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Magnetotransport Studies on GdBa$_2$Cu$_3$O$_7$
Superconducting Film

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Abstract. We report the results of temperature dependent magnetotransport measurements on PLD grown GdBa$_2$Cu$_3$O$_7$ (Gd-123) film in the superconducting transition region, T$_{C0} < T < T_{Conset}$. It is observed that, on application of magnetic field (0 – 14T), T$_{Conset}$ (temperature at which superconducting transition starts) remains unchanged while T$_{C0}$ (temperature at which resistance becomes zero) gets suppressed with field, resulting in the increase in superconducting transition width ($\Delta T_C$). Effect of applied field on the flux dynamics, in superconducting transition region, has been understood in the light of thermally activated flux flow (TAFF) model and variation in pinning energy ($U_0$) in Gd-123.

Keywords: Magnetotransport, Superconductivity, TAFF, Pinning Energy

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INTRODUCTION

Research on high-T$_C$ superconductors (HTSC) is presently aimed at finding the possible solutions to overcome the weak flux pinning behavior and considerable decrease in current density ($J_C$) under applied field, necessary for their practical applicability in high-T$_C$ transistors, non-volatile resistive switches, field effect devices, etc [1 – 3]. Reports are available on the studies on flux dynamics in HTSC using various models such as phase slip, flux line melting-cutting, field induced Lorentz force, thermally activated flux flow (TAFF), etc [4 – 6]. Sharma et al have shown that, T$_{Conset}$ (temperature at which superconducting transition starts) is not affected by the sintering temperature while field induced superconducting transition width ($\Delta T_C$) increases with sintering temperature in Bi-based sol-gel grown polycrystalline HTSC, which has been ascribed to the sintering temperature induced modifications in the grain morphology of the samples [7]. They have discussed the variation in pinning energy ($U_0$) with field in the context of TAFF mechanism and found that, TAFF process can be controlled by the grain morphology.

In this communication, an attempt is made to find out possible mechanism responsible for the field induced modifications in the superconductivity in GdBa$_2$Cu$_3$O$_7$ (Gd-123) film and to study the effect of field on the vortex motion responsible for variation in pinning energy, $U_0$.

EXPERIMENTAL TECHNIQUES

GdBa$_2$Cu$_3$O$_7$ (Gd-123) film (thickness ~ 200nm) was grown on SrTiO$_3$ (STO) (100) substrate using pulsed laser deposition (PLD) by ablating the well characterized single phasic polycrystalline bulk Gd-123 target with KrF excimer laser (wavelength ~ 248nm) having fluence ~ 200mJ/cm$^2$. During deposition, substrate temperature ~ 780°C was kept with oxygen partial pressure ~ 400mTorr at a substrate-to-target distance ~ 45mm. XRD studies were carried out to confirm the phase purity and structure of film. Transport measurements were performed using d.c. four probe method, without and with field, in the temperature range 2–400K using physical property measurement system (PPMS, Quantum Design) (0–14T) facility at UGC-DAE CSR, Indore.
RESULTS AND DISCUSSION

Analysis of XRD data confirms the single phasic nature of the film (not shown here). Temperature dependent resistivity measurements on Gd-123 film under various applied fields show that, $T_{\text{Conset}} \sim 90\text{K}$, exhibited by the film, remains unchanged with field while $T_{\text{C0}}$ (temperature at which resistance becomes zero) decreases from 77.86K ($H = 0$) to 36.15K ($H = 14T$), resulting in the increase in transition width ($\Delta T_C$) with field (figure 1). Variation in $T_{\text{C0}}$ and $\Delta T_C$ with applied field is shown in the inset of fig. 1.

FIGURE 1. Temperature dependent resistivity under various applied fields for Gd-123 film. Inset: Variation in $T_{\text{C0}}$ and $\Delta T_C$ with applied field.

Various mechanisms responsible for the field induced flux dynamics in HTSC have been discussed earlier [4 – 7]. For the validity of TAFM model, two conditions, namely, (i) invariance of $T_{\text{Conset}}$ and (ii) $\Delta T_{\text{H}} [T_{\text{H}} (H = 0) - T_{\text{H}} (H = H)] \propto H^{2/3}$, should be satisfied. During present study, it is observed that, $T_{\text{Conset}}$ remains unchanged with field (fig. 1) indicating that, the first condition is satisfied in Gd-123 film. Inset of fig. 2 shows the plot of $\Delta T_{\text{H}}$ vs. $H^{2/3}$ depicting the linear dependence, confirming that, the second condition is also satisfied in the present case. According to TAFM model, $\rho = \rho_0 (H,T) \exp(-U_0/K_B T)$, wherein, resistivity is caused due to the flow of vortices under field which are thermally activated.

Fig. 2 shows the plots of normalized resistivity $\ln\left(\rho/\rho_{90}\right)$ vs. $T^{-1}$ under various fields for Gd-123 film. Straight line fits to all the plots in the superconducting transition region confirm that, magnetotransport obeys TAFM mechanism. Values of pinning energy, $U_0$, calculated using the TAFM model show a decrease from $2.35eV$ ($H = 0$) to $0.1eV$ ($H = 14T$) indicating that, the energy dissipation caused by vortex motion results in the decrease in $U_0$ and increase in $\Delta T_C$.

FIGURE 2. $\ln(\rho/\rho_{90})$ vs. $T^{-1}$ plots under various applied fields for Gd-123 film. Straight lines are fitted using TAFM model.

CONCLUSIONS

We show that, magnetotransport in Gd-123 superconductor film can be explained by TAFM mechanism. Application of magnetic field results in the increase in superconducting transition width ($\Delta T_C$), while pinning energy ($U_0$), associated with flux motion, decreases.

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Studies on charge transport in Al–doped La$_{0.7}$Ca$_{0.3}$Mn$_{1-x}$Al$_x$O$_3$ manganites

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In this communication, we report the results of the studies on the effect of non-magnetic Al$^{3+}$–doping on structure and properties of La$_{0.7}$Ca$_{0.3}$Mn$_{1-x}$Al$_x$O$_3$ (LCMAO) manganites synthesized by conventional solid state reaction (SSR) route. The Rietveld refinement of the X-ray diffraction (XRD) data confirms the single phase nature of the samples without any detectable impurities. All the samples exhibit metal to insulator transition ($T_f$) which decrease with increase in Al$^{3+}$ doping concentration while it increases with applied magnetic field. To understand the nature of charge transport in metallic and insulating regions of resistivity, various models and mechanisms have been used to fit the observed experimental data.

1. Introduction

Manganites with chemical stoichiometry A$_{1-x}$B$_x$MnO$_3$, A=La, Pr, Nd, etc and B=Ca, Sr, Ba, etc, possess interesting and interrelated properties along with strong structure–property correlation [1,2]. Undoped manganite ($x=0.0$) is antiferromagnetic insulator (AFM) state. On application of magnetic field, resistivity decreases resulting in the magnetoresistance (MR) effect [3] which can be explained on the basis of zener double exchange (ZDE) mechanism [4]. Since only ZDE cannot explain the fundamental properties of manganites i.e. MR effect and metal to insulator transition (at $T_f$), Jahn–Teller (JT) effect [5] is taken into account. In addition to ZDE mechanism and JT effect, charge ordering (CO), orbital ordering (OO), spin ordering (SO), size disorder, tolerance factor, average cation size, electron–phonon coupling, electron–lattice interactions, electron–electron scattering, electron–magnon interactions, phase segregation, phase coexistence, phase separation, etc are also important to understand MR behavior of manganites.

Manganites are known to exhibit metal insulator (M–I) transition at $T_f$ which is concomitant with ferromagnetic to paramagnetic (FM–PM) transition at $T_C$ which is useful in spintronic based applications. However, these properties are dependent on the local lattice distortion and mismatch between rare earth (at A–site) and alkaline elements (at B–site) [2,6,7]. Structural, transport and magnetic properties of manganites and phase transition temperatures ($T_f$ and $T_C$) are mainly governed by the following three factors:

(a) Goldschmidt tolerance factor [8] defined by $T=\frac{(r_A+r_O)}{[\sqrt{2 \times (r_B+r_O)}]}$, where $r_A$ and $r_B$ are average A-site and B-site cationic radii while $r_O$ is oxygen anionic radius.

(b) Charge carrier density determined by the amount of hole doping ($x$ in A$_{1-x}$B$_x$MnO$_3$) which decides the bandwidth of the system and hence movement of charge carriers.

(c) Size variance calculated using the formula:

$$\sigma_x^2(r_A) = \langle r_A^2 \rangle - \langle r_A \rangle^2 = \Sigma_i \langle r_i^2 \rangle - \langle \Sigma_i r_i \rangle^2$$

or

$$\sigma_B^2(r_B) = \langle r_B^2 \rangle - \langle r_B \rangle^2 = \Sigma_i \langle r_i^2 \rangle - \langle \Sigma_i r_i \rangle^2$$

which depends on average A-site or B-site cationic radius ($x_i$ is fraction occupancy, $r_i$ is corresponding ionic radius).

Earlier studies have shown simultaneous effect of grain morphology and size disorder on the resistivity and MR behavior of sol–gel grown nanostructured manganites [7]. Tomioka and Tokura have reported A-site disorder induced enhancement in CO/ OO fluctuations and its effect on magnetic phase transition in manganite [8]. Hwang et al. [9] have reported that, with increase
in tolerance factor \( t \), electrical and magnetic transitions shift toward higher temperatures in doped LaMnO\(_3\) manganites while nonlinear relationship between \( T_P \) and \( t \) has been reported due to presence of A-site size mismatch [10]. Rana et al. [11] have reported size disorder effect in (LaTb)\(_{0.5}\)(CaSr)\(_{0.5}\)MnO\(_3\) manganites wherein Tb and Sr concentration were selected so that average A-site cationic radius remains constant (\( \sim 1.215 \text{ Å} \)) while size disorder increases with doping level. They have observed the fall in transition temperatures and disappearance of disparity between \( T_P \) and \( T_C \) values with size disorder [11].

