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Effects of electrochemical reduction on the magnetotransport properties of $La_{0.67}Ca_{0.33}MnO_{3\pm\delta}$ nanoparticles

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Abstract

We report on the effect of electrochemical reduction on the magnetic and transport properties of $La_{0.67}Ca_{0.33}MnO_{3\pm\delta}$ nanoparticles. We have observed a large displacement of the metal–insulator transition temperature (but not of the Curie temperature, T_c) in reduced samples. This behaviour is consistent with the existence of a magnetically inhomogeneous state below T_c, caused by random oxygen elimination. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Colossal magnetoresistance; Nanoparticles; Electrochemistry

There is renewal interest in manganese perovskites due to the colossal magnetoresistance (CMR) effect that these compounds develop near their spin-ordering temperature (T_c), [1]. Particularly, $La_{1-x}Ca_xMnO_3$ ($0.2 \leqslant x < 0.5$) shows a transition from a ferromagnetic metallic (FMM) to paramagnetic-insulating (PMI) state with increasing temperature [2]. Following the double exchange (DE) theory first proposed by Zener [3], the conduction is due to the existence of e_g mobile electrons between the Mn^{3+}/Mn^{4+} pairs, strongly coupled (Hund's rule) to the static t_{2g} spin core ($S = \frac{3}{2}$). The DE model qualitatively explains the coincidence of the metal–insulator transition temperature (T_{MI}) and T_c and also the existence of CMR associated with these transitions: application of a magnetic field tends to align the spins and to reduce the magnetic scattering of the mobile electrons.

The aim of this work is to change the Mn^{3+}/Mn^{4+} ratio at very low temperatures (near room temperature). Changing the oxygen content by avoiding high annealing temperatures makes it possible to distinguish between the effects of oxygen stoichiometry and grain size on the magnetotransport, separately. For this, we have carried out the electrochemical reduction of $La_{0.67-y}Ca_{0.33}MnO_{3\pm\delta}$ ($y = 0; 0.03$) prepared by the sol–gel method [4]. The particles were annealed at 800°C for 8 h ($D_{TEM} \approx 70$ nm). X-ray analysis revealed the absence of spurious phases. Electrochemical reduction of the samples was carried out in a thermostated beaker, filled with a 1 M NaOH solution. The samples were pelleted in disk shape, and attached to a Pt wire with silver painting. An epoxy-resin was used to cover the electric contacts. The exposed surface area was always about 1.5 cm^2. The reference samples were also immersed in the solution for the same time as the treated samples, but without applying electrical current. The value of the used reduction potential (≈ -0.19 V) was derived from previous cyclic voltamograms of the sample in the same medium [5].

The electrical resistivity was measured ($77\text{ K} < T < 300\text{ K}$) using the four-probe standard method. A vibrating sample magnetometer was employed to obtain magnetisation data between $77\text{ K} < T < 1000\text{ K}$.

The experiments were carried out by varying both time and temperature and keeping the potential constant (potentiostatic mode) in order to study the effects of these two parameters on the final composition of the sample. The presence of a small amount of La^{3+} defects ($y = 0.03$) was found which facilitate the exit of the

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Table 1
Oxygen content and transition temperatures determined for reference and electrochemical reduced samples

	Electrochem. treatment	T_{MI} (K)	T_c (K)	$3 \pm \delta$
Reference	—	240	248	3.01
Sample 1	72 h room temp.	234	245	3.00
Sample 2	72 h 50°C	180	245	2.97

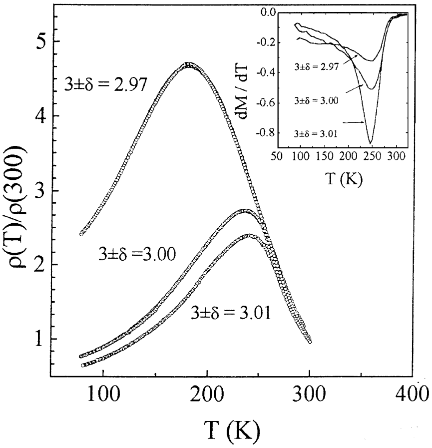

Fig. 1. Temperature dependence of normalized resistivity for reference and reduced samples. Oxygen stoichiometry is indicated. T_c does not follow T_{M-I} displacement with oxygen content (inset).

oxygen electroactive species [5]. Iodometric analysis of the samples gave the compositions listed in Table 1. The transition temperatures for these samples were determined and are also shown in this table.

