4. Temperature dependence of reduced resistivity for sol-gel sample sintered at 800°C and ceramic samples of La_{0.67}Ca_{0.33}MnO₃. Metal-insulator transition temperature is the same in both cases, $T_{M-I} = 266$ K.

behavior:

- The residual resistivity is larger in the sol-gel samples, being twice the value of the ceramic close to metal-insulator transition.
- Sol-gel samples show a wider metal-insulator transition in temperature.

The temperature behavior of the MR% is clearly different for the two samples (Fig. 5). The ceramic sample shows a sharp peak ($\sim 7\%$ at 1.5 kOe) in $T_{\text{M-I}}$, characteristic of an intrinsic CMR in double exchange (DE) perovskites. The sol-gel samples do not show this peak, but the MR% below the transition temperature is always larger than for ceramic samples, increasing this difference toward lower temperatures.

A plausible explanation of this fact could be that the magnetic order extends to different lengths in the ceramic and sol–gel samples. The ceramic sample shows a longer ferromagnetic correlation range than the sol–gel one, due to the presence of spin disorder at the grain boundaries. However, we could not overlook completely the chemical disorder (but retaining stoichiometry) in the sol–gel samples, that could lead to a similar result. Nevertheless, according to the analysis done in our samples, we believe that this is negligible with respect to



Fig. 5. Temperature dependence of %MR at 5 kOe for sol-gel samples sintered at 800°C and ceramic samples.

spin disorder. Moreover, sharp peaks in the MR versus temperature curves have been observed for single crystal samples [22–24], without grain boundaries and with very long range magnetic order. The large percentage magnetoresistance at low temperature is attributed to spin-polarized tunneling at grain boundaries, as it will be discussed.

Low-field magnetoresistance can be explained successfully in terms of ferromagnetic grains with no parallel magnetic moments. The influence of spin-polarized tunneling in the magnetoresistance properties was first studied on granular metallic films [25–28], but applied later in perovskite oxides [18,29]. Low-field magnetoresistance can be fitted to the equation:

$$\frac{\Delta\rho}{\rho_0} = -\left(\frac{JP}{4k_{\rm B}T}\right) [m^2(H,T) - m^2(0,T)],\tag{2}$$

where J is the intergrain exchange constant, P the electron polarization (\cong 1) [30,31], and m the magnetization normalized to the saturation value. The high spin polarization degree is one of the reasons why low field MR is so important in manganese perovskites.

Starting from magnetization loops (Fig. 6) and using J as an arbitrary fitting factor, we have obtained theoretical approximations to experimental magnetoresistance data. The M versus H curves of the sol-gel samples show a pronounced hysteresis,



Fig. 6. Hysteresis loops for samples of $La_{0.67}Ca_{0.33}MnO_3$ at various temperatures from 77 to 225 K. (a) Sol–gel sample sintered at 800°C. (b) Ceramic sample.

with larger coercive fields. In spite of the differences, theoretical calculations are valid due to the presence of a ferromagnetic state inside the grains, and give us appropriate values for both cases.

Although the agreement between experimental and theoretical data is not completely satisfactory, the model describes adequately the main features of the experimental MR values for the sol-gel and ceramic samples (Fig. 7). ΔH is defined as the difference in magnetic field between the two maxima of the magnetoresistance versus magnetic field curve. Its presence in sol-gel samples is accounted for in the model, whereas for ceramic samples ΔH is negligible. The tendency to saturation that presents sol-gel particles is another characteristic derived from the general equation. This coincidence between experimental and theoretical data validate successfully the model.



Fig. 7. Experimental (open circles) and theoretical (line) data of low-field MR at 125 K for samples of $La_{0.67}Ca_{0.33}MnO_3$. (a) Sol–gel sample sintered at 800°C. (b) Ceramic sample.

The hysteresis loop in magnetoresistance and the decrease in ΔH with temperature (Fig. 8) are clearly related with the coercive field. Ceramic samples do not show this effect, but also present spin-polarized tunneling at grain boundaries, but it is not so important as in samples with smaller grain size.

We obtain a ferromagnetic coupling between grains (J > 0) that goes down with increasing temperature, achieving zero value near $T_{\rm C}$ (Fig. 8). The value of the coupling constant is about one order of magnitude larger than for other compounds (i.e. Ni particles) [27], but the reason for this fact is not clear today.

