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Magnetoresistance behavior in $La_{0.7}Ca_xMnO_3$ ($x=0$, 0.2, and 0.3) thin films

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A systematic investigation focused on the magnetoresistance (MR) behavior of $La_{0.7}Ca_xMnO_3$ ($x=0$, 0.2, and 0.3) thin films has been carried out. As indicated by the unit chemical formula, $La_{0.7}Ca_xMnO_3$ films with $x=0.3$, 0, and 0.2 represent external, internal, and mixed (external and internal) doped lanthanum manganite systems, respectively. Thin films of these materials have been grown *in situ* on (100) $LaAlO_3$ substrates using a pulsed laser deposition technique. Microstructural characterization carried out on these films has shown that the films are smooth, free from impurities, and highly textured. Electrical resistance and magnetoresistance have been measured in the 10–300 K range in magnetic field up to 5 T using a superconducting quantum interference device magnetometer. The MR ratios of $La_{0.7}Ca_{0.3}MnO_3$ ($x=0.3$), $La_{0.7}MnO_3$ ($x=0$), and $La_{0.7}Ca_{0.2}MnO_3$ ($x=0.2$) films are found to be 825%, 700%, and 750% at 200 K, 240 K, and 220 K, respectively. The variation in the insulator to metal transition and the MR ratio is attributed to internal chemical pressure and vacancy localization effects. [S0163-1829(98)08438-0]

$LaMnO_3$ is the basic compound among lanthanum-based manganite systems, the transport properties of which can be varied dramatically by means of partial substitution of trivalent lanthanum ions with divalent cations.[1–14] This sparked off a tremendous interest in studying the magnetotransport properties of the doped perovskite manganite $La_{1-x}M_xMnO_3$ ($M=$Ba, Ca, Sr, Pb) because of their potential in technological applications such as magnetic read-write heads and magnetic sensors. In numerous papers,[2–15] it has been shown that over an appreciable range of doping these materials exhibit a very large magnetoresistance effect at temperatures close to those where they undergo a ferromagnetic-paramagnetic transition. The presence of divalent alkaline earth cations on the La sites of the perovskite induces a Mn^{3+}/Mn^{4+} mixed valence state which is responsible for both metallic conductivity and ferromagnetism in accordance with the double exchange (DE) interaction.[16–19]

Although the magnetoresistance effects brought about by the partial doping of lanthanum sites with divalent cations have been studied extensively,[1–14] there are very few papers in the literature reporting the transport and magnetic properties of self-doped lanthanum manganites.[20–23] Self-doped lanthanum manganites can be synthesized using lanthanum deficiency at lanthanum sites. According to neutron diffraction and x-ray diffraction studies carried out on $LaMnO_3$ this compound exists as a single phase defect perovskite with a range of vacancies principally on the lanthanum sites.[24] The chemical composition of the lanthanum deficient compounds can be represented by a general formula, $La_{1-x}MnO_3$. The electronic doping in lanthanum deficient $La_{1-x}MnO_3$ should be similar to that in other lanthanum manganites obtained by divalent substitution. In other words, the nonstoichiometric $LaMnO_3$ compound will have mixed Mn^{3+}/Mn^{4+} valence in a manner similar to that in the divalent substituted compounds $La_{1-x}M_xMnO_3$.

In the present paper, we report the growth and characterization of $La_{0.7}Ca_xMnO_3$ ($x=0$, 0.2, and 0.3) systems in thin-film form. The three different compositions have been chosen to differentiate and understand the effects of external, internal, and a combination of external and internal (mixed) doping on the transport and magnetic properties of lanthanum manganites with the same ratio of Mn^{3+} and Mn^{4+} ions. If M substitution is equivalent to hole doping, $La_{0.7}Ca_{0.3}MnO_3$ ($x=0.3$), $La_{0.7}MnO_3$ ($x=0$), and $La_{0.7}Ca_{0.2}MnO_3$ ($x=0.2$) represent external, internal, and mixed doped systems. In order to show the mixed valency of manganese ions in these systems, their chemical formulas can be written as $La_{0.7}Ca_{0.3}Mn_{0.7}(III)Mn_{0.3}(IV)O_3$, $La_{0.7}Mn_{0.7}(III)Mn_{0.3}(IV)O_3$, and $La_{0.7}Ca_{0.2}Mn_{0.7}(III)Mn_{0.2}(IV)Mn_{0.1}(IV)O_3$, respectively. These formulas clearly indicate that the Mn^{3+}:Mn^{4+} ratio is the same (7:3) in all the samples.

