Electronic and magnetic properties of $La_{0.4}Ba_{0.1}Ca_{0.5}MnO_{3-y}$ thin films

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We investigated the transport and magnetic properties of $La_{0.4}Ba_{0.1}Ca_{0.5}MnO_{3-y}$ thin films to see the effect of substitution of the small atom Ca by Ba, which is much bigger. $La_{0.4}Ba_{0.1}Ca_{0.5}MnO_{3-y}$ thin films have been fabricated by a pulsed laser deposition technique. The electrical resistance has been measured in the range of 20–200 K under the field from zero up to 9 T. Under zero field, at $T \sim 37$ K, an insulator-to-metal (IM) transition was observed, as expected. However, we found that the magnetic field dependence of the resistivity seems to be anomalous since T_{IM} shifts to a lower temperature when the magnetic field is increased and the magnetoresistance at low temperature is positive. Magnetization measurements imply that in the metallic region, canted antiferromagnetic and ferromagnetic states coexist. Phase separation is suggested. © *2000 American Institute of Physics.* [S0021-8979(00)41708-1]

I. INTRODUCTION

Recently, the magnetotransport property of perovskite manganese oxides has been an interesting topic for many research groups. These oxides, $RE_{1-x}AE_xMnO_3$ (where RE is a trivalent rare-earth element and AE is a divalent alkaline earth element), present an exotic magnetoresistance (MR) effect, whereby magnetic fields induce large changes in their resistivity. That effect has been the so-called ''colossal'' magnetoresistance (CMR) and basically explained by double-exchange (DE) theory. Recent extensive studies have revealed that the doped manganites show a variety of interesting phenomena besides the large MR effect,[1–3] such as a charge-ordering transition, magnetic field induced insulator-to-metal (IM) transition, and so on, and it is found that those phenomena are rather complex and DE theory seems to be insufficient to explain them.

The MR behavior in manganites relates strongly to the exchange interaction between two magnetic cations separated by an anion. The change of size of the A site cation can modify the Mn–Mn distance and the Mn–O–Mn angles.[4] For perovskite manganites with a fixed x, transport properties including CMR phenomena can be strongly modified by changing the combination of perovskite A-site ions (RE and AE). Based on those factors, we have chosen Ba as a dopant for $La_{0.4}Ca_{0.6}MnO_{3-y}$ in order to clarify the role of the size of the A cations in the magnetic and transport properties. $La_{0.4}Ca_{0.6}MnO_{3-y}$ was selected due to its insulating behavior and being adjacent to the region of $x \sim 0.5$ which has complicated phase diagrams due to the competition between ferromagnetic (FM) metallic and antiferromagnetic (AF) insulating states. By replacing Ca by Ba which has a much bigger ionic radius, we expect the transition from an insulating to a metallic state.

II. EXPERIMENT

A Ba-doped $La_{0.4}Ca_{0.6}MnO_{3-y}$ (LCMO) target (2 cm diameter, 4 mm thickness) with nominal composition $La_{0.4}Ba_{0.1}Ca_{0.5}MnO_{3-y}$ (LBCMO) was synthesized by mixing stoichiometric proportions of La_2O_3, $BaCO_3$, $CaCO_3$, and MnO_2 and then heating in air at 1250 °C for 5 h, at 1380 °C for 12 h, and at 1390 °C for 20 h with intermediate grindings. Film deposition on (100) $LaAlO_3$ substrates was carried out by a pulsed-laser-deposition technique using a Lambda Physik 248 nm KrF excimer laser with 8 Hz repetition rate and 1.1 J/cm^2 energy density. Two series of samples, with different deposition conditions, were prepared. For the first series of samples, the substrate temperature was 760 °C and the oxygen pressure was 70 mTorr during film deposition (92% O_2 and 8% O_3), while those were 800 °C and 300 mTorr for the second series of samples. After deposition, films were annealed at 450 °C for 1 h and then cooled to room temperature in the same atmosphere as during deposition. The typical thickness of the films is 1200 Å. X-ray diffraction analysis confirmed that all films are c-axis oriented. The electrical resistance has been measured in the range of 20–200 K from zero field up to 9 T using a conventional four-probe method and a superconducting magnet. The magnetization has been measured by a Quantum Design superconducting quantum interference device magnetometer.