Several studies report the A-site doping effects on the transport and magnetic properties of mixed valent manganites [1,2,12,13]. Since, manganites are known to exhibit electronic and magnetic phase transitions as well as colossal magnetoresistance (CMR) effect, all the physical properties of manganites strongly depend on the B-site magnetic lattice of Mn ions [6]. Various lower and higher valence ions have been substituted at B-site (such as Bi\(^{3+}\), Zn\(^{2+}\), Zr\(^{4+}\), Ta\(^{5+}\), W\(^{6+}\), Nb\(^{5+}\), Ru\(^{4+}/5+\), Cu\(^{2+}\), Cr\(^{3+}\), Ti\(^{4+}\), Al\(^{3+}\), Ga\(^{3+}\), etc.) and their effect on transport and magnetic properties of manganites has been studied [6,14–21]. Krichene et al. [6] have reported the effect of B-site Bi doping effect on the structural, transport and magnetic properties of La\(_{0.5}\)Ca\(_{0.5}\)MnO\(_3\) manganites. Lakshmi et al. [14] have reported the studies on charge modulation, structural disorder effect in (LaTb)\(_{0.5}\)(CaSr)\(_{0.5}\)MnO\(_3\) manganites. Diagnomic Nb\(^{5+}\)-substitution induced phase transition has been reported in polycrystalline La\(_{0.45}\)Sr\(_{0.55}\)(Mn\(_{1-\text{Nb}}\)\(_{\text{O3}}\)) manganites [15]. Effect of fluctuating valence of Ru\(^{4+}/5+\)-substituted at Mn-site on the magnetic field dependent thermoelectric power (TEP) of Pr\(_{0.5}\)Sr\(_{0.5}\)MnO\(_3\) has been studied [16]. CMR behavior and its dependence on Cu\(^{2+}\) [17] and Cr\(^{3+}\) [18] substitution in manganites has been also studied. Liu et al. [19] have studied the effect of Ti-substitution in La\(_{0.7}\)Ca\(_{0.3}\)Mn\(_{1-\text{Ti}}\)O\(_3\) manganites on the transport, MR and magnetic properties. Tiwari et al. [20] have reported the effect of nonmagnetic A\(^{3+}\)-doped La\(_{0.7}\)Ca\(_{0.3}\)MnO\(_3\) manganites and reported the control over the conduction by disorder induced localization of charge carriers. Teresa et al. [21] have theoretically predicted the quantum critical point in La\(_{2/3}\)Ca\(_{1/3}\)Mn\(_{1-\text{Ga}}\)O\(_3\) manganites.

Keeping in mind all the above aspects of studies on mixed valent manganites and role of B-site substitution in governing the structural and transport properties of A\(^{3+}\)-doped La\(_{0.7}\)Ca\(_{0.3}\)MnO\(_3\) manganites. Results obtained have been discussed in the context of B-site structural disorder and modifications in the magnetic lattice.

### 2. Experimental techniques

Polycrystalline bulk samples of La\(_{1-x}\)Ca\(_{x}\)Mn\(_{1-y}\)Al\(_y\)O\(_3\) (LCMAO: \( x = 0.00, 0.02, 0.04, 0.06, 0.08 \) and 0.10) (hereafter referred as A0, A2, A4, A6, A8 and A10, respectively) were synthesized using conventional ceramic route [22] by stoichiometric mixing of the respective metal oxides (of lanthanum, manganese and aluminum) and carbonates (of calcium) and then subjected to successive grindings. The calcined powder was pelletized and sintered at various temperatures between 950 °C and 1150 °C with intermittent grindings. All the samples were characterized for their structural properties using X-ray diffraction (XRD) measurements at RT and phase purity was verified by Rietveld analysis. Transport and magnetotransport properties were studied using standard four probe dc method in the temperature range: 5–300 K and magnetic field range: 0–8 T.
(d\rho/dT < 0) transition at \( T_p \). With increase in Al content, resistivity increases while \( T_p \) shifts towards lower temperature under applied magnetic field which can be understood as: (i) substitution of non-magnetic \( \text{Al}^{3+} \) at \( \text{Mn}^{3+} \) site results in the reduction in magnetic Mn ion density and hence degrade the ZDE mechanism thereby enhancing the resistivity and shifting \( T_p \) towards lower temperature and (ii) substitution of \( \text{Al}^{3+} \) at \( \text{Mn}^{3+} \) site introduces the structural and magnetic disorders in the lattice resulting in the suppression in hopping of \( e_g \) electrons between Mn ions thereby increasing resistivity and suppressing \( T_p \). In addition, application of magnetic field, resistivity is found to decrease while \( T_p \) increases suggesting an existence of negative MR which is mainly due to field induced suppression in magnetic disorder, reduced scattering of charge carriers at Mn–O–Mn bonds and strengthening of ZDE of mechanism.

As shown in Fig. 3, presently studied LCMO-AO manganites exhibit metallic and semiconducting behavior below and above \( T_p \), respectively, under the applied magnetic field, with exception of, A0 sample which shows only metallic behavior up to 300 K under 5 and 8 T fields. To understand the charge transport in semiconducting region above \( T_p \) in all the LCMO manganites, the observed resistivity data were fitted using various mechanisms and models such as nearest neighbor hopping [27], adiabatic nearest neighboring hopping model for small polaron conduction [28], Shklovskii–Efros (SE) type of variable range hopping (VRH) model [29] and Mott type VRH model for uncorrelated carriers [30,31]. Three of them, namely, (i) nearest neighbor hopping model \([\rho = \rho_0 \exp(E_g/\kappa T)]\), (ii) small polaron conduction \([\rho = A T \exp(E_g/\kappa T)]\) and (iii) Mott type VRH model \([\rho = \rho_0 \exp(T_0/T)^{1/4}]\) were fitted to resistivity data under zero applied field for pure LCMO (A0) manganite sample as shown in Fig. 4. It is clearly seen that, resistivity data in semiconducting region does not follow nearest neighboring hopping model or small polaron conduction mechanism [Fig. 4a] while linear fittings of data to \( \ln \rho \) vs. \( T^{-0.25} \) suggests that in semiconducting region, resistivity of A0 sample follows Mott type VRH mechanism throughout the temperature range studied [Fig. 4b].

Fig. 5 depicts the fitting of resistivity data using VRH model for \( \text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Al}_x\text{O}_3 \) \((x=0.02, 0.04, 0.06, 0.08\) and 0.10) manganites showing a good agreement between the linear fit and semiconducting resistivity data confirming that Mott type VRH model is obeyed by the semiconducting resistivity behavior under all the applied fields studied. Mott type VRH model having the form: \( \rho = \rho_0 \exp(T_0/T)^{1/4} \), where \( T_0 \) is the carrier localization length having the relation with activation energy, \( E_a \) as: \( E_a = T_0/K \) [\( K \) is the Boltzmann constant \( (K=8.617 \times 10^{-5} \text{ eV/K}) \)]. Activation energy of pure LCMO (A0 sample) calculated from the fitting shown in Fig. 4b is found to be \(-0.094 \text{ eV} \) under zero applied field.

Fig. 6 shows the variation in activation energy calculated from fitting the resistivity data shown in Fig. 5 for \( \text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Al}_x\text{O}_3 \) \((x=0.02, 0.04, 0.06, 0.08\) and 0.10) manganites. It can be seen that, with increase in applied magnetic field, activation energy decreases which can be ascribed to the field induced suppression in localization length favouring the hopping of charge carriers and hence reduction in activation energy. Also, with increase in \( \text{Al}^{3+} \) content in \( \text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Al}_x\text{O}_3 \) from 2% to 10%, activation energy is found to increase which is due to the fact that substitution of smaller nonmagnetic \( \text{Al}^{3+} \) ion at larger \( \text{Mn}^{3+} \) results in the enhancement in the structural and magnetic disorder in the system resulting in reduction in hopping of charge carriers and hence increase in activation energy with \( \text{Al}^{3+} \) content.

Few reports are available on the use of ZDE polynomial law fitting of the resistivity data in metallic region [23,24] wherein Salmon and Jaime [32] have reported electron–electron scattering mechanism having \( \rho \alpha T^2 \) relation, responsible for resistivity while Kudo and Ohata [33] have observed the variation in resistivity with \( T^{2.5} \) attributing it to one magnon scattering and Akimoto et al. [34] have suggested un-conventional one magnon scattering as mechanism of charge transport with the dependence of resistivity on \( T^7 \). Recently, our group has investigated ZDE polynomial low fitted to resistivity data collected for \( \text{La}_{0.8}\text{Pr}_{0.2}\text{Sr}_{0.5}\text{Mn}_3\text{O}_7 \) manganite films and found two magnon scattering law and higher order
exponent \( n \) suggesting higher order spin fluctuation mechanisms responsible for the metallic charge transport in manganite films [2].

Presently studied LCMAO manganites exhibit metal to insulator transition at \( T_p \) under 0, 5 and 8 T fields. To understand the electrical charge transport mechanism responsible for the metallic behavior of these samples, we have fitted resistivity data using ZDE polynomial law having the form:

\[
\rho(T) = \rho_0 + \rho_2 T^2 + \rho_n T^n,
\]

where \( \rho_0 \) is residual resistivity, \( \rho_2 \) is the resistivity contributed by electron–electron, electron–phonon and electron–magnon scattering mechanism, \( n \) is the higher order term and \( \rho_n \) is the corresponding resistivity coefficient [2]. In the present case, we have specifically fitted resistivity data in temperature range: 50–140 K for the better comparison as shown in Fig. 7. Obtained values of \( n \) for all the samples under 0, 5 and 8 T fields are listed in Table 1. Values of \( n \) for \( x = 0.00 \) to 0.08 are found to be \( n \approx 2 \) for the samples with \( x = 0.00 \) to 0.08 suggesting a strong electron–electron scattering under zero and all the applied fields. It is clearly seen that \( n \) increases slightly from \( x = 0.00 \) (A0; \( n = 1.8931 \); \( H = 0 \) T) to \( x = 0.08 \) (A8; \( n = 2.0106 \); \( H = 0 \) T) with increase in \( \text{Al}^{3+} \) content revealing the enhanced spin fluctuations with non-magnetic ion density in magnetic lattice. Upon application of magnetic field, \( n \) is found to decrease slightly (Table 1) indicating the field induced suppression in spin fluctuations and increase in spin polarization in all the samples having \( x < 1.0 \). A10 sample shows \( n \approx 7.5 \) under 0 T field.
suggested higher order spin fluctuations in the magnetic lattice mainly due to presence of non-magnetic ion substitution. Under 5 T field, n becomes ~4.5 (in A10) suggesting the field induced suppression in higher order spin fluctuations. For higher applied field of 8 T, n ~ -3 implies un-conventional one magnon scattering mechanism. Field induced suppression in spin fluctuations can be understood on the basis of double exchange theory [4]. According to double exchange model, the hopping of itinerant charge carriers, i.e., $e_g$ electrons of Mn ions, is impeded, if neighboring Mn sites are not parallel, i.e. sites are orthogonal. Transfer integral ($t$) of $e_g$ electrons of Mn ions between the neighboring Mn sites is strongly dependent upon the value of cosine of the angle ($\theta$) between the neighboring spins, i.e. $\cos\theta$. Upon the application of magnetic field, Mn spins get aligned parallel in the direction of applied magnetic field resulting in the $\cos\theta$ → 1 thereby allowing the itinerant Mn $e_g$ electrons to gain kinetic energy and suppress the resistance of the system.

