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Colossal enhancement of magnetoresistance in $La_{0.67}Sr_{0.33}MnO_3$ thin films: possible evidence of electronic phase separation

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Abstract
A gigantic three orders of magnitude change of resistivity in $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) thin film, on application of magnetic field, has been observed. The transport and magnetic properties are characteristic of electronic phase separation between ferromagnetic metallic and antiferromagnetic charge-ordered insulating regions, unusual for a canonical double exchange system such as LSMO.

(Some figures in this article are in colour only in the electronic version)

The compound $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) is regarded as the canonical double exchange system having the largest conduction bandwidth among the manganites, and the high kinetic energy of the conduction electron favors a purely ferromagnetic ground state [1]. However, unlike other manganites, it fails to exhibit some of the most interesting phenomena such as electronic phase separation into charge-ordered insulating and ferromagnetic metallic regions [2], metastability in transport and magnetic properties [3], gigantic change in resistivity on application of magnetic field [4], etc. It does show appreciable magnetoresistance around the Curie temperature but this is miniscule when compared to other ferromagnetic systems such as $La_{0.67}Ca_{0.33}MnO_3$ (LCMO) and $Nd_{0.67}Sr_{0.33}MnO_3$, etc. The transition metal oxides, particularly manganites having narrow bandwidth, are electronically inhomogeneous [2, 5]. The length scale of these inhomogeneities or electronic phase separation varies from nanometers up to a few microns. Moreover, these inhomogeneities can be manipulated by external magnetic field [2, 5], or internal magnetic field generated in ferromagnetic metal–charge-ordered insulator multilayers [6], resulting in colossal magnetoresistance. In this article, we will demonstrate that, below a certain thickness, LSMO film exhibits transport and magnetic properties characteristic of systems having electronic phase separation between ferromagnetic metallic and antiferromagnetic charge-ordered insulating regions along with colossal change in resistivity (three orders of magnitude) on application of magnetic field.

There are a few reports on observation of electronic phase separation resulting in a highly insulating state in $La_{0.67}Ca_{0.33}MnO_3$ (LCMO) ultra-thin films, which is attributed to the structural inhomogeneities caused due to non-uniform distribution of strain in the film [7, 8]. It has been observed that, for narrow bandwidth systems, there is a tendency towards phase separation into ferromagnetic metallic and antiferromagnetic charge-ordered insulating regions. LCMO is a narrow bandwidth system and hence it is not so surprising that the system would be prone to phase separation.

Thin films of LSMO having different thicknesses in the range 10–100 nm were deposited on single crystalline $SrTiO_3(100)$ substrates using the pulsed laser ablation technique. The substrate temperature was 800 °C and the oxygen pressure 350 mTorr. The Curie temperature for the as prepared LSMO films turns out to be around 310 K (10 nm)–360 K (100 nm), consistent with a previous report [9]. The film composition was verified by energy dispersive x-ray spectroscopy (EDX), which differs from the expected stoichiometry within margins of 1%. The absence of impurities and interdiffusion of substrate element into the film was confirmed using secondary ion mass spectroscopy. The surface morphology of all the films was analyzed using atomic force microscopy (AFM) (figures 1(A) and (B)). A study in magnetic
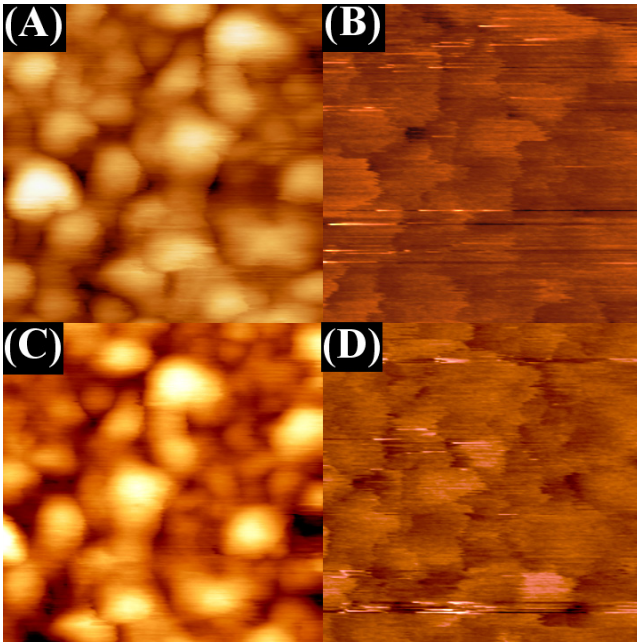
Figure 1. (A) AFM taken over a 500×500 nm^2 area of a thin LSMO/STO (10 nm) film, (B) corresponding frequency modulated MFM picture, (C) AFM taken over a 500×500 nm^2 area in another part of the same film and (D) corresponding amplitude modulated MFM picture. All the measurements have been carried out at room temperature.