The bulk samples of nominal composition $La_{0.7}MnO_3$, $La_{0.7}Ca_{0.2}MnO_3$, and $La_{0.7}Ca_{0.3}MnO_3$ were prepared by a ceramic method. The required quantities of respective oxide or carbonate powders were mixed and sintered at 1400 °C for 24 h. The films of these materials were grown *in situ* using a pulsed laser ablation system. A detailed description of the deposition system is mentioned elsewhere.[25] In brief, a 248 nm KrF pulsed laser with 5 Hz repetition rate and 1.6 J/cm^2 energy density was used. A substrate temperature of 700–800 °C and oxygen pressure of 250 mTorr were used during the deposition of the films. The films deposited were characterized using scanning electron microscopy (SEM), energy dispersive x-ray analysis (EDX), atomic force microscopy (AFM), and x-ray diffraction (XRD) measurements. The temperature dependence of resistance of the films was examined in zero and applied field using four-probe technique and the quantum design superconducting quantum interference device (SQUID) magnetometer. Both the transport current and applied field were in the film plane. The magnetoresistance (MR) ratio, $\Delta R/R(H)$, was calculated using

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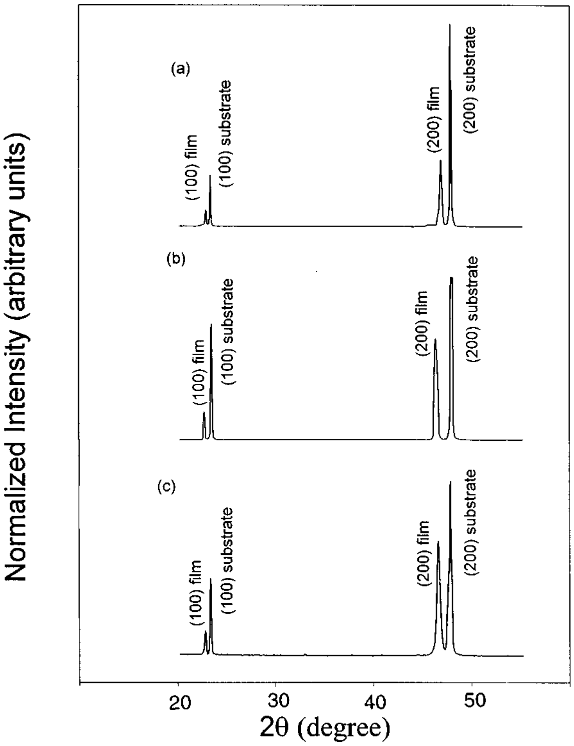

FIG. 1. X-ray diffraction patterns of (a) $La_{0.7}Ca_{0.3}MnO_3$, (b) $La_{0.7}Ca_{0.2}MnO_3$, and (c) $La_{0.7}MnO_3$ films grown at 700 °C on (100) $LaAlO_3$ substrates.

$\Delta R/R(H)=[R(H)-R(0)]/R(H)$, where $R(H)$ and $R(0)$ are resistances in applied and zero field.

XRD patterns of $La_{0.7}Ca_{0.3}MnO_3$, $La_{0.7}Ca_{0.2}MnO_3$, and $La_{0.7}MnO_3$ grown on (100) $LaAlO_3$ substrate at 700 °C are shown in Fig. 1. From the figure it is clear that all the films have a single phase with $(00l)$ peaks with $l=1$ and 2. The presence of only $(00l)$ peaks implies the highly textured growth of all the films on (100) $LaAlO_3$ substrate with lattice parameters of 3.87, 3.91, and 3.90 Å, for $La_{0.7}Ca_{0.3}MnO_3$, $La_{0.7}Ca_{0.2}MnO_3$, and $La_{0.7}MnO_3$ films, respectively. The root mean square (rms) roughness of these films measured using AFM was found to be 2 ± 0.5 nm. The value of rms roughness obtained here suggests that as-deposited manganite thin films in the present study are very smooth as this value of rms roughness is significantly low compared to the values reported in the literature.[7]