4. Conclusion

In conclusion, we have successfully studied the properties of La$_{0.7}$Ca$_{0.3}$MnO$_3$ thin films, Physica B 406 (2011) 1466.

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Transport studies on La$_{0.8-x}$Pr$_{0.2}$Sr$_x$MnO$_3$ manganite films

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ABSTRACT

In this communication, we report the results of the studies on structural, microstructural, transport and magnetotransport behavior of La$_{0.8-x}$Pr$_{0.2}$Sr$_x$MnO$_3$ (LPSMO) ($x=0.1$, $0.2$ and $0.3$) manganite films grown on (100) single crystalline SrTiO$_3$ (STO) substrate using low cost chemical solution deposition (CSD) method. Films with similar compositions were also grown using sophisticated pulsed laser deposition (PLD) technique and results of structural and transport studies obtained for CSD grown films were compared with PLD grown films. Structural studies show that all the CSD and PLD grown films possess single crystalline nature with compressive and tensile strain, respectively. Surface morphology, studied using atomic force microscope (AFM), reveals the island like grain morphology in CSD grown films while PLD grown films possess smooth film surfaces. Carrier density dependent transport properties of the films have been discussed in the context of zener double exchange (ZDE) mechanism. Lower resistivity and higher transition temperature ($T_c$) observed in CSD grown films as compared to PLD grown films have been discussed in the light of structural strain and surface morphology of the films. Various models and mechanisms have been employed to understand the charge transport in CSD and PLD grown films. Also, observation of low temperature resistivity minima behavior in all the CSD and PLD grown LPSMO films has been explained in the context of electron–electron scattering mechanism.

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1. Introduction

Hole doped manganites having ABO$_3$ type perovskite structure exhibit colossal magnetoresistance (CMR) effect which is a topic of considerable interest [1,2] due to their potential in bolometric applications, magnetic field sensors, magnetic recording and read-write heads. One of the fruitful endeavors in this field is to grow good quality thin films with appreciably large magnetoresistance (MR) and high ferromagnetic to paramagnetic (FM–PM) transition temperature ($T_c$) along with metal to insulator/semiconductor (M–I/S) transition temperature ($T_p$), preferably around room temperature (RT). Structural, transport, magnetotransport and magnetic properties of CMR oxide films are very sensitive to the processing parameters such as deposition technique [3–5], growth temperature [6], annealing temperature and environment [7], film thickness [8,9] and substrate used [10]. Amongst all the thin film deposition methods, Chemical Solution Deposition (CSD) is a low cost and simple method for depositing films on large surface areas, as compared to commonly used physical methods such as Pulsed Laser Deposition (PLD), Magnetron Sputtering Deposition (MSD), Molecular Beam Epitaxy (MBE), etc. It is reported that, CSD grown La$_{0.75}$Sr$_{0.3}$MnO$_3$ (LSMO) film exhibits $T_p > 390$ K and MR$>17.7$% at 360 K under 3 T field [11] while La$_{0.7}$Ca$_{0.3}$MnO$_3$ (LCMO) and LSMO films exhibit better transport and magnetotransport behavior as compared to PLD grown films with similar compositions [3]. Similarly, Markna et al. have observed three times larger temperature sensitivity in CSD grown LCMO film as compared to that of PLD grown films [5].

In this communication, an effort is made to study the properties of CSD grown La$_{0.8-x}$Pr$_{0.2}$Sr$_x$MnO$_3$ (LPSMO) ($x=0.1$, $0.2$ and $0.3$) films and to understand the effect of A-site size variance on the structural, microstructural, transport and magnetotransport properties of the films grown on SrTiO$_3$ (STO) (100) single crystalline substrate. Also, the comparison of the properties of CSD grown LPSMO films with the PLD grown films has been carried out in the context of various properties and magnetotransport
behavior exhibited. A commonly observed problem of low quality films deposited using CSD arise due to number of reasons such as improper substrate, non-optimized growth conditions, uncontrolled grain morphology, purity of chemicals used, etc. Similar problems are faced in other techniques such as PLD, MSD, MBE, etc. Our main aim of the present study is to grow good quality crystalline films of LPSMO on STO substrate using CSD route and to study their structural, microstructural, transport and magneto-transport properties. The effect of structural strain arising due to film lattice-substrate mismatch has been studied and compared with PLD grown films.

2. Experimental techniques

La$_{0.8-x}$Pr$_{0.2}$Sr$_x$MnO$_3$ (LPSMO) [x=0.1, 0.2 and 0.3] manganite films were grown on STO (100) single crystalline substrate using Chemical Solution Deposition (CSD) technique by following the steps as shown in Fig. 1. Acetates of La, Pr, Sr and Mn in stoichiometric ratio were dissolved in acetic acid and double distilled water (1:1 volume ratio) and stirred at 90 °C for 30 min. Transparent light yellow solution was further stirred to achieve clear solution of La$_{0.8-x}$Pr$_{0.2}$Sr$_x$MnO$_3$. LPSMO films were grown on STO substrate using spin-coating with a rotation of 4000 rpm for 25 s and then dried at 150 °C for 30 min in order to remove the excess water. The films were calcined at 350 °C for 30 min so as to expel the organics. The calcined films were then annealed at 1000 °C for 24 h in O$_2$ environment. In order to grow the desired thickness (~100 nm) of the films, spin coating, drying, calcination and annealing process was repeated twice. Films having similar thickness were synthesized using PLD technique for comparing the structural, microstructural, transport and magnetotransport properties. Single phase LPSMO targets for PLD were synthesized using conventional solid state reaction (SSR) route. The parameters used for PLD technique were: laser = 248 nm KrF excimer, substrate temperature = 700 °C, target-substrate distance = 55 mm, oxygen partial pressure = 400 mTorr and film thickness = ~100 nm. La$_{0.8-x}$Pr$_{0.2}$Sr$_x$MnO$_3$ manganite films (grown by CSD and PLD) on STO (100) substrates (LPSMO/STO) now referred as LPSMO I, LPSMO II and LPSMO III for x=0.1, 0.2 and 0.3, respectively, were characterized for structure using X-ray Diffraction (XRD) with Cu Kα radiation at room temperature (RT) while Atomic Force Microscopy (AFM) was used to study surface properties and microstructure. Thickness ~96 and 100 nm for CSD and PLD grown films, respectively, was measured using thickness profilometer. Resistivity data were obtained under various applied fields (0, 1, 5 and 9 T) in the temperature range 2–380 K and MR vs. H isotherms were recorded at various temperatures under 0–9 T using Physical Properties Measurement System (PPMS, Quantum design).

3. Results and discussion

Fig. 2a shows the XRD patterns of CSD grown LPSMO/STO films collected at RT revealing single crystalline growth of films in (100) direction. Bifurcation in LPSMO film and STO substrate peaks reveal the presence of strain in the films which is negligibly small in LPSMO I indicating the lower lattice mismatch between film and substrate. Bifurcation increases from LPSMO I to LPSMO III film indicating the increase in lattice mismatch and hence strain at the interface. The lattice mismatch or strain was calculated using the formula $\delta \% = \left(\frac{d_{\text{sub}}}{} - d_{\text{film}}\right) / d_{\text{sub}} \times 100$ (where $d_{\text{sub}}$ = 3.905 Å). The values of average A-site ionic radius $(r_A)$ |$(r_A) = \sqrt{\sum x_i r_i}$|, size variance at A-site $(\sigma^2_A)$ |$(\sigma^2_A = 2^2 - \langle r_A^2 \rangle - \langle r_A \rangle^2)$|, tolerance factor $(t) = \left(\frac{r_A + r_O}{\sqrt{2}}(r_A + r_O)\right)$ and lattice strain $(\delta \%)$ for all the LPSMO films are listed in Table 1. The $(r_A)$, $\sigma^2_A$ and t increase with increase in Sr$^{2+}$ content. Negative values of the strain indicate the presence of compressive strain at the interface. Strain value $(\delta \%)$ increases from ~0.05 to ~0.15% in LPSMO I to LPSMO III films wherein the size mismatch is gets doubled from LPSMO I to LPSMO III. Though, the compressive strain increases with x in LPSMO III/STO film, the mismatch value is only ~0.15%. Fig. 2b and c shows the XRD patterns of LPSMO I/STO films grown using PLD and CSD, respectively. Both the films are oriented in (h00) direction. As shown in the insets of Fig. 2b and c, (200) XRD peak intensity is larger in CSD grown film as compared to PLD indicating better crystallinity (which is also confirmed by the width of the peaks in the insets, i.e. FWHM). Bifurcation in (200) peaks of film and substrate for, both PLD and CSD grown LPSMO I/STO films, indicates the strained interface. PLD grown LPSMO I/STO film (having large bifurcation) possesses +0.1% (tensile) strain at the interface while CSD grown film (lower separation in peaks) possesses only ~0.05% (compressive) strain.

