

Percolative transport in the vicinity of charge-order ferromagnetic transition in a hole-doped manganite

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Abstract. We report measurements of non-linear charge transport in epitaxial $(\text{La}_{1-x}\text{Pr}_x)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ thin films fabricated on (100) oriented SrTiO_3 single crystals by pulsed laser deposition. The end members of this series, namely $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ are canonical charge-ordered (CO) and ferromagnetic manganites, respectively. The onset of the CO state in $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ is manifested by a pronounced insulating behavior below ~ 200 K. The CO state remains stable even when a large ($\sim 2 \times 10^5$ V/cm) electric field is applied across the thin film samples. However, on substitution of Pr with La, a crossover from the highly resistive CO state to a state of metallic character is observed at relatively low electric fields. The current–voltage characteristics of the samples at low temperatures show hysteretic and history dependent effects. The electric field driven charge transport in the system is modelled on the basis of an inhomogeneous medium consisting of ferromagnetic metallic clusters dispersed in a CO background.

Keywords. Hole-doped manganite; percolative transport; charge-order; ferromagnetic transition.

PACS Nos 75.30.Vn; 75.50.Dd

1. Introduction

The intermediate bandwidth manganites of general formula $(\text{La}_x\text{Pr}_{1-x})_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ are candidate materials for observing fascinating effects such as colossal magnetoresistance, charge and spin ordering, and coexistence of phase segregated states [1]. The end members of this family of manganites, namely $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ are a charge delocalized ferromagnetic (CDFM) metal and charge-ordered (CO) insulator, respectively. The highly resistive, charge-ordered state among manganites originates from the specific C–E type arrangement of manganese d_Z^2 orbitals in (001) plane due to dominant electron–phonon interaction as proposed by Goodenough [2], and can be illustrated by regular checker-board arrangement of Mn^{3+} and Mn^{4+} ions onto two separate crystallographic sublattices. The charge-ordering phenomenon is most robust when Mn^{3+} and Mn^{4+} ions are in due proportion (i.e., $\text{Mn}^{3+} : \text{Mn}^{4+} :: 1 : 1$) and average ionic radius $\langle r_A \rangle$ is substantially small ($\langle r_A \rangle = 1.15$ Å). Here $\langle r_A \rangle$ is the average ‘A’ site ionic radius of the perovskite AMnO_3 . The charge-ordered phase for incommensurate distribution of manganese ions (i.e., the ratio $\text{Mn}^{3+}/\text{Mn}^{4+} > 1$), is also very stable at smaller values of $\langle r_A \rangle$ (≤ 1.15 Å). The system $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ is a good example of this. The CO state undergoes

a first-order melting transition under the application of strong magnetic and electric fields [3,4], and high energy photon flux [5]. The critical strength of these perturbations required to initiate the melting transition is expected to become smaller if $\langle r_A \rangle$ is increased by substitution at the rare earth or alkaline earth sites, as such substitutions increase the bandwidth of the e_g electrons. In this paper we investigate the relative stability of the CO and CDFM states in $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ system when the Pr^{3+} sites are gradually replaced by La^{3+} ions. Since La^{3+} is a much larger ion than Pr^{3+} , substitution with La would lead to increase in $\langle r_A \rangle$, and hence, a gradual increase in the bandwidth.

2. Experimental details

Targets of $(\text{La}_x\text{Pr}_{1-x})_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ for laser ablation were prepared by following the solid-state reaction method. Mixture of Pr_6O_{11} , CaCO_3 , La_2O_3 and Mn_2O_3 in stoichiometric proportion was first ground and then fired in air at 1150°C for 12 h. This cycle was repeated 3 times before pressing the mixture into 22-mm diameter pellets, which were subsequently annealed at 1400°C for 10 h. Epitaxial films of thickness $\sim 2500 \text{ \AA}$ were deposited on (001) cut SrTiO_3 substrates using the technique of pulsed laser deposition (PLD). The film deposition parameters such as substrate temperature, pulse laser energy density, target-to-substrate distance and oxygen partial pressure were maintained at 800°C , 3 J/cm^2 , 5 cm and 400 mbar, respectively throughout the process. After completion of film deposition, the chamber was backfilled with oxygen to atmospheric pressure and the film was cooled to room temperature at the rate of $\sim 5^\circ\text{C/min}$. Standard $(\theta-2\theta)$ X-ray diffraction measurements were performed to confirm epitaxial growth of the films. The measurements of current-voltage ($I-V$) characteristics, resistivity and magnetoresistance were carried out in the temperature range of 4.2 K to 300 K.