Figure 2. Temperature dependence of resistivity of LSMO films deposited on STO substrate showing enhanced upturn with lowering of temperature below a certain thickness. Inset: the low temperature minima for the thick LSMO/STO (100 nm) film is shown.

force microscopy (MFM) on LSMO/STO (10 nm) film at room temperature, as shown in figure 1, shows that, similar to the grain size and their distribution, there is a wide distribution in magnetic domain size.

The temperature dependence of resistivity of all the samples, measured in the temperature interval 4–300 K using a conventional four probe technique, shows that if the thickness of the film is reduced below a certain value the resistivity upturn, the position of the resistivity minima and the resistivity value itself are enhanced significantly (figure 2). The position of the resistivity minima of LSMO/STO film of thickness 10 nm is at a strikingly higher temperature compared to thicker films (inset, figure 2), which have resistivity values close to that of a single crystal. The origin of low temperature resistivity minima in thicker films has been discussed elsewhere [10]. The average roughness of the LSMO/STO (10 nm) film is 2 nm, sufficiently less than the thickness of the film that the film can be assumed to be continuous.

Extraordinary enhancement of magnetoresistance (MR, defined as $\Delta\rho/\rho_H = \rho(H) - \rho(0)/\rho(H)$) has been observed over a broad temperature range, which is rare for LSMO films. Figure 3(A) shows appreciable enhancement of MR when the film thickness is reduced to 10 nm. The values of MR for thicker films are almost identical (figure 3(A)). The highest MR at any temperature below 300 K is 375% for LSMO/STO (10 nm) (figure 3(C)). At low temperature, the MR increases as temperature is increased, shows a maximum and then falls off with increasing temperature. An additional minima is observed at 200 K, the Curie temperature for the film being well above 300 K. Here, we have used the so called
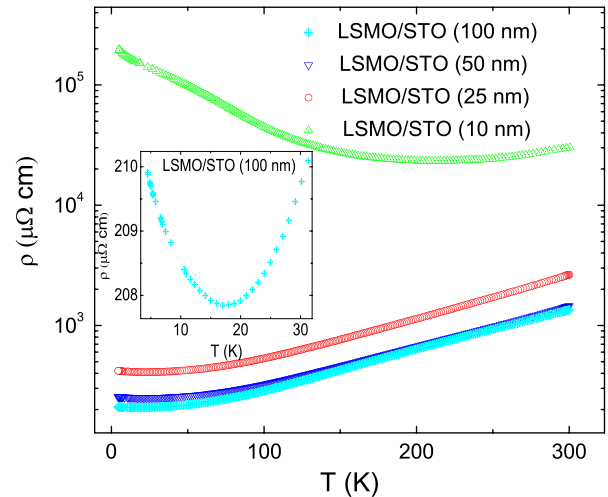
'inflationary' definition of MR instead of the conservative definition, which cannot give an MR value more than 100%. If the conservative definition is used and if the MR value is very high (as in our case), it becomes difficult to follow the variation of MR with temperature.