Microstructural studies carried out using AFM measurements show that LPSMO/STO films grown using CSD possess well connected island like grains, as evident from Fig. 3. Values of average grain size and root mean square (rms) surface roughness of the films are listed in Table 1. It can be seen that, films are relatively flat (because the roughness is <5 nm for each film) and dense
(dense granular structure). With increase in charge carrier density \((x)\), average grain size and rms surface roughness increases which may be due to the increased concentration of larger \(\text{Sr}^{2+}\) ion at smaller La-site. Similar observation can be seen in AFM micrographs of PLD grown LPSMO films (Fig. 3 bottom row) revealing isolated island like grain growth having almost smooth surface.

Fig. 4 shows the \(\rho\)-\(T\) plots for all the CSD grown LPSMO/STO films in the absence and presence of an applied magnetic fields \(\sim 1\), 5 and 9 T in the temperature range 2–360 K. All the films exhibit metal–insulator/semiconductor (M–I/S) transition. With increase in \(x\), the residual resistivity \((\rho_0)\) and peak resistivity \((\rho_p)\) decreases along with increase in metal–insulator/semiconductor transition temperature \((T_p)\) (Table 2). For instance, in LPSMO I, \(\rho_0\) and \(\rho_p\) are \(\sim 50\) times higher than that in LPSMO III, whereas the \(T_p\)\(\sim 238\) K in LPSMO I becomes \(\sim 377\) K in LPSMO III film. Fig. 5 shows the \(\rho\)-\(T\) plots for (a) CSD and (b) PLD grown LPSMO I/STO film in the absence and presence of an applied field \(\sim 5\) T whereas Fig. 5 shows the \(\rho\)-\(T\) plots for (c) CSD and (d) PLD grown LPSMO II and LPSMO III films under 0 T field. It can be seen that all the films exhibit M–I/S transition at \(T_p\). Values of \(\rho_0\), \(\rho_p\) and \(T_p\) under zero applied field are listed in Table 2.

It can be seen from Table 2 that, in both, CSD and PLD grown LPSMO/STO films, the values of resistivity get suppressed with increasing Sr content \((x)\) while \(T_p\) increases. From comparison point of view, resistivity in CSD grown LPSMO/STO films is quite lower as compared to that in PLD grown films while \(T_p\) is higher in CSD grown LPSMO I and LPSMO III films than that of PLD films. LPSMO II/STO films grown by CSD and PLD exhibit almost similar \(T_p\) \((\sim 305\) K). An applied field suppresses the resistivity as well as shifts \(T_p\) towards higher temperature and hence maximum CMR effect exist around \(T_p\).

Urushibara et al. have reported that 10% doping of \(\text{Sr}^{2+}\) at rare earth site (A-site) in manganites results into an insulating behavior throughout the temperature range studied [12]. However, in the presently studied LPSMO I/STO films having 10% Sr-doping at La-site, \(T_p\)\(\sim 178\) K (PLD) and 238 K (CSD) have been observed. Also, with increase in Sr-doping concentration, \(T_p\) increases and becomes \(\sim 347\) K (PLD) and 377 K (CSD) for 30% \(\text{Sr}^{2+}\)-doping. Possible reason for the better transport and large M–I transition at reasonably higher temperatures in Sr-doped \(\text{La}_{0.8-x}\text{Pr}_{0.2}\text{Sr}_x\text{MnO}_3\) manganites are given below.

Smaller sized \(\text{Pr}^{3+}\) substituted at La-site in \(\text{LaMnO}_3\) results in the reduction in \(\text{Mn}–\text{O}–\text{Mn}\) bond angle from \(180^\circ\) making superexchange competitive with Zener Double Exchange (ZDE) [13]. Substitution of \(\text{Sr}^{2+}\) in \(\text{La}_{0.8-x}\text{Pr}_{0.2}\text{Sr}_x\text{MnO}_3\) system results in the increase in lattice parameters and \(\text{Mn}–\text{O}–\text{Mn}\) bond angle towards \(180^\circ\). Sr-doping induces more compressive strain in the lattice resulting in the enhancement in \(T_p\) and suppression in resistivity [14,15]. Increase in \(\text{Sr}\)-concentration (from \(x=0.1\) to 0.3) enhances the \(e_g\) electron bandwidth due to larger size of \(\text{Sr}^{2+}\) ion, promoting the motion of more itinerant electrons between \(\text{Mn}^{3+}\) and \(\text{Mn}^{4+}\) which in turn suppresses resistivity and enhances \(T_p\). In addition, due to substitution of \(\text{Sr}^{2+}\) \((x)\) at La-site, average grain size increases and grain boundary density decreases (Fig. 3) resulting in the suppression in scattering of \(e_g\) electrons which in turn increases \(T_p\) [16–18]. It is reported that grain boundaries can be considered as highly strained while core of the grains possess lower strain in the films [8,9]. With increase in \(\text{Sr}^{2+}\) \((x)\) content, grain size increases and grain boundary density decreases.

![Fig. 3. AFM images of (top) CSD and (bottom) PLD grown LPSMO/STO films.](image-url)
electron, electron–phonon and electron–magnon scattering mechanisms. In metallic region, Salmon and Jaime have reported $T^2$ dependent resistivity (electron–electron scattering) [21] while Kubo and Ohata have observed a variation in resistivity with $T^{2.5}$ attributed to the one magnon scattering [22]. Akimoto et al. have suggested the dependence of resistivity on $T^3$ which is due to unconventional one magnon scattering law [23]. Also, two magnon scattering mechanism has been also reported by Kubo and Ohata to understand the charge transport in metallic region [22].

As shown in Fig. 4, CSD grown LPSMO I/STO film exhibits metallic and semiconducting regions below and above $T_p$, respectively, whereas LPSMO II/STO and LPSMO III/STO films exhibit metallic behavior up to RT. In order to understand the charge transport in semiconducting region above $T_p$ in LPSMO I/STO film, the observed resistivity data were fitted using various mechanisms and models such as nearest neighbor hopping [24], adiabatic nearest neighboring hopping model for small polaron conduction [25], Schklovskii–Efros (SE) type of Variable Range Hopping (VRH) model [26] and Mott type VRH model for uncorrelated carriers [27,28]. Three of them, namely, (i) nearest neighboring hopping model $[\rho=\rho_0\exp(E_d/KT)]$, (ii) small polaron conduction $[\rho=AD\exp(E_d/KT)]$ and (iii) Mott type VRH model $[\rho=\rho_0\exp(T_o/T)^{1/4}]$ were fitted to resistivity data under zero field as shown in Fig. 6. It is clearly seen that resistivity data does not follow the small polaron conduction or nearest neighboring hopping conduction (Fig. 6a) while linear fit to $\ln\rho$ vs. $T^{0.25}$ data suggests that resistivity under zero field (as well as 1, 5 and 9 T fields) follows the Mott type VRH model throughout the temperature range studied (Fig. 6b). Fig. 6c shows the fitting of resistivity data using VRH model for PLD grown LPSMO I/STO film indicating a good agreement between the linear fit and semiconducting region suggesting that Mott type VRH model is obeyed by the semiconducting resistivity behavior under all the applied fields studied. In Mott type VRH model, $T_o$ is related to carrier localization length. The values of activation energy at different fields calculated using the equation, $E=\epsilon_0/2K$, where $\epsilon_0$ is the activation energy and $K$ is Boltzmann constant ($8.617 \times 10^{-5}$ eV/K) are 53.54, 51.93, 44.35 and 39.44 K under 0, 1, 5 and 9 T fields, respectively, for CSD grown films and 54.24 and 48.27 K at 0 and 5 T fields, respectively, for PLD grown films. It can be seen that the activation energy decreases with increase in field suggesting that the localization length is suppressed, favoring the hopping of charge carriers with the increase in field. In addition, values of activation energy are higher in PLD grown films as compared to CSD which may be due to the better transport in CSD grown film.

In order to understand the charge transport responsible in metallic region, small polaron conduction mechanism, zener double exchange (ZDE) polynomial model, etc. have been reported [19,29,30]. Theory of low temperature small polaron conduction mechanism has been explained in the form of resistivity equation given by:

$$\rho(T)=\rho_0 + [\omega_o/\sinh^2(\delta/4\pi K T)] + B T^n$$

where $\omega_o$ is an average frequency of softest optical mode. ZDE polynomial law can be given as:

$$\rho=\rho_0 + \rho_2 T^2 + \rho_3 T^3$$

where $\rho_2$ is the residual resistivity, $\rho_3$ is the resistivity contributed by the electron–electron, electron–phonon and electron–magnon scattering mechanism, $n$ is a higher order term and $\rho_p$ is the corresponding resistivity

---

**Table 2**

Values of $\rho_p$, $\rho_2$ and $T_p$ for CSD and PLD grown LPSMO/STO films under zero applied field.

<table>
<thead>
<tr>
<th>LPSMO/STO (100)</th>
<th>CSD</th>
<th>PLD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\rho_p$ (m$\Omega$ cm)</td>
<td>$\rho_2$ (m$\Omega$ cm)</td>
</tr>
<tr>
<td>LPSMO I</td>
<td>13.440</td>
<td>408.560</td>
</tr>
<tr>
<td>LPSMO II</td>
<td>2.326</td>
<td>28.905</td>
</tr>
<tr>
<td>LPSMO III</td>
<td>0.273</td>
<td>6.961</td>
</tr>
</tbody>
</table>
coefficient. Fig. 7 shows the resistivity data of CSD grown LPSMO I/STO film carried out under 0 T field fitted using small polaron conduction mechanism (Fig. 7a) and ZDE polynomial law (Fig. 7b) for the temperature range: 2–235 K (i.e. $T_T$ of the film). Both the models fit properly throughout the temperature range studied. To confirm appropriateness of the model in this region, the difference resistivity, $\rho_{\text{exp}}-\rho_{\text{theory}}$, has been calculated and plotted as a function of temperature in Fig. 7c suggesting that ZDE mechanism is more appropriate for the metallic behavior in the films under study. Responsible transport mechanisms in metallic region of all the CSD grown LPSMO/STO films can be understood by fitting the resistivity data to a ZDE Polynomial law. For one magnon scattering process, $n$ is found to be equal to 2.5 and 3 and for two magnon scattering phenomena, it is 4.5 and 7.5. It is reported that, for $n=5.5$ and 6.5 corresponds to the higher $T^0$ law indicating the importance of spin fluctuations to the low temperature resistivity [19]. Figs. 8–10 show the metallic resistivity fittings to ZDE polynomial law (in linear scale) for CSD grown LPSMO I, LPSMO II and LPSMO III films, respectively, carried out using the proposed models under various applied fields.

LPSMO/STO films under various fields show the different electron–magnon scattering phenomena. As shown in Fig. 8, in LPSMO I/STO film, value of $n$ in ZDE polynomial law continuously decreases with increase in applied magnetic field, suggesting the magnetic field induced suppression in the spin fluctuations, lattice vibrations and JT polarons. For 0 T field, the metallicity follows the two magnon scattering law which becomes one magnon scattering phenomenon at 9 T field due to the field induced suppression in lattice vibrations. In LPSMO II/STO film (Fig. 9), resistivity data follows the one magnon scattering law in the absence and presence of various applied fields. In LPSMO III/STO film (Fig. 10), the resistivity data can be fitted to two magnon scattering law; where under 0 and 1 T fields it follows higher $T^0$ law indicating the high spin fluctuations in lower field transport which get suppressed under 5 and 9 T applied fields exhibiting low order $T^n$ law, indicating the field induced suppression in spin fluctuations. From LPSMO II/STO to LPSMO III/STO film, the one magnon scattering phenomenon becomes two magnon scattering process due to the effect of large size disorder in LPSMO III/STO than LPSMO II/STO film.

An unusual observation in $\rho$–$T$ behavior of presently studied LPSMO manganite films grown by CSD and PLD techniques is the occurrence of resistivity upturn (resistivity minima) at low temperature. Several theories have been suggested to explain the resistivity minima behavior observed at low temperatures in manganites in the form of polycrystalline bulk, single crystal or thin film [31–34]. Presently studied LPSMO films exhibit resistivity minima at $\sim$50 K (30 K) for PLD (CSD) grown films. The possible reasons for such a behavior in $\rho$–$T$ are, grain boundary localization [35], kondo effect [36], electron–electron scattering due to enhanced coulomic interactions and weak localization [33,36], etc. PLD grown LPSMO films possess almost smooth surface (AFM images) and hence absence of grain boundaries and hence their contribution to resistivity minima can be ruled out. Few reports suggest the co-existence of kondo effect and electron–electron scattering mechanism responsible for resistivity minima in manganites [31,37,38]. In order to justify whether kondo effect and/or electron–electron scattering are responsible for the observed resistivity minima in LPSMO manganite films, the low temperature $\rho$–$T$ data (2–80 K) have been fitted using $\rho=[1/(\sigma_0+B \ln T)]+\rho_B T^n$ (kondo effect) and $\rho=[1/(\sigma_0+B T^{1/2})]+\rho_0 T^n$ (electron–electron scattering effect) equations as shown in Fig. 11, where $\sigma_0$ signifies residual conductivity, $B$ signifies coulomic interactions which correlates the depth of minima ($B$ is inversely proportional to minima depth) and $n$ represents the power law exponent. In these equations, first term relates with elastic scattering of charge

Fig. 5. $\rho$ vs. $T$ plots of (a) CSD and (b) PLD grown LPSMO I/STO films under 0 and 5 T field (c) CSD and (d) PLD grown LPSMO II/STO and LPSMO III/STO films under 0 T field.
carriers while second term signify the inelastic scattering of charge carriers. Lower (third) panel of Fig. 11 shows that resistivity difference between experimental and theoretical values is comparatively lower for electron–electron scattering mechanism as compared to kondo effect suggesting the validation of electron–electron scattering mechanism responsible for the observation of low temperature resistivity behavior in LPSMO films.

As shown in Fig. 12, electron–electron scattering mechanism calculated (theoretical) data fits nicely to the experimental observation which is evident from low $\chi^2$ values (Table 3) for all the CSD and PLD grown films. Table 3 lists the values of parameters derived from the fitting of electron–electron scattering mechanism to the experimental data in the temperature range: 2–80 K under different applied fields. $T_{\text{min}}$ shifts towards lower temperature with increase in Sr$^{2+}$ content for CSD and PLD grown films indicating doping induced enhanced inelastic scattering while for all the films, magnetic field suppresses inelastic scattering, i.e. increase in $T_{\text{min}}$ with applied field. $T_{\text{min}}$ is found to be maximum in PLD grown LPSMO I/STO film. Depth parameter B increases with increase in Sr$^{2+}$ content and applied magnetic field suggesting the reduction in resistivity minima depth for all the films understudy mainly due to enhanced tolerance factor ($t$) (Table 1). This can be understood as – increase in tolerance factor results into the suppression in coulombic interactions (i.e. supportive transport...
behavior in higher $Sr^{2+}$ sample), weak localization and reduced electron–electron scattering at low temperatures. Also, resistivity minima depth is more prominent in PLD grown films as compared to CSD grown films mainly due to better crystallinity and presence of compressive strain at the interface in CSD grown films.

To understand the systematic variation in MR with field in CSD grown LPSMO/STO films and to compare it with that observed in PLD grown films, MR vs. H isotherms were recorded at various temperatures. The results are shown in Fig. 9, which displays the plot of $\rho$ vs. $T$ for LPSMO II/STO film under 0, 1, 5, and 9 T fields. A similar analysis was carried out for LPSMO III/STO film, and the results are shown in Fig. 10, which displays the plot of $\rho$ vs. $T$ for LPSMO III/STO film under (a) 0 and 1 T and (b) 5 and 9 T fields. The analysis revealed that the systematic variation in MR with field in CSD grown LPSMO/STO films is different from that in PLD grown films.

To further understand the nature of the resistivity behavior, the low temperature resistivity data were fitted to the laws $\rho = \left[1/(s_0 + BT^{1/2})\right] + \rho_n T^n$ (electron–electron scattering mechanism) and $\rho = \left[1/(s_0 + BT^{1/2})\right] + \rho_n T^n$ (Kondo effect). The fitting results are shown in Fig. 11 and Fig. 12. The lower panel of these figures shows the difference between the experimental and theoretical data for both the laws.
temperatures in the field up to 9 T for all the CSD grown films as shown in Fig. 13 (in PLD grown films, measurements were carried out up to 8 T field). The suppression in resistivity and shift in $T_P$ to higher temperatures (Fig. 4) under applied field, results in the negative MR having maximum value at $\sim T_P$ which decreases with the increase in Sr ($x$) concentration. In LPSMO I/STO film, MR 75% is observed at 200 K (close to $T_P \sim 238$ K) under 9 T which decreases to 35% at 300 K (near $T_P \sim 304$ K) under 9 T in LPSMO II/STO film. In LPSMO III/STO film, MR $\sim 30\%$ is exhibited at 360 K (near $T_P \sim 377$ K) under 9 T with appreciably large low temperature MR $\sim 42\%$ (at 5 K). Enhanced CMR effect in CSD grown LPSMO I/STO film can be attributed to the strong effect of magnetic field on the electron–lattice interaction. With increasing Sr ($x$) content, the lattice distortion is suppressed and CMR effect is pronounced. Also, due to the presence of smaller grains, grain boundary effect is prominent in LPSMO I/STO film, the magnetic field aligns more spins at non-magnetic grain boundaries resulting in higher MR.

Fig. 14 depicts the MR vs. $H$ isotherms at 5 K for LPSMO III/STO films grown by CSD and PLD techniques. It can be seen that, at 5 K, PLD grown film exhibits MR $\sim 4\%$ under 8 T while CSD grown film exhibits MR $\sim 41\%$ under similar conditions which can be attributed to the spin polarized tunneling (SPT) or spin dependent scattering (SDS) effect [39,40]. These observations clearly indicate that, the CSD grown LPSMO/STO films possess better magnetotransport as compared to PLD grown films.

### Table 3

Parameters obtained from fitting the resistivity data to the equation $\rho = \frac{1}{s_0 + BT^{1/2}} + \rho_n T^n$ (electron–electron scattering mechanism) law (for definition of parameters, see text).

<table>
<thead>
<tr>
<th>LPSMO/STO</th>
<th>$H$ (T)</th>
<th>$T_{\text{min}}$ (K)</th>
<th>$\sigma_0$ (m$\Omega$ cm)$^{-1}$</th>
<th>$B$ (m$\Omega$ cm K$^{1/2}$)$^{-1}$</th>
<th>$\rho_n$ (m$\Omega$ cm/K$^n$)</th>
<th>$n$</th>
<th>$\chi^2 (10^{-3})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSD</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LPSMO I</td>
<td>0</td>
<td>17.81</td>
<td>0.0717</td>
<td>0.00176</td>
<td>0.00085</td>
<td>2.025</td>
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<tr>
<td>LPSMO II</td>
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<td>11.31</td>
<td>0.4026</td>
<td>0.00279</td>
<td>0.00005</td>
<td>2.206</td>
<td>0.03</td>
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<tr>
<td>LPSMO III</td>
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<td>3.6494</td>
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<tr>
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<td>0.64</td>
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<tr>
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<td>0.00219</td>
<td>0.00065</td>
<td>2.207</td>
<td>0.82</td>
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<tr>
<td>LPSMO I (CSD – 9 T)</td>
<td>9</td>
<td>23.19</td>
<td>0.0802</td>
<td>0.00241</td>
<td>0.00057</td>
<td>2.313</td>
<td>0.09</td>
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<td>PLD</td>
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<td>LPSMO I</td>
<td>0</td>
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<td>0.00036</td>
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<td>0.00483</td>
<td>2.06E$-$5</td>
<td>2.207</td>
<td>7E$-$8</td>
</tr>
</tbody>
</table>

Fig. 13. MR vs. $H$ isotherms for CSD grown LPSMO/STO films at collected various temperatures.

Fig. 14. MR vs. $H$ isotherms for CSD and PLD grown LPSMO III/STO films collected at 5 K.
4. Conclusions

We have successfully synthesized La$_{0.8-x}$Pr$_x$Sr$_x$MnO$_3$ (LPSMO) [x=0.1, 0.2 and 0.3] manganite films onto the single crystalline SrTiO$_3$ (STO) (100) substrate using low cost and simple Chemical Solution Deposition technique (CSD). Structural analysis using X-ray Diffraction (XRD) confirms the (001) oriented film growth while surface and morphological studies using AFM reveal the island like grain growth observed in CSD grown films while PLD grown films possess smooth surface with isolated island grain growth. Increase in compressive strain and enhanced grain size (and hence reduced grain boundary density) with Sr$^{2+}$ content (x) support the ZDE mechanism which results into the improved transport, decrease in resistivity and increase in $T_h$. CSD grown films show better transport as compared to PLD films due to the better crystallinity and compressive strain at the film–substrate interface. The responsible mechanism for the charge transport in semiconducting region of CSD and PLD grown films is VRH type hopping of charge carriers indicating the field induced reduction in activation energy which is lower in CSD grown films as compared to PLD grown films. In metallic region, size variance at A-site plays an important role in governing the charge transport revealing that, CSD grown LPSMO II film obeys one magnon scattering process which becomes two magnon scattering process in LPSMO III/STO due to the large size variance. Enhancement in tolerance factor with Sr$^{2+}$ content results into the suppression in coulombic interactions between the charge carriers, weak localization and reduced electron–electron scattering mechanism at low temperature and hence consequences in the modifications in resistivity upturn behavior. Peak MR near $T_h$ is governed by the ZDE mechanism while low temperature large MR has been attributed to the spin polarized tunneling (SPT) or spin dependent scattering (SDS) effect. Pr$^{3+}$ can induce the M–I/$\lambda$ transition along with large MR value in the CSD grown LPSMO I/STO film. Better transport and magnetotransport properties observed in CSD grown films as compared to PLD grown films can be attributed to the better crystallinity, presence of compressive strain at the interface and improved grain morphology in CSD grown LPSMO/STO films.

Acknowledgment

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Swift Heavy Ion Irradiation Studies on the Transport in La$_{0.8-x}$Pr$_{0.2}$Sr$_x$MnO$_3$ Manganite Films

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**Keywords:** SHI Irradiation, Manganites. Transport

**Abstract.** Thin films of La$_{0.8-x}$Pr$_{0.2}$Sr$_x$MnO$_3$ (LPSMO) ($x = 0.1, 0.2, 0.3$) manganite, synthesized using pulsed laser deposition (PLD) technique, were irradiated by 200MeV Ag$^{+15}$ ions with an ion fluence of $5 \times 10^{11}$ ions/cm$^2$. Structural and microstructural characterizations have been carried out using XRD and AFM show single crystalline nature of the films having island like grain growth. The structural and grain morphology modifications due to irradiation has been observed. Temperature dependent resistivity measurements have been carried out for all the films before and after irradiation, which reveal a reduction in the resistivity and enhancement in insulator - metal (I-M) transition temperature ($T_P$) with Sr content ($x$) resulting in improved transport (reduced resistivity and enhanced $T_P$) in the films which can be attributed to the irradiation induced improved crystallinity and grain morphology. Temperature coefficient of resistance (TCR) improves on irradiation which is useful for practical applications.

**Introduction**

Studies on hole doped perovskite structured manganites with stoichiometric composition La$_{1-x}$A$_x$MnO$_3$ (A = Ca$^{2+}$, Sr$^{2+}$, Pb$^{2+}$, Ba$^{2+}$, etc) exhibiting colossal magnetoresistance (CMR) effect has attracted considerable attention due to their potential applications in temperature and magnetic field sensors, magnetic recording, read-write heads, bolometric devices etc. Various functionalities exhibited by these mixed valent manganites can be explained using different phenomena such as zener double exchange mechanism (ZDE), Jahn-Teller (JT) distortion, charge ordering (CO), spin ordering (SO), orbital ordering (OO), size variance ($\sigma_A^2$), etc [1, 2]. In addition, they are known to exhibit large magnetoresistance (MR) around their metal – insulator transition at $T_P$ (in concomitant with ferromagnetic – paramagnetic transition at $T_C$) which is highly affected by the structural parameters such – tolerance factor $t$ and $<r_A>$ (and hence by size variance, $\sigma_A^2$) [3, 4], quantified as: $t = (r_A + r_O) / \sqrt{2} (r_B + r_O)$, $<r_A> = \sum_i r_i$ and $\sigma_A^2 = \sum_i r_i^2 - <r_A>^2 = <r_A^2> - <r_A>^2$. Markna et al have reported the effect of structural disorder on the transport and magnetotransport in manganite thin films [5]. The dependence of the structural, microstructural, transport, magnetotransport and magnetic properties of manganites on structural parameters results into a strong structure – property correlations in the manganites [6 – 8].

For practical applications, the materials should be grown in the form of thin films having physical properties different of than their bulk counterparts, mainly due, to the structural strain present at the film – substrate interface. Manganite based thin films can be fabricated, either by physical or chemical techniques, such as pulsed laser deposition (PLD), physical vapor deposition (PVD), molecular beam epitaxy (MBE), sputtering, metal oxide chemical vapor deposition (MOCVD), chemical solution deposition (CSD), dip coating, spin coating, sol-gel, etc. PLD Using PLD technique, one can grow high quality films in controlled manner. Several reports exist on the
studies on PLD grown manganite films having large temperature and field sensitivity [5, 9, 10]. Markna et al have observed a large cationic size disorder induced high temperature sensitivity (~60%K$^{-1}$) in PLD grown La$_{0.5}$Pr$_{0.2}$Ba$_{0.3}$MnO$_3$ manganite film [5].

Swift Heavy Ion (SHI) irradiation is a fascinating tool to create defects in controlled manner and localized strain in various manganite based thin films. SHI irradiation results in the structural and morphological modifications which in turn affect the physical properties of manganite films [11–13]. Irradiation induced improvement in the transport has been reported at one hand while enhancement in resistivity and suppression in $T_P$ have been observed on the other hand in manganite film [9, 14].

In this communication, we discuss the effect of 200MeV Ag$^{15+}$ ion irradiation on the modification in structural, microstructural and transport properties of PLD grown La$_{0.8-x}$Pr$_{0.2}$Sr$_x$MnO$_3$ (LPSMO) ($x$ = 0.1, 0.2 and 0.3) manganite films. Our main aim is to study the simultaneous effect of structural parameters [$t$, $<r_A>$ and $\sigma_A^2$] and irradiation in modifying structural and microstructural properties which affect transport in 100nm LPSMO films.

**Experimental Details**

Bulk polycrystalline targets of LPSMO samples were synthesized using solid state reaction route$^7$ while high quality LPSMO films on single crystalline (100) SrTiO$_3$ (STO) substrate were grown using PLD technique as reported earlier [5]. 15 UD Tandem Accelerator, at Inter University Accelerator Centre (IUAC), New Delhi was used for irradiating LPSMO films at 200MeV Ag$^{15+}$ ions with a fluence of $5 \times 10^{11}$ ions/cm$^2$. Irradiation was performed at a low angle with respect to the ion beam to avoid the channeling effect. The ion beam was focused onto a spot of $\sim$ 1mm diameter on the sample and was scanned over a $10 \times 10$ mm$^2$ area using a magnetic scanner in order to ensure that, irradiation in LPSMO films is uniform. Pristine and irradiated films were characterized using X-ray diffraction (XRD) for structural phase purity and atomic force microscopy (AFM) for surface morphology. $\rho$–$T$ measurements were carried out using standard d.c. four probe technique (PPMS quantum design).

**Result and Discussion:**

X-ray diffraction patterns of PLD grown 100nm pristine and irradiated LPSMO [$x$ = 0.1 (LPS I), 0.2 (LPS II) and 0.3 (LPS III)] thin films (fig.1) show oriented growth of the films in (h00) direction.
The separation between LPSMO film and STO substrate peaks reveal the presence of strain in the films which is negligibly small in LPS I indicating lower lattice mismatch between the LPS I and STO. Separation increases from LPS I - III indicating an increase in lattice mismatch and hence strain at the interface. The lattice mismatch or strain was calculated using the formula $\delta\% = \frac{(d_{\text{substrate}} - d_{\text{film}})}{d_{\text{substrate}}} \times 100$ ($d_{\text{STO}} = 3.905\text{Å}$). The values of average A - site ionic radius ($<r_A>$), size variance at A - site ($\sigma_A^2$), tolerance factor (t) and lattice strain ($\delta\%$) for all the LPS pristine and irradiated films are listed in Table 1. Positive values of the strain indicate the presence of compressive strain at the interface. Film relaxation decreases with increasing Sr$^{2+}$ content and hence with increase in average A - site cationic radius and size mismatch at A – site. The value of strain reduces after irradiation due to local annealing effect of SHI Irradiation.

Table 1. Values of $<r_A>$, $\sigma_A^2$, t and $\delta$ (pristine and irradiated) for PLD grown LPSMO/STO films

<table>
<thead>
<tr>
<th>LPSMO/STO (h00)</th>
<th>$&lt;r_A&gt;$ [Å]</th>
<th>$\sigma_A^2$ [Å$^2$]</th>
<th>t</th>
<th>$\delta%$ Pristine</th>
<th>$\delta%$ Irradiated</th>
</tr>
</thead>
<tbody>
<tr>
<td>LPS I</td>
<td>1.2180</td>
<td>0.00115</td>
<td>0.8327</td>
<td>0.81</td>
<td>0.62</td>
</tr>
<tr>
<td>LPS II</td>
<td>1.2274</td>
<td>0.00191</td>
<td>0.8914</td>
<td>0.87</td>
<td>0.685</td>
</tr>
<tr>
<td>LPS III</td>
<td>1.2368</td>
<td>0.00249</td>
<td>0.9393</td>
<td>0.1</td>
<td>0.81</td>
</tr>
</tbody>
</table>

Studies on the effect of SHI irradiation have shown the formation of track like defects in manganites [15]. Presently, 200 MeV Ag$^{15+}$ ions were used for modifying various properties of LPS I - III films. Calculated values of electronic energy loss ($S_e$) are $S_e \sim$13.86KeV/nm, 13.37KeV/nm, 13.61KeV/nm and nuclear energy loss ($S_n$) are $S_n \sim$38.21eV/nm, 37.78eV/nm, 37.34eV/nm for LPS I - II respectively, (using SRIM-2008) [16]. The projected range of Ag$^{15+}$ ions was $\sim$22.86µm, 23.07 µm, and 23.28 µm for LPS I to III which is very high as compared to film thickness $\sim$100 nm, ensuring that the bombarded ions pass through the film completely and finally get deposited in the substrate.
Microstructural studies on LPS I – III (pristine and irradiated) films, carried out using atomic force microscope (AFM) show island like grain growth [figure 2 (a to f)]. It can be seen that, with increasing Sr concentration, average grain size and root-mean-square (RMS) roughness increases in all the films. Figure 2 (d to f) clearly shows the 2D images of the irradiated surfaces showing modifications in the pristine films due to Ag\(^{+15}\) ion bombardment (circles indicates damaged part). Irradiation with \(5 \times 10^{11}\) ions/cm\(^2\) fluence, shows the formation of track-like defects and spike-like structures [inset of fig. 2(d-f)] on the surface. The track-like defects possess the average diameter of \(\sim 100\)nm which is quite large than columnar defects.

**Figure 2.** AFM micrograph of pristine and irradiated (2d images) of LPS films. Inset [fig. 2(d-f)] show 3d images of irradiated LPS films

Temperature dependence of resistivity of pristine and irradiated LPS I - III films, is shown in figure 3.
Substitution of Sr$^{2+}$ at La - site in La$_{0.8-x}$Pr$_{0.2}$Sr$_x$MnO$_3$ results in an increase in lattice parameters and hence increases in Mn-O-Mn bond angle towards 180°. Sr - doping induces more compressive strain in the lattice resulting in the enhancement in $T_P$ and suppression in resistivity. Smaller size Pr$^{3+}$ substituting at La - site in LaMnO$_3$ results in the reduction of Mn-O-Mn bond angle from 180° making super exchange competitive with Zener Double Exchange (ZDE) [17]. The increase in the Sr - doping concentration (from $x = 0.1$ to 0.3) at La (A) - site in La$_{0.8-x}$Pr$_{0.2}$Sr$_x$MnO$_3$, enhances the $e_g$ electron bandwidth due to larger size of Sr$^{2+}$ ion, promoting the motion of itinerant electrons between Mn$^{3+}$ and Mn$^{4+}$ which in turn suppresses resistivity and increases the $T_P$ (Table 2). In addition, due to the substitution of Sr$^{2+}$ ($x$) at La - site, the average grain size increases and the grain boundary density decreases resulting into the suppression in the scattering of $e_g$ electrons which in turn increases $T_P$. The passage of energetic ion through LPS films, results in the deposition of energy on the film, which reduces structural distortion resulting in local release of strain and improvement in the crystallinity of the film favouring electronic transport and suppression in resistivity and hence increases in $T_P$. The amount of suppression in resistivity LPS II is lower as compared to LPS I and LPS III which may be due to lower electronic energy loss in LPS II.

The temperature sensitivity values for LPS films (pristine and irradiated) were calculated using (TCR % = 1/R × dR/dT × 100) and plotted in the temperature range 5-400K in fig. 4. Values of TCR are -2.12%K$^{-1}$, 0.35%K$^{-1}$, 2.65%K$^{-1}$ for LPS I - III respectively. An increase in $\langle r_A \rangle$ and $\sigma_A^2$ with Sr$^{2+}$, enhances the drop in $\rho$ near $\sim T_P$ resulting the increases in TCR value for pristine films. In irradiated LPS films, the TCR values are -2.04%K$^{-1}$, 0.56%K$^{-1}$, 2.10%K$^{-1}$ respectively for LPS I - III. Irradiation induced changes in TCR values, are useful for bolometric applications.

**Table 2.** Values of $T_P$ (pristine and irradiated) for PLD grown LPS films

<table>
<thead>
<tr>
<th>Films</th>
<th>Pristine</th>
<th>Irradiated</th>
</tr>
</thead>
<tbody>
<tr>
<td>LPS I</td>
<td>179K</td>
<td>188K</td>
</tr>
<tr>
<td>LPS II</td>
<td>305K</td>
<td>310K</td>
</tr>
<tr>
<td>LPS III</td>
<td>311K</td>
<td>318K</td>
</tr>
</tbody>
</table>

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Figure 4. TCR vs. T plots for LPS pristine and irradiated films

Conclusions

Effect of 200MeV Ag$^{+15}$ irradiation with $5 \times 10^{11}$ ions/cm$^2$ fluence and size variance ($\sigma_A^2$) on the modifications in structural and transport properties of LPS I-III films have been studied. Increases in Sr$^{2+}$ content results in an increase in $\sigma_A^2$ which improves transport and enhances $T_P$. In addition, SHI irradiation, further improves transport and $T_P$ due to the release in structural strain. Temperature sensitivity of the LPS I-III films get modified with Sr$^{2+}$ content and SHI irradiation in the films studied.

Acknowledgements

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References


Role of strain and microstructure in chemical solution deposited La$_{0.7}$Pb$_{0.3}$MnO$_3$ manganite films: Thickness dependent swift heavy ions irradiation studies

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HIGHLIGHTS

- Chemical solution deposition (CSD) technique is low cost, simple and easy to handle.
- Prominent strain effect in lower thickness manganite films.
- Microstructural changes with thickness modify the transport in the manganite films.
- Modifications in the properties of manganite films due to swift heavy ion irradiation.
- On SHI irradiation, improvement in temperature and field sensitivity

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ABSTRACT

Owing to the higher magnetic transition temperature ($T_C$), above RT and large magnetoresistance (MR) exhibited by La$_{0.7}$Pb$_{0.3}$MnO$_3$ (LPMO) manganite, we have carried out the studies on the effect of 200 MeV Ag$^{+15}$ ion irradiation on LPMO films. It is interesting to note that, the modifications in the surface grain morphology and roughness in higher thickness (> 200 nm) LPMO films, due to irradiation, affects the transport and magnetotransport, in a prominent manner, which has been understood in the light of enhancement in the scattering of charge carriers. The results of the structural, microstructural, transport and magnetotransport properties of pristine and irradiated LPMO films (150–350 nm) have been discussed in this communication.

1. Introduction

Last decade has witnessed a phenomenal growth in research on mixed valent manganites exhibiting colossal magnetoresistance (CMR) effect, owing to their scientific and technological applications (Chahara et al., 1993; Von Helmolt et al., 1993; Jin et al., 1994). Several interesting aspects such as interplay between spin, charge and lattice degrees of freedom, charge and orbital ordering, structure–property correlations, etc exhibited by CMR manganites, lead to understanding various properties exhibited by them. Earlier, it was felt that, Zener double exchange (ZDE) mechanism successfully explains the simultaneous occurrence of ferromagnetism and metallic behavior in mixed valent manganites (Zener, 1955), but later, it was confirmed that, ZDE cannot alone explain all the properties exhibited by CMR manganites. Important role played by the structural strain in modifying the transport and magnetic properties of manganites have been investigated (Hwang et al., 1995; Sharma et al., 1996).

La$_{0.7}$Pb$_{0.3}$MnO$_3$ (LPMO) manganite is well studied in the form of polycrystalline bulk, single crystal and thin film forms (Young et al., 2002; Mahendiran et al., 1995; Solanki et al., 2009, 2011; Jia et al., 1995; Manoharan et al., 1994; Srinivasan et al., 1995; Lisauskas et al., 2001; Solanki and Choudhary et al., 2011) due to the high magnetic ordering temperature (above RT) and large magnetoresistance (MR) exhibited under relatively low applied fields (Solanki et al., 2011; Solanki and Choudhary et al., 2011). LPMO manganite is suitable for application because it possesses ferromagnetic metallic ground state at RT (Young et al., 2002).
Mahendiran et al. (1995) have reported the observation of large MR at RT in polycrystalline La$_{1-x}$Pb$_x$MnO$_3$ while nanostructured LPMO exhibits large low temperature negative MR ($\sim$300) under 1 T with insulator—metal transition temperature ($T_F$) at $\sim$350 K (Solanki et al., 2009). PLD grown Pb-doped LaMnO$_3$ films grown on single crystalline LAO (0 0 1) substrates exhibit MR~40 and 41% at RT and 266 K under 6.5 and 0.7 T fields, respectively (Manoharan et al., 1994; Lisaukas et al., 2001).

Most of the applications of manganites involve thin films, where in, the physical properties are different from their bulk counterparts, mainly due to the presence and nature of strain and its effect (Li et al., 2002). Chemical solution deposition (CSD) technique for thin film deposition is a simple and cost-effective method for the growth of good quality and homogeneous manganite films on suitable substrates. A strong dependence of transport and magnetotransport on the film thickness and annealing conditions used in the CSD grown CMR manganite films have been reported (Solanki et al., 2011; Solanki and Choudhary et al., 2011). High purity lanthanum acetate [La (CH$_3$CO$_2$)$_3$ XH$_2$O], lead carbonate (PbCO$_3$) and manganese acetate (Mn (CH$_3$CO$_2$)$_2$ X 4 H$_2$O) were taken as starting materials in stoichiometric ratio. The precursor solution was prepared by dissolving the constituents (precursors/starting materials) in double distilled water (DDW) and acetic acid (AA) with desired composition. The optimum ratio of DDW and AA of 1:1 was maintained in proper volume to yield of 0.3 M solution. Then, the solution was stirred at 90 °C using magnetic stirrer until a clean and transparent solution was obtained. LAO substrates were cleaned by keeping in (i) DDW at 90 °C, (ii) tri chloro ethylene (TCE) at 60 °C, (iii) DDW at 90 °C, (iv) methanol at 60 °C, (v) DDW at 90 °C and finally (vi) acetone at 60 °C, for 5 min in each. Films were prepared by spin coating the solution at 4000 rpm for 25 s on cleaned LAO (1 0 0) substrates to attain 50 nm film thickness. The film was then dried at 150 °C for 30 min on heater to remove the excess water from the surface and the dried film was calcined at 350 °C for 30 min in furnace. To achieve the desired thicknesses of 150 to 350 nm, the successive coatings were made. Finally, the films were annealed at 1000 °C for 24 h in O$_2$ environment. All the films were irradiated using 200 MeV Ag$^{+15}$ ions with $5 \times 10^{11}$ ions/cm$^2$ ion dose using 15 UD Tandem PELLETRON accelerator at Inter University Accelerator Centre (IUAC), New Delhi. XRD measurements performed using Bruker X-ray diffractometer (model: D8 Advanced) confirmed the single crystalline nature and oriented growth of all the films. AFM micrographs were obtained using NANO NICS make Academia model while the four probe resistivity measurements (with and without field) in the temperature range 5–375 K were performed using PPMIS (quantum design, physical property measurement system) in a field up to 9 T.

3. Results and discussion

Enlarged views of the (2 0 0) XRD reflections of pristine and irradiated LPMO films (150–350 nm) on LAO substrates are shown in Fig. 1. Existence of the lattice mismatch $(\delta)$ between the film and substrate, quantified using $\delta (%)=|q_{\text{substrate}}-q_{\text{film}}|/q_{\text{film}}$
$a_{\text{substrate}} \times 100$, where $a$ is the lattice parameter of film/substrate, is evident from the separation between the film and substrate peaks. Values of compressive strain (negative $\delta$ value) calculated for all the films have been given in Table 1. For pristine films, strain is suppressed with increasing film thickness, while for irradiated films, it first increases from 150 to 200 nm film and then decreases with film thickness (Table 1). Increase in strain for 200 nm film is due to irradiation induced effects, which can be understood as the estimated range of 200 MeV Ag$^{+15}$ ions in LPMO films, under study, is in the range of $\sim \mu$m (calculated using SRIM-2008) which is much larger than the film thicknesses. Passage of energetic Ag-ions, through LPMO films (150–350 nm), results in, either (i) release in strain at the interface, locally, by reducing the structural distortion around the ion path, as well as, improvement in the interface structure quality due to annealing effect at interface or (ii) creation of defects at the interface (Markna et al., 2007) (and in film volume) resulting in the enhancement in strain.

In 150 nm film, ion energy is sufficient to induce the annealing effect at the interface leading to comparatively less strain while in 200 nm film, the effect (ii) becomes more prominent resulting in the enhancement in strain. In higher thickness films (> 200 nm), the lattice relaxation due to irradiation becomes dominant which results in the decrease in strain in irradiated films.

Fig. 2 shows the AFM micrographs of all the pristine and irradiated LPMO/LAO films. The values of grain size and surface roughness, obtained from the analysis of AFM data, are given in Table 1. From the micrographs, it can be seen that, all the films possess island like grain morphology, having diffused grain boundaries in 150 nm film which becomes sharp and clear, due to irradiation, in higher thickness films. pristine films (300 and 350 nm) possess almost elongated shaped grains (shown in black circles), which on irradiation, becomes spherical with the reduction in surface roughness.

$\rho$–$T$ measurements, in the temperature range 5–375 K under zero applied field (Fig. 3), show that all the pristine and irradiated LPMO/LAO films.

Table 1

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>Strain $\delta$ (%)</th>
<th>Surface roughness (nm)</th>
<th>Grain size (nm)</th>
<th>$\rho_p$ (m$\Omega$ cm)</th>
<th>$T_p$ (K)</th>
<th>MR (%) at 9 T</th>
<th>TCR (%K$^{-1}$)</th>
<th>FCR (%T$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150 pristine</td>
<td>$-2.123( \pm 0.002)$</td>
<td>29.83</td>
<td>$180( \pm 20)$</td>
<td>802.0</td>
<td>254</td>
<td>4</td>
<td>85</td>
<td>42</td>
</tr>
<tr>
<td>150 irradiated</td>
<td>$-1.963( \pm 0.005)$</td>
<td>7.38</td>
<td>$270( \pm 30)$</td>
<td>313.6</td>
<td>263</td>
<td>15</td>
<td>84</td>
<td>50</td>
</tr>
<tr>
<td>200 pristine</td>
<td>$-2.036( \pm 0.001)$</td>
<td>18.64</td>
<td>$250( \pm 10)$</td>
<td>685.9</td>
<td>256</td>
<td>10</td>
<td>81</td>
<td>43</td>
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<tr>
<td>200 irradiated</td>
<td>$-4.752( \pm 0.002)$</td>
<td>12.28</td>
<td>$300( \pm 30)$</td>
<td>3689</td>
<td>245</td>
<td>11</td>
<td>82</td>
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</tr>
<tr>
<td>300 pristine</td>
<td>$-2.035( \pm 0.001)$</td>
<td>12.28</td>
<td>$150( \pm 10)$</td>
<td>312.3</td>
<td>261</td>
<td>15</td>
<td>77</td>
<td>44</td>
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<tr>
<td>300 irradiated</td>
<td>$-4.751( \pm 0.001)$</td>
<td>19.54</td>
<td>$300( \pm 25)$</td>
<td>2225</td>
<td>247</td>
<td>16</td>
<td>81</td>
<td>36</td>
</tr>
<tr>
<td>350 pristine</td>
<td>$-1.949( \pm 0.003)$</td>
<td>15.24</td>
<td>$600( \pm 80)$</td>
<td>247.6</td>
<td>269</td>
<td>18</td>
<td>74</td>
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<tr>
<td>350 irradiated</td>
<td>$-3.294( \pm 0.005)$</td>
<td>15.24</td>
<td>$350( \pm 50)$</td>
<td>2002</td>
<td>250</td>
<td>20</td>
<td>84</td>
<td>41</td>
</tr>
</tbody>
</table>

Fig. 2. AFM micrographs of (top) pristine and (bottom) irradiated LPMO/LAO films.
films exhibit metal (dρ/dT > 0) to insulator (dρ/dT < 0) transition at T_P below RT. The values of peak resistivity (ρ_p) and T_P, for all the films, are given in Table 1. The increase in T_P [254 K (prist.) to 263 K (irrad.)] and the suppression in ρ_p throughout the temperature range studied, in 150 nm films, may be attributed to the reduction in strain, improved crystallinity and reduced surface roughness. Irradiation results in the stretching of Mn–O–Mn bond angles to 180° leading to the increase in hoping of charge carriers between adjacent Mn^{3+} and Mn^{4+} sites which in turn decreases the resistivity and enhances T_P in 150 nm LPMO film. In higher thickness films (200, 300 and 350 nm), the ρ_p increases appreciably while T_P is suppressed (Table 1) on irradiation. The resistivity enhancement in higher thickness films, on irradiation, can be attributed to the deterioration in crystal structure, as well as increased strain at the interface. Irradiation-induced decrease in grain size and hence increase in grain boundary density consequences the increase in magnetic disorder and non-magnetic phase fraction resulting in the increase in resistivity and decrease in T_P (Table 1).

In order to understand the magnetotransport behavior of all the pristine and irradiated films, the temperature dependent resistivity measurement carried out in the temperature range 5–375 K under 0, 1, 5 and 9 T fields are shown in Fig. 4. It can be seen that, the resistivity decreases while T_P shifts towards higher temperature suggesting negative CMR effect in the films which can be due to the field induced suppression in the magnetic disorder and charge carrier scattering in the films especially at the grain boundaries, as well as improvement in the Mn–O–Mn bonds towards 180° supporting ZDE.

In order to understand the effect of SHI irradiation on the magnetotransport of LPMO films, MR isotherms (MR = [(ρ_H/ρ_0)/ρ_0] × 100), recorded at 5, 240 and 300 K, for all the pristine and
irradiated films are shown in Fig. 5 (calculated MR values shown in Fig. 5 are negative). Values of MR at 5, 240 and 300 K under 9 T field are tabulated in Table 1. At 5 K, all the films exhibit a sharp rise in MR–H plots at ~1 T field, known as low field MR (LFMR). Observation of LFMR ~10% at 5 K, in all the pristine and irradiated films (Fig. 5) indicates the absence of intergranular spin polarized tunneling. At 240 K (near $T_P$), maximum MR has been observed in all the films due to intrinsic magnetotransport which can be attributed to the field induced suppression in the scattering of the charge carriers at the grain boundaries and magnetic disorder at Mn–O–Mn bond angle. It can be clearly seen that, with increasing film thickness, the MR increases in all the films which may be due to the field induced suppression in the three dimensional disorder in the films which increases with increasing film thickness (Solanki et al., 2011; Solanki and Choudhary et al., 2011). In low thickness (150 nm) films, irradiation with $5 \times 10^{11}$ ions/cm² Ag-ions dose consequences in the improvement in grain size and surface roughness resulting in the reduction in grain boundary density and disorder at Mn–O–Mn bonds which in turn, suppresses the field induced suppression of scattering and magnetic disorder leading to marginal effect on MR at 5 and 240 K (Table 1). In higher thickness films (> 200 nm), decrease in grain size and enhanced surface roughness results in the enhancement in the scattering of charge carriers as well as magnetic disorder at the grain boundaries, leading to an increase in MR at 5 and 240 K (Table 1). Also, at 300 K, MR increases from 42% (prist.) to 50% (irrad.) due to irradiation, which is useful for practical applications.

Further, to explore the application potential of CSD grown pristine and irradiated LPMO films, we have calculated the temperature and field sensitivities of resistivities quantified by temperature coefficient of resistance \( \text{TCR} = \frac{1}{R} \left( \frac{dR}{dT} \times 100 \, \% \, K^{-1} \right) \) and field coefficient of resistance \( \text{FCR} = \frac{1}{R} \left( \frac{dR}{dH} \times 100 \, \% \, T^{-1} \right) \), respectively. Fig. 6 shows the temperature dependent variation in TCR under 0 T field for (a) pristine and (b) irradiated LPMO/LAO films. In similar way, field dependent variation in FCR at 300 K is shown in Fig. 7 for (a) pristine and (b) irradiated LPMO/LAO films. Values of TCR (around $T_P$) and FCR (at 9 T) are listed in Table 1. In all the irradiated films, significant enhancement in positive TCR and negative FCR values near RT (Table 1) suggests the usefulness of SHI irradiated CSD grown LPMO/LAO films for bolometric and magnetic sensing applications.

### 4. Conclusions

In this communication, we report the results of the studies on the effect of 200 MeV Ag$^{+15}$ ion irradiation in modifying the transport and magnetotransport in CSD grown LPMO manganite films. It is observed that the SHI irradiation effect is more pronounced in higher thickness (> 200 nm) LPMO films which has been attributed to the enhancement in the scattering of charge carriers due to the decrease in grain size and increase in surface roughness. In addition, the observation of enhancement in the positive TCR and negative FCR values at RT, due to irradiation