The variation of electrical resistance in zero and applied field (5 T) as a function of temperature for $La_{0.7}Ca_{0.3}MnO_3$, $La_{0.7}Ca_{0.2}MnO_3$, and $La_{0.7}MnO_3$ films are shown in Fig. 2. All three films were grown under identical conditions so that film thickness and oxygen contents of all the films could be kept identical. It is important to keep these two parameters (thickness and oxygen content) identical in order to resolve the effects of the nature of doping on magnetotransport properties in these films. According to the variation of resistance shown in Fig. 2, all three films have similar qualitative magnetotransport behavior. That is, all the films undergo an insulator-to-metal (I-M) transition as the temperature is lowered and the resistance of all the films is suppressed significantly with the application of magnetic field. As observed frequently by others in several manganite systems,[1–14] here also the suppression in film resistance in each case is maximum near the resistivity peak in zero field. However, the temperature at which the I-M transition takes place in each system is different from each other. The internal doped system ($La_{0.7}MnO_3$) attains the metallic state earliest (240 K), followed by the mixed doped system ($La_{0.7}Ca_{0.2}MnO_3$), and external doped ($La_{0.7}Ca_{0.3}MnO_3$) system with I-M transitions around 220 and 200 K, respectively. Thus, it appears that the electronic doping in self-doped compounds is similar to that of the compounds with external doping.

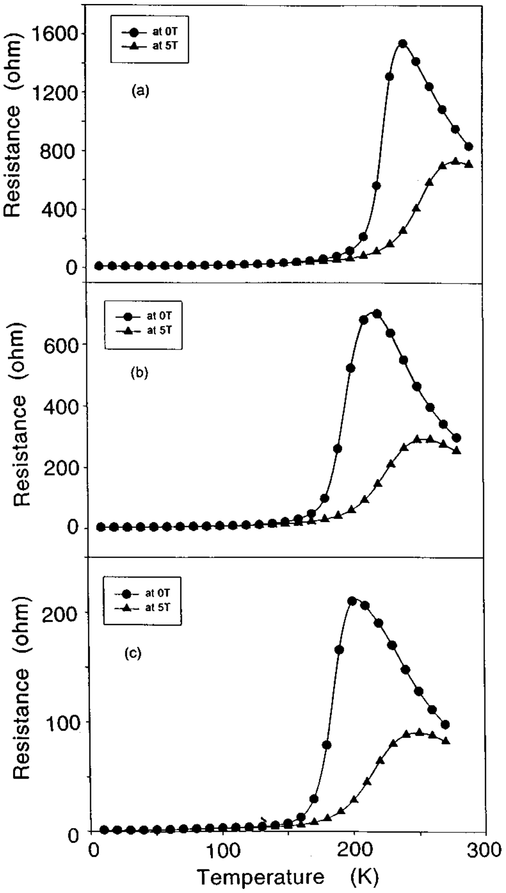

FIG. 2. Resistance vs temperature plots for (a) $La_{0.7}MnO_3$, (b) $La_{0.7}Ca_{0.2}MnO_3$, and (c) $La_{0.7}Ca_{0.3}MnO_3$ films in 0 and 5 T magnetic field.

The difference in the values of the I-M transition temperature in the systems we have studied here may be explained on the basis of a tolerance factor (t). The tolerance factor essentially determines the Mn-O-Mn bond angle, which in turn controls the effective electron transfer between Mn^{3+} and Mn^{4+} within the framework of a double exchange mechanism.[26] The deviation in t from unity is a measure of the mismatch between the equilibrium bond lengths La-O and Mn-O in a perovskite-structured lanthanum manganite system.[27] The room-temperature, ambient-pressure value of t is calculated from the sums of the empirical ionic radii given in tables, e.g., those of Shannon and Prewitt[28] and Jin *et al.*[5] A $t<1$ places the Mn-O bonds under compression and La-O bonds under tension. If these internal stresses are not relieved due to structural hindrance in rotation of MnO_6 octahedra,[27] the lattice will be in the state of internal pressure.[29,30] The tolerance factors of the compounds investigated in the present study, $La_{0.7}Ca_{0.3}MnO_3$, $La_{0.7}Ca_{0.2}MnO_3$, and