Observation of such large magnetoresistance far away from the Curie temperature is possibly due to charge ordering. In order to further illustrate the influence of charge ordering in LSMO/STO (10 nm), the magnetotransport properties have been studied in greater detail. The magnetic field dependence of resistivity at low temperature (figure 3(B)) shows distinct hysteresis giving rise to a metastable state when the magnetic field is switched off. The temperature dependence of both zero-field-cooled resistivity and magnetization exhibit hysteresis during the heating and cooling cycle, which are the characteristic features of phase separation and metastability (inset, figures 3(B) and 4(A)). The metastable state consists of spatially segregated ferromagnetic and antiferromagnetic charge-ordered patches, with the volume fraction of the charge-ordered and ferromagnetic metallic regions changing with time.

This metastability has been directly verified from magnetic relaxation measurements. The relaxation measurements were carried out at various constant temperatures over the range 4–250 K, and for each temperature a magnetic field of 50 kOe was applied for 60 s, after which the field was removed, followed by data collection over a time-span of 2 h. After the magnetic field is removed, the charge-ordered antiferromagnetic patches seek re-birth at the expense of ferromagnetic regions, resulting in the observed magnetic relaxation. The long-time relaxation is clearly logarithmic and the negative slope-value of the reduced magnetization versus time curves increases systematically up to a certain temperature, above which a completely opposite trend is observed (figures 4(B) and (C)). The magnetic relaxation at long timescales can be described approximately by the
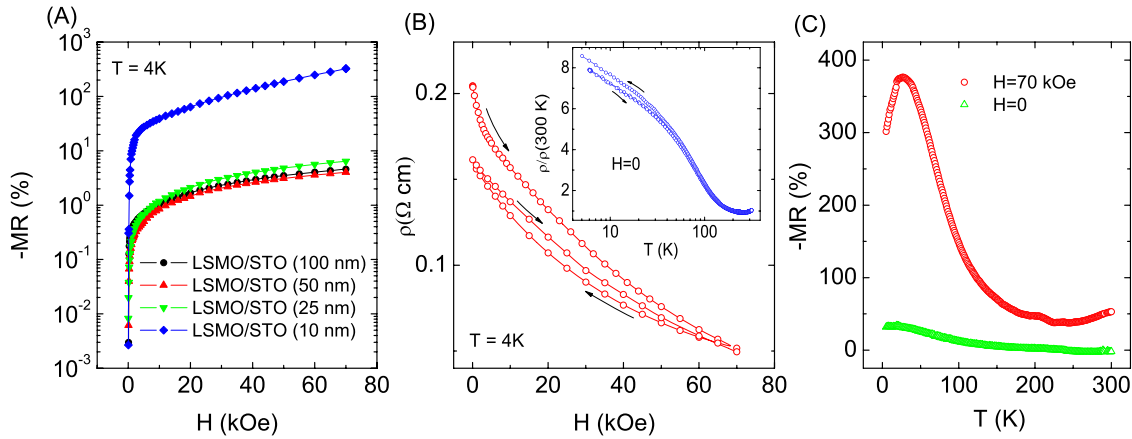
Figure 3. (A) The magnetic field dependence of MR at 4 K for all the films deposited on STO showing abrupt enhancement of MR when the thickness of the film is reduced to 10 nm. (B) The magnetic field dependence of resistivity for LSMO/STO (10 nm) at 4 K, showing hysteresis; the metastable state at $H = 0$ after the film is exposed to strong magnetic field is clearly visible. Inset, the irreversibility in the temperature dependence of resistivity; the sample is zero-field-cooled followed by data collection during the warming and cooling cycle. (C) The temperature dependence of MR for LSMO/STO (10 nm) at 5 and 70 kOe.
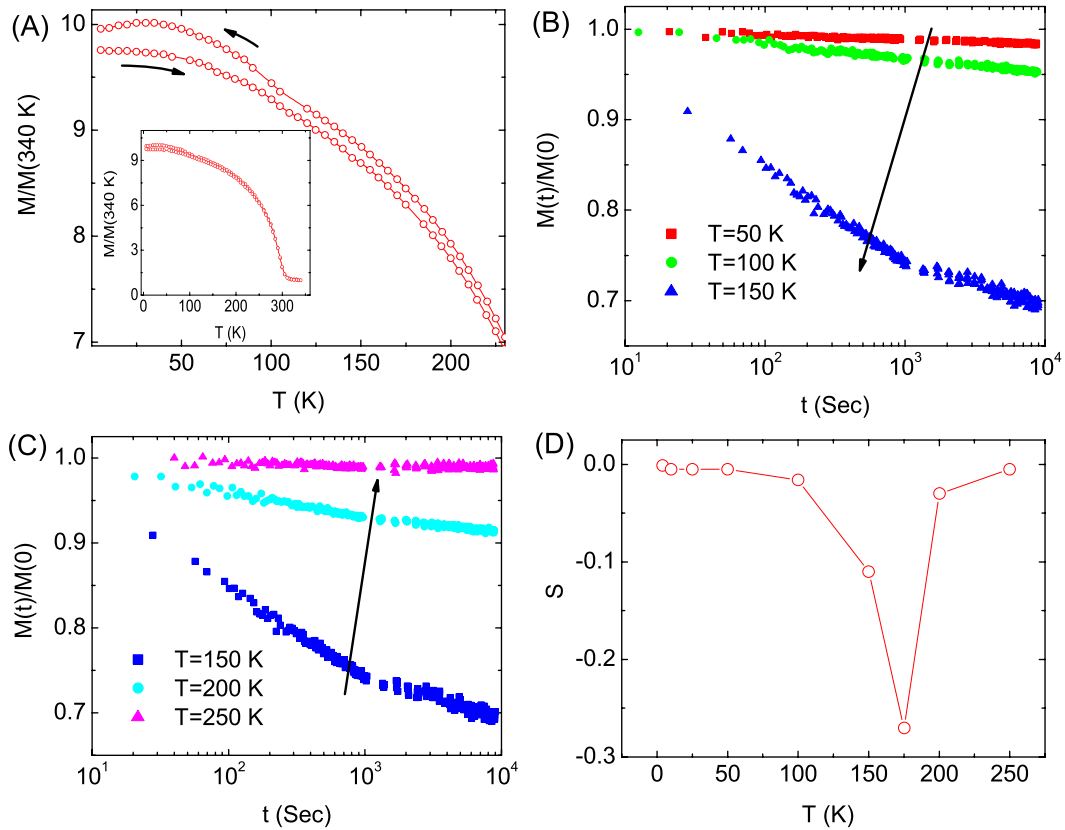