III. RESULTS AND DISCUSSION

The variation of electrical resistance of Ba-doped LCMO films as a function of temperature in zero and applied fields is shown in Fig. 1. Under zero field at high temperature, for the sample of the first series, with the oxygen pressure at 70 mTorr, the resistance of the film increases as the temperature decreases. A transition from an insulating to a metallic state, as expected, occurred at about 37 K. By doping only 10% of Ba for LCMO, an IM transition was obtained even at $H=0$. According to the literature reported so far, $La_{0.4}Ca_{0.6}MnO_3$ is an insulator over the whole range of temperature.[5–7] Since the ionic radius of Ba is rather big, the idea of Ba-doping is to intentionally induce the chemical pressure inside the lattice to cause the reduction of resistance. In general, the cations with smaller ionic radii in (RE, AE) sites of $RE_{1-x}AE_xMnO_3$ cause a big lattice distortion,

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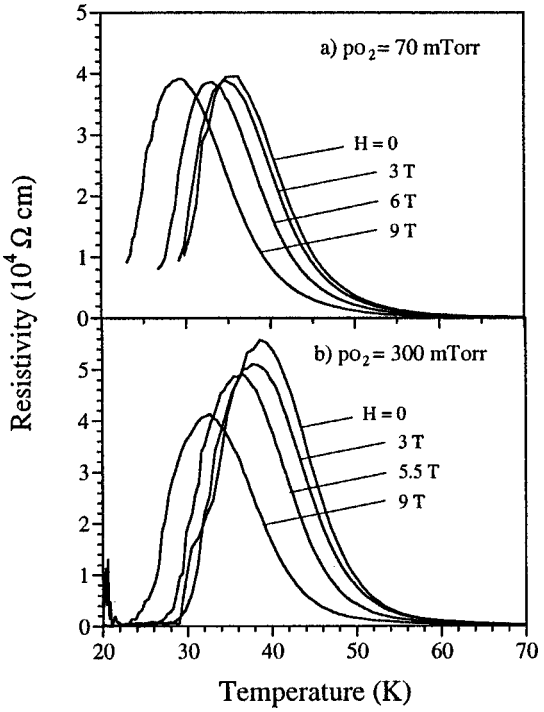

FIG. 1. The temperature dependence of resistivity at various fields for $La_{0.4}Ba_{0.1}Ca_{0.5}MnO_{3-y}$ thin films deposited with the oxygen pressure of (a) 70 mTorr and (b) 300 mTorr.

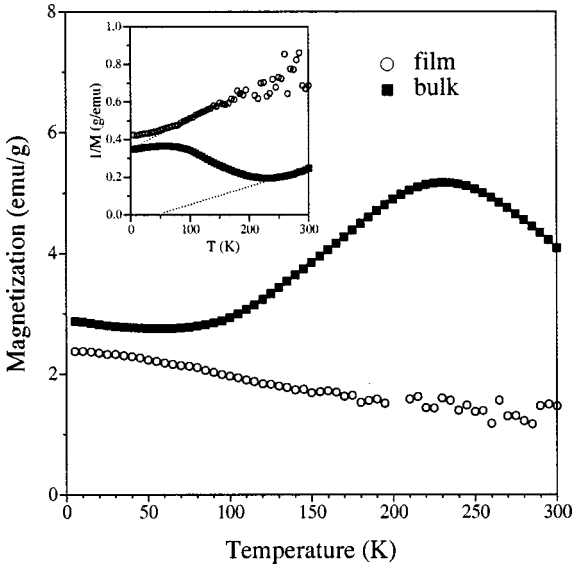

FIG. 2. The temperature dependence of magnetization at 3 T for $La_{0.4}Ba_{0.1}Ca_{0.5}MnO_{3-y}$ thin films (deposited with an oxygen pressure of 70 mTorr) and bulk. The inset shows $1/M$ vs T, and the interceptions of the dashed lines and T axis indicate θ.

and as a result it reduces the transfer interaction between Mn sites and a one-electron bandwidth in those manganites causing a charge ordering state and simultaneously stabilizes the AF spin structure.[1,4] Ba-doping induces the chemical pressure in this manner to relax the lattice distortion and enable the IM transition.

When the magnetic field is increased, the $\rho(T)$ curve shifts towards the low temperature side. In other words, the transition temperature (T_{IM}) decreases as the magnetic fields increases ($T_{IM}=28$ K at 9 T) while the peak height of the $\rho(T)$ curve remains almost the same. When $T \geqslant T_{IM}$ the MR is negative, when it is somewhat below T_{IM} the MR is positive. We notice that there is no big difference between the $\rho(T)$ measured on warming and cooling. The bottom panel in Fig. 1 shows that when the oxygen pressure is increased up to 300 mTorr, under the application of a higher field, the resistance of the film is suppressed a bit, but the tendency that T_{IM} shifts towards the low temperature side and the positive MR under the application of a higher field were obtained again. This effect has also been observed in $La_{0.45}Ba_{0.05}Ca_{0.5}MnO_{3-y}$ thin films which has been reported elsewhere[8] as well as in $La_{0.4}Sr_{0.1}Ca_{0.5}MnO_{3-y}$ thin films with different fabrication conditions. For LBCMO thin films postannealed at 800 °C for 10 h in the oxygen atmosphere, however, there is no IM transition under $H=0$ and under an applied magnetic field the resistance is suppressed drastically as a normal CMR effect. These facts show that the anomalous behavior is a rather universal one, however, it seems to depend sensitively on the fabrication conditions. Referring to other reports concerning this kind of material,[6,9,10] not only in La–Ca–Mn–O systems but also in other manganites, the application of a magnetic field usually enhances T_{IM} and the resistance is significantly suppressed (CMR phenomena). In other words the conductive property can be explained very well by a DE mechanism. In our films, the applied magnetic field causes an opposite effect on T_{IM}. The positive MR was also reported in Ref. 11, but it is observed at the charge-ordering phase transition (at the paramagnetic (PR)-FM transition, the MR is negative as expected from DE theory). The tendency of a magnetic field dependence of T_{IM}, as well as the positive MR observed in our films, cannot be explained in terms of a DE mechanism.