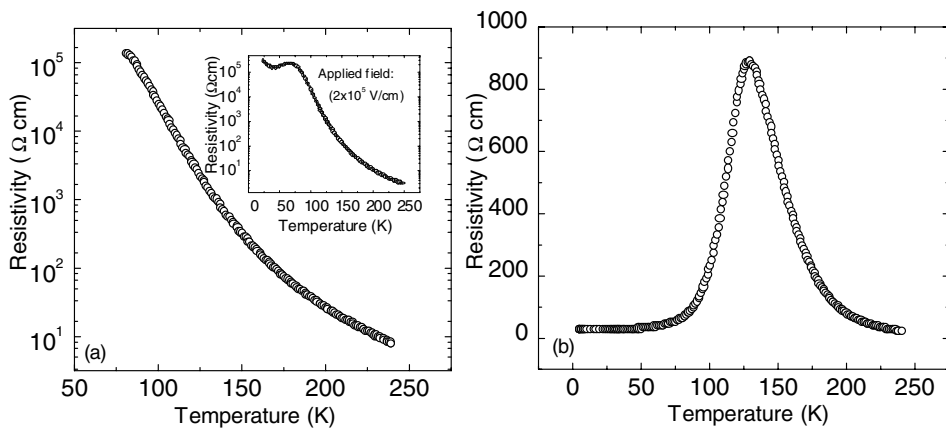


Figure 1. (a) and (b) show the resistivity profiles of the compositions $x = 0.35$ and $x = 0.5$, respectively as a function of increasing temperature at zero magnetic field. These are constant current mode measurements. The inset shows resistivity of composition $x = 0.35$ measured in a constant voltage mode. The electric field used in the temperature range 20–120 K was $2 \times 10^5 \text{ V/cm}$.

3. Results and discussion

In figures 1a and 1b, we show electrical resistivity of compositions $x = 0.35$ and $x = 0.5$ measured in a constant current mode. The sample $x = 0.35$ undergoes charge-ordering transition below 200 K. The steep growth in the resistivity of this sample below ~ 200 K suggests transport in a CO state. The resistivity continues to grow down to 70 K and below this temperature the constant current method does not work due to impedance related restrictions imposed by our voltmeter. In the inset of figure 1a, we show the electrical resistivity of the $x = 0.35$ film measured in a constant voltage mode. The applied electric field across the sample in the temperature range 20–120 K was 2×10^5 V/cm. To minimize sample heating, the strength of the electric field was dropped to 6×10^3 V/cm for temperatures above 120 K. At these higher electric fields, a strikingly different behavior is seen. The resistivity on cooling below ~ 200 K first shows a sharp increase. This is followed by a drop in resistance on decreasing the temperature. The resistivity reaches a minimum at $T \approx 30$ K and then increases on further lowering the temperature. The observed metallic behavior in the temperature window of 40 K–70 K is a signature of electric field-induced melting of the CO state. On increasing the lanthanum concentration (x) to 0.5, a markedly different behavior is seen in the resistivity of these samples. As shown in figure 1b the resistivity of this sample is weakly insulating down to 200 K. Below 200 K it grows rapidly and reaches a peak value at $T_p = 130$ K. On lowering the temperature further, the resis-