Figure 4. (A) Field-cooled M versus T curves at $H = 100$ Oe for LSMO/STO (10 nm) during the heating and cooling cycle (inset: the whole temperature range is shown). (B), (C) Magnetic relaxation measurements on the same sample after the removal of 50 kOe magnetic field. (D) The temperature dependence of magnetic viscosity as defined in the text.

expression $M(t)/M(t_n) = 1 + S \log(t/t_n)$. Here, S is called magnetic viscosity, and t_n and $M(t_n)$ are the normalization time and the corresponding magnetization at that point in time, respectively. The logarithmic relaxation can be attributed to a free energy landscape containing local minima corresponding to different equilibrium states separated by energy barriers. The spatial phase separation into inhomogeneous mixtures of ferromagnetic and antiferromagnetic clusters after the

magnetic field is removed produces frustration at the phase boundary, which gives rise to glassy behavior at low temperature and the system gets trapped in a frozen state, which almost refuses to relax with time. The magnitude of S becomes maximum near about 175 K (figure 4(D)), which possibly marks the onset of the phase-coexistence regime.

The in-plane lattice mismatch between the LSMO and SrTiO$_3$ substrate is -0.5%, which results in bi-axial tensile
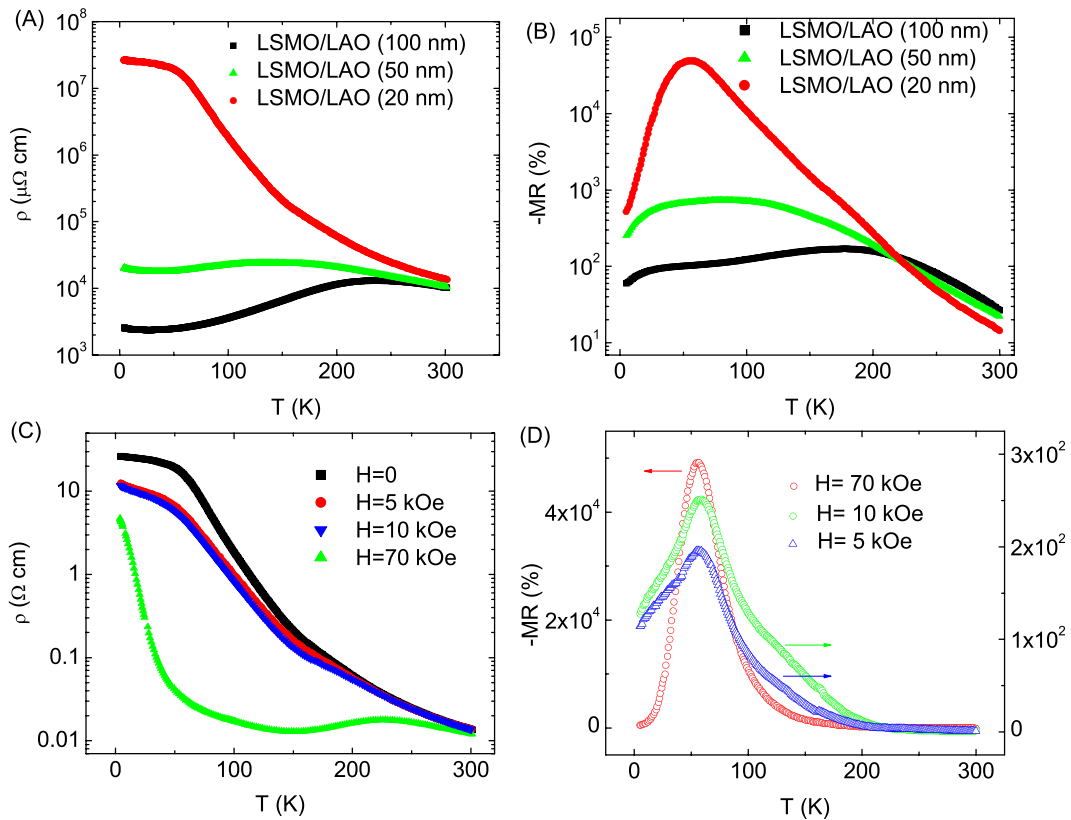
Figure 5. (A) Temperature dependence of resistivity of LSMO films deposited on LAO substrate showing distinct insulating behavior for LSMO/LAO (20 nm). (B) Temperature dependence of MR at $H = 70$ kOe for all the LSMO/LAO films showing significant enhancement of MR with lowering thickness below 200 K. (C) The temperature dependence of resistivity for LSMO/LAO (20 nm) film at different magnetic fields. (D) The temperature dependence of MR for LSMO/LAO (20 nm) at different magnetic fields.

stress. The bi-axial strain can influence two important parameters which determine the co-operative interaction and hence the transport or the magnetic properties: (1) the extension or contraction of the Mn–O–Mn bond-length leads to a large reduction or enhancement of the electronic hopping amplitude; (2) the increased Jahn–Teller distortion leads to localization of electrons. The reduction in film thickness leads to the situation where the film is highly strained. The resulting lattice distortion reduces the hopping amplitude, thereby bringing other competing interactions into play, which produces electronic phase separation. It has been experimentally observed that the in-plane compressive strain favors the C-type antiferromagnetic ordering and the in-plane tensile strain favors the A-type antiferromagnetic ordering [11, 12]. While the bi-axial strain stabilizes the antiferromagnetic charge-ordered state, the non-uniform distribution of the strain gives rise to the phase-coexistence. Hence, although the lattice mismatch is minimal in LSMO/STO, the distribution in grain size (figure 1) means that there is a distribution of strain. For example, the top of a large grain should be relatively strain relaxed, while the periphery of the grain or the portion close to the substrate should be highly strained. The growth of the ferromagnetic metallic patches at the expense of the charge-ordered insulating regions on application of magnetic field leads to huge negative magnetoresistance in LSMO/STO (10 nm) film.