The temperature seems to play a crucial role in the exit of oxygen electroactive especies, the final oxygen content being highly dependent on this parameter. After the reduction treatment, X-ray analysis did not show any changes in the symmetry group of the samples (Pbnm) or the appearance of secondary phases.

Reduction of Mn^{4+} to Mn^{3+} gives rise to oxygen elimination in order to keep the electrical neutrality of the structure. This results in large shifts of even more than 60 K in the metal to insulator transition temperature (T_{MI}) with respect to those of the untreated samples (Fig. 1). The most striking result is that in the reduced samples, T_c remains constant and is equal to ≈ 245 K (see inset of Fig. 1), creating relatively large zones with oxygen vacancies that disturb the electrical conductivity. However, the dM/dT curve for the reduced samples shows that the magnetic transition occurs over a large temperature interval, probably due to random distribution of oxygen vacancies.

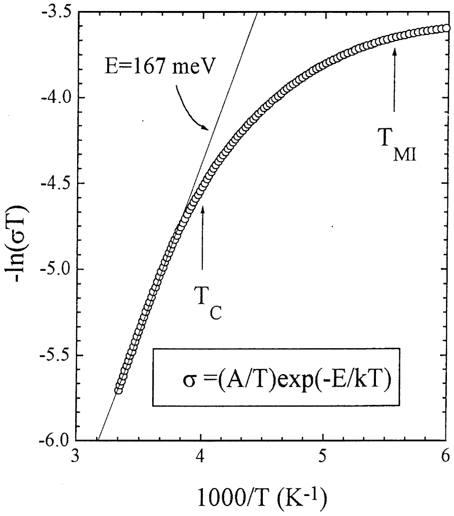

Fig. 2. Conductivity of $3 \pm \delta = 2.97$ sample in the adiabatic limit. The adjustment of high temperature data gives an activation energy of 167 meV for the hopping motion. Note also the separation near T_c, which indicates higher electron mobility in the insulating range between T_c and T_{MI}.

We have fitted the high temperature conductivity data (insulating phase) to a small-polaronic conduction mechanism in the adiabatic limit (Fig. 2) [6]. The linear fit indicates an activation energy (E) of 167 meV, nearly twice that reported in $La_{0.67}Ca_{0.33}MnO_3$ films by Jaime et al. [7]. Close to T_c the deviations from the Arrhenius behaviour become more significant, indicating higher electron mobility, even in the insulating phase ($T_{MI} < T < T_c$).

To explain this behaviour, we propose the formation of a new phase with disordered oxygen vacancies. The elimination of the oxygen bond destroys the conduction pathways for e_g mobile electrons, at least in a long range, and insulating behaviour becomes predominant in a larger temperature range. At low temperatures we have an FM and metallic material, but with oxygen defects which makes the resistivity greater than in the reference samples (see Fig. 1). With the increase in temperature, these defects lead to the increase of the resistivity and to the appearance of an insulating phase. Finally, a reoxidation of the samples has been observed by heating them in static air atmosphere ($T \approx 800$°C), but the composition of the original material cannot be achieved in this way. In summary, we have demonstrated the ability of electrochemistry to change the Mn^{3+}/Mn^{4+} ratio in manganites, and hence their magnetotransport properties. Moreover, these changes can be achieved near room temperature ($\leqslant 50$°C), which avoids secondary effects due to size changes in nanoparticles.

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