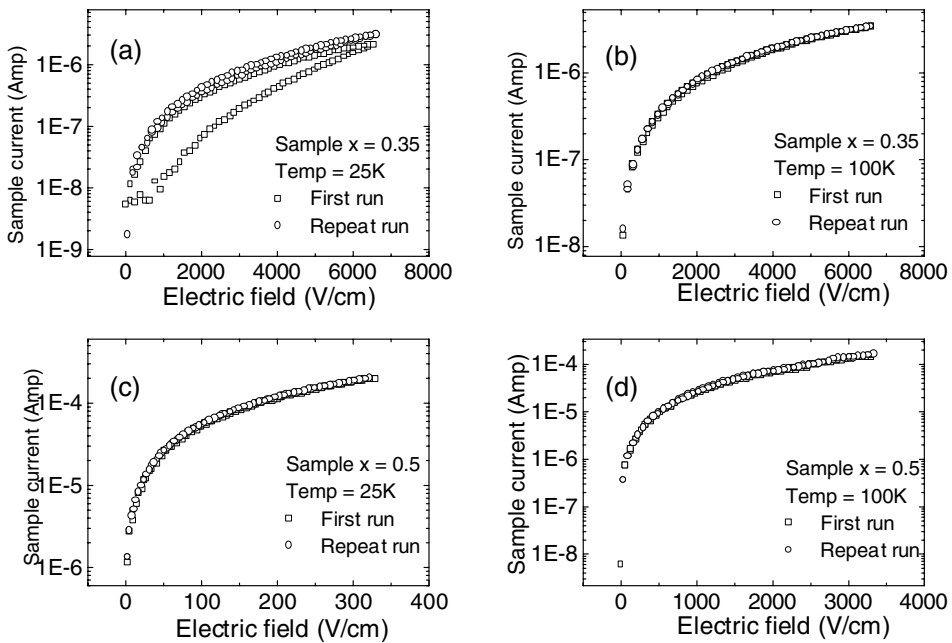


Figure 2. I – V characteristics for composition $x = 0.35$, (a) and (b) and $x = 0.5$, (c) and (d), at specified temperatures. Each run was carried out twice to confirm history (memory) and hysteresis related effects. In each individual scan, the open squares represent the first run whereas the open circles represent the repeat run.

tivity shows a drop which is symmetrical to its behavior between 130 K and 200 K. A similar behavior of the resistivity is seen in the parent compound $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, which is a charge delocalized ferromagnetic metal below T_P . In figure 2 we present the current–voltage characteristics of compositions $x=0.35$ and $x=0.5$, performed at 25 K and 100 K. For composition $x=0.35$, nonlinearity accompanied by a large hysteresis in the $I-V$ scans suggest an inhomogeneous charge-ordered state which is melted by applying large electric field $\sim 6 \times 10^5$ V/cm. This is why the forward branch of the $I-V$ curve is nonlinear while the reverse branch is linear with current following the Ohm’s law. In the subsequent runs at the same temperature, the $I-V$ scans are fully reversible and ohmic. The large hysteresis observed in first scan no longer exists in the repeated scans. For measurement performed at 100 K, the $I-V$ scans are fully reversible and ohmic. The hysteretic $I-V$ curves showing history dependent nonlinearities at temperatures in the vicinity of the minimum ($T \approx 30$ K) in figure 1a (inset) suggest opening up of percolative metallic channels in the sample. The competing energy scales of the CO and the metallic states permit the channels to remain open when the field is brought back to zero. For the composition $x = 0.5$ (see figures 2c and 2d), the $I-V$ scans are fully reversible and ohmic in both first and repeat runs taken at temperatures 25 K and 100 K. These observations clearly show that the CO system $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ becomes a charge delocalized ferromagnetic metal when 50% of the Pr sites are replaced with La^{3+} ions.

4. Conclusion

In summary, the ground state of the $(\text{La}_{1-x}\text{Pr}_x)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ hole-doped mixed manganite changes from CO to CDFM at $x = 0.5$. For lower lanthanum concentration ($x = 0.35$), we see a weak CO state, which undergoes percolative metallic transport at high electric fields. The percolative transport is hysteretic and history dependent.

Acknowledgements

This research was supported by a grant from the Department of Science and Technology, Government of India, through the project no. SP/S2/M-53/94.

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