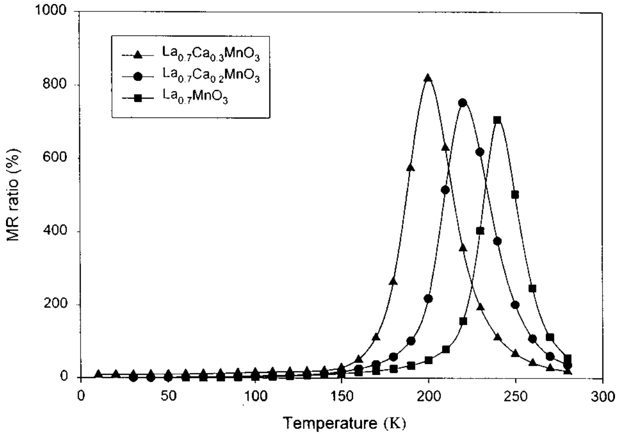

FIG. 3. Variation of MR ratio with temperature for $La_{0.7}MnO_3$ (filled square), $La_{0.7}Ca_{0.2}MnO_3$ (filled circle), and $La_{0.7}Ca_{0.3}MnO_3$ (filled triangle) films.

$La_{0.7}MnO_3$, were calculated to be 0.90, 0.85, and 0.80, respectively. Therefore, in accordance with previous reports by Yoshizawa *et al.*[29] and Raveau, Maignan, and Caignaert,[30] these compounds with varying tolerance factors are likely to experience different internal stresses, and hence, different chemical pressures. As a result of difference in chemical pressure, the insulator-to-metal transition in each system occurs at a different temperature: $La_{0.7}MnO_3$ films which have the largest deviation of t from unity, and hence, the highest internal chemical pressure undergo an I-M transition at higher temperature (240 K) compared to I-M transitions of $La_{0.7}Ca_{0.2}MnO_3$ (I-M transition: 220 K) and $La_{0.7}Ca_{0.3}MnO_3$ (I-M transition: 200 K) films.

The MR ratios of $La_{0.7}Ca_{0.3}MnO_3$, $La_{0.7}Ca_{0.2}MnO_3$, and $La_{0.7}MnO_3$ films were calculated using the data in Fig. 2. The MR ratios obtained are plotted in Fig. 3 as a function of temperature at 5 T. The figure shows that $La_{0.7}Ca_{0.3}MnO_3$ has the highest MR ratio (~825%) which is followed by $La_{0.7}Ca_{0.2}MnO_3$ (MR ratio ~750%) and $La_{0.7}MnO_3$ (MR ratio ~700%) systems. The variation in MR ratios of these compounds is explained as follows. The occupancy of the e_g band is expected to be similar for all three systems assuming that oxygen remains divalent and the Mn^{3+}/Mn^{4+} ratio is the same in all systems. However, due to the difference in vacancies at La sites (arising from lanthanum deficiency), the localization effects, and hence, the mobility of charge carriers are different in different systems. Since the density of lanthanum deficiency is more in the $La_{0.7}MnO_3$ system (internal doped), the localizing effect of random vacancies is stronger in $La_{0.7}MnO_3$ films than that in the $La_{0.7}Ca_{0.2}MnO_3$ (mixed doped) film. Therefore, the random potential fluctuations due to missing La^{3+} ions will favor the Anderson localization more strongly in the former system than in the latter system.[31] As a result of this, the MR ratio obtained for $La_{0.7}MnO_3$ film is less than that of $La_{0.7}Ca_{0.2}MnO_3$ film. There is no such localization effect in stoichiometric $La_{0.7}Ca_{0.3}MnO_3$ films due to absence of vacancies, which is manifested with the realization of the highest MR ratio among the three systems discussed here.

In summary, we have presented the studies of magnetoresistance behavior in $La_{0.7}Ca_{0.3}MnO_3$, $La_{0.7}MnO_3$, and $La_{0.7}Ca_{0.2}MnO_3$, which are external, internal, and mixed doped systems with the same Mn^{3+}/Mn^{4+} ratio. The results obtained have shown that the electronic doping in nonstoichiometric compounds is similar to that of the compounds with divalent substitution. The variation in insulator-to-metal transition and the MR ratio in these systems have been explained using the concept of internal chemical pressure and localization effects.

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