The in-plane lattice mismatch between the LSMO and LaAlO$_3$ (LAO) substrate is $+2\%$, which results in bi-axial compressive stress. We have already established that bi-axial strain in LSMO deposited on STO can lead to electronic phase separation. The lattice mismatch being higher in LSMO/LAO compared to LSMO/STO, one can expect that the manifestation of phase separation should be more pronounced in LSMO/LAO. Keeping this factor in mind, we also deposited LSMO films in the thickness range of 100–20 nm on LAO substrate under the same conditions as mentioned earlier. The Curie temperature for the films turn out to be 330–250 K, consistent with a previous report [9]. The average surface roughness of all the films varies between 0.5 and 0.6 nm. It is observed that, with lowering of thickness, for LSMO/LAO (20 nm) film, the metallic regime is completely suppressed (figure 5(A)), although the room temperature resistivity remains almost the same. Even for LSMO/LAO (50 nm) film, the resistivity at low temperature is high ($\sim$20 mΩ). Figure 5(B) shows that the high field MR increases significantly with lowering of thickness. It is noteworthy that the MR is far more sensitive to film thickness in LSMO/LAO films compared to that in LSMO/STO films, possibly a result of the pronounced bi-axial strain in the former. As speculated earlier, it turns out that for LSMO/LAO (20 nm) the evidence of charge ordering is more distinct compared to LSMO/STO (10 nm). On application of strong magnetic field, metallic

resistivity is recovered (figure 5(C)), which is a characteristic signature of charge order melting. At low temperature, however, a sharp resistivity upturn is still observed, which can be attributed to a fraction of charge-ordered patches left undisturbed by magnetic field at low temperature. The effect of inter-granular transport [13, 14] cannot be ruled out either. The highest MR for LSMO/LAO (20 nm) is about 50 000% (figure 5(D)), which means a gigantic three orders of magnitude change in resistivity, typical of charge-ordered systems. The low field MR around the liquid nitrogen temperature is 200% for LSMO/LAO (20 nm). The high value of low temperature resistivity and MR for LSMO/LAO (50 nm) suggests that electronic phase separation might be playing a part. This is not so surprising, since bi-axial strain is known to be influential even at a thickness of 50 nm [15]. The cross-over to insulating behavior on reduction of thickness in LSMO films has been observed previously [16]. However, in that case, the magnitude of MR is very small ($\sim$1%) and the phenomenon is attributed to the reduced Curie temperature of the magnetic dead layer in the film. The enhancement of insulating behavior and high field MR (although, in our case, the effect is much more pronounced) due to the reduction of particle size in a bulk ferromagnetic perovskite manganite have been reported earlier [17]. However, such a phenomenon is attributed to the inter-granular Coulomb gap and surface-spin disorder in the grains respectively, rather than any intrinsic property of the manganites. Here the recovery of metallic state on application of magnetic field clearly indicates that the origin of insulating behavior is different from that stated in [17]. The MR in the case of LSMO/LAO (20 nm), which has a smooth surface, being much higher compared to LSMO/STO (10 nm), which has a relatively rough surface, proves that the origin of such huge enhancement in MR is intrinsic in nature and not arising from the surface roughness of the films. That the bi-axial strain is playing a part can be ascertained from the fact that the LSMO/STO film around the same thickness as that of the thinnest LSMO/LAO film shows normal metallic behavior. Experimentally, till now, there is hardly any evidence of the influence of phase separation on the macroscopic properties like transport or magnetism in a canonical double exchange system such as LSMO.

To summarize, colossal enhancement of magnetoresistance (an unprecedented three orders of magnitude change in resistivity) has been observed in LSMO films as the film thickness is reduced. The transport and magnetic properties strongly suggest electronic phase separation into ferromagnetic metallic and antiferromagnetic charge-ordered insulating regions. It seems that a sufficiently large bi-axial strain leading to Mn–O octahedral distortion can possibly induce phase separation even in a canonical double exchange system such as LSMO.

Acknowledgment

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