3.2. Oxygen stoichiometry dependence

For the purpose of discussing the dependence of the magnetotransport properties on the oxygen



Fig. 8. Top panel: experimental and theoretical data of ΔH for La_{0.67}Ca_{0.33}MnO₃ sol–gel sample sintered at 800°C. Bottom panel: intergrain coupling constant (*J*) for the cited sol–gel and ceramic samples.

stoichiometry, we used a technique which allows us to change this oxygen content without affecting the grain size. This can be reached by means of the electrochemical reduction in alkaline medium. As it is carried out at very low temperatures ($\leq 50^{\circ}$ C), the grain size remains invariant during the treatment. Several works [32,33] have showed the ability of the method to change the oxygen stoichiometry of perovskite related materials not only in the surface, but also in the bulk. Reducing the Mn⁴⁺ to Mn³⁺, the oxygen is forced to leave the structure to keep the electrical neutrality.

No oxygen content change could be obtained with perfect stoichiometry samples probably due to its perfect structure. To make easy the exit of the diffusion species we made slightly La^{3+} deficient ($\cong 5\%$) samples. No change in the symmetry from Pbnm was induced by this small cationic deficiency, and the other main features of the sol-gel samples remains unchanged, with the exception of the shift of $T_{\rm C}$ to 245 K (265 K for the stoichiometric sample). However, $T_{\rm C}$ is close to the metal-to-insulator transition temperature. Due to the little differences between stoichiometric and La deficient samples, it is possible to use La³⁺ deficient samples to study the influence of the oxygen content. For this purpose, two different treatments were performed on these samples:

Treatment 1: Electrochemical reduction for 72 h at room temperature at V = -0.18 V.

Treatment 2: Electrochemical reduction for 72 h at 50°C at V = -0.18 V.

As reference material, a similar sample immersed in the alkaline solution for the same time but without applying any current was used.

For all the samples oxygen content was determined after several iodimetric titrations [21], and are listed below:

Reference: $La_{0.63}Ca_{0.33}MnO_{3.01}$,

Treatment 1: La_{0.63}Ca_{0.33}MnO_{2.99},

Treatment 2: La_{0.63}Ca_{0.33}MnO_{2.97}.

As it is shown in Fig. 9, the variation in the oxygen content achieved in the second treatment shifts the T_{M-I} more than 60 K, with respect to those of the reference sample. The residual resistiv-



Fig. 9. Temperature dependence of normalized resistivity for an La_{0.63}Ca_{0.33}MnO_{3- δ} sol-gel sample with different oxygen stoichiometry: (a) $3 \pm \delta = 3.01$, (b) $3 \pm \delta = 2.99$, (c) $3 \pm \delta = 2.97$.



Fig. 10. Derivative of magnetization versus temperature curves for an La_{0.63}Ca_{0.33}MnO_{3- δ} sol-gel sample with different oxygen stoichiometries: (a) $3 \pm \delta = 3.01$, (b) $3 \pm \delta = 2.99$, (c) $3 \pm \delta = 2.97$.

ity in the reduced samples is also larger, due to the oxygen faults that make difficult conduction between Mn ions. There is a clear influence of the temperature in the final composition, as the oxygen ion diffusion coefficient is dependent on T. However, the fact that $T_{\rm C}$ does not follow the shift of T_{M-I} (Fig. 10) creating vast zones of ferromagnetic-insulator (FMI) behavior is striking. This experimental evidence has been explained on the basis of the DE model, assuming the formation of small ferromagnetic clusters, which are large enough to give a magnetic contribution but not to allow metallic conductivity [34]. The origin of these zones could come from the oxygen removed but only from the grain boundaries. Electrochemical experiments on ceramic samples are on the way, just to clarify the influence of the boundaries in the treatment. Anyway, we proved that the temperature at which a metal-to-insulator transition occurs, dramatically depends on the Mn³⁺ to Mn⁴⁺ ratio, and hence on the oxygen content of the samples.

4. Conclusions

In summary, in this work we have tested grain size and oxygen stoichiometry contributions to magnetotransport properties of $La_{0.67}Ca_{0.33}$ MnO_{3± δ} changing separately grain size and oxygen stoichiometry to avoid mixing the influence of both changes.

Samples with very different grain size were produced via sol–gel method and solid state reaction, and show us that neither $T_{\rm C}$ nor $T_{\rm M-I}$ are functions of this variable. Instead, great differences in resistivity and low field magnetoresistance are produced by the different contribution of the grain boundaries. This contribution has been understood under a spin-polarized tunneling model that has led us to an acceptable accuracy between experimental and theoretical data.

The electrochemical method at low temperatures has allowed us to reduce the oxygen content in the La³⁺ deficient samples without changing their grain size. $T_{\rm C}$ remains at the same value for different δ content, while $T_{\rm M-I}$ decreases by more than 60 K from the reference sample in the case of the more efficient treatment. This leads to the appearance of a zone of FMI behavior.

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