According to DE theory, the material used to be FM when it was in the metallic state. Therefore, we supposed that we may find a FM transition at T_{IM} from magnetization measurements. The magnetization vs temperature $[M(T)]$ vs magnetic field $[M(H)]$ of LBCMO films are shown in Figs. 2 and 3(a). $M(T)$ of the film does not show any bulk effect of the FM phase and no sign of change from PR to FM could be observed as well (the curve is monotonous and the magnitude is very small). We may say that the volume of the FM phase is rather small. Besides, $M(H)$ curves give some evidence for the existence of a canted antiferromagnetic (CAF) state not only above but also below T_{IM} (this is in accord with the negative θ which can be referred from the inset of Fig. 2). To explain the magnetic phase of the metallic region in our film, we presume two possibilities. One is that the metallic region may be in an AF state (in fact, an AF metallic state was discovered recently,[12] but even in this case we still may expect some change in magnetization at an IM transition thus the experimental results suggest that the volume of this AF metallic phase is very small). Another assumption, which seems to be more persuasive, is the possibility of small FM domains. To clarify the intrinsic magnetic properties of LBCMO thin films, we examine the magnetization of LBCMO bulk (a piece cut from the target) which is also shown in Figs. 2 and 3(b). $M(H)$ of the bulk sample at 250

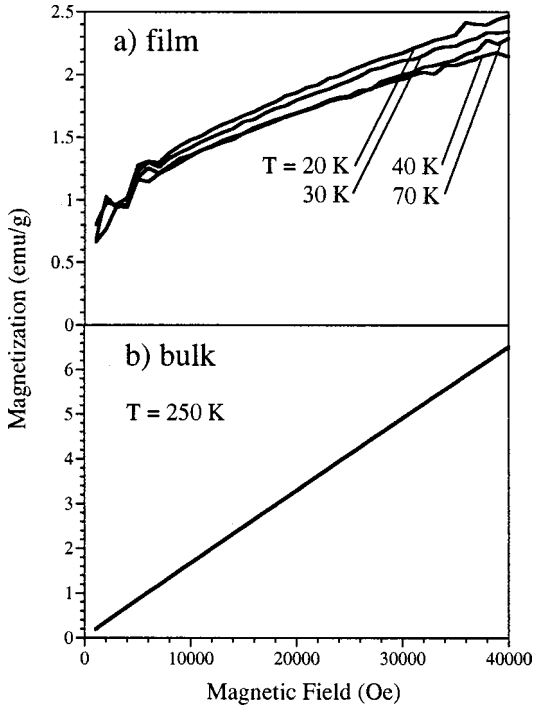

FIG. 3. The field dependence of magnetization at various temperatures for $La_{0.4}Ba_{0.1}Ca_{0.5}MnO_{3-y}$ thin films (deposited with the oxygen pressure of 70 mTorr) and bulk.

K indicates that it has PR behavior at a high temperature and $M(T)$ shows that below 230 K the material turns out to be AF. We should say its state must be CAF since the magnetization retains some certain value (about 3 emu/g) at a low temperature region. As seen in the inset of Fig. 2, the bulk sample $\theta = 50\,\mathrm{K}$ (determined by the interception of the dashed line and T axis), is much smaller than that of LCMO which was reported by Schiffer *et al.*,[6] but it is still a positive value. Therefore, we may assume that at low temperature LBCMO bulk may also have a FM structure with small volume. Returning to the $M(T)$ of the LBCMO thin film at a low temperature region, we found out that even though it has a smaller magnitude compared to that of the bulk it behaves very similarly. Concerning the metallic state observed in the film, the assumption about FM domains seems to be reasonable. Those small FM domains must be connected to each other in the form of FM stripes thus they can contribute to the conductivity of the material. The coexistence of CAF and FM domains in LBCMO thin films seems to be related to the so-called ''phase separation'' for compositions which are near to the critical point $x = 0.5$ which was mentioned by Moreo *et al.*[5]

IV. CONCLUSION

We have obtained the insulator-to-metal transition in Ba-doped LCMO thin films that were grown by the pulsed-laser-deposition technique. This effect is expected since the decrease in resistance is supposed to be caused by the effect of the big radius of Ba ions, but what is more surprising is the anomalous response of the system to the magnetic field. When the magnetic field increases, T_{IM} shifts to a lower temperature and positive MR was observed. These cannot be explained by DE theory. Besides, our results imply the coexistence and the competition of CAF and FM states at a low temperature region and it may be the evidence of phase separation which has been claimed for the magnetic properties of manganites with $x \sim 0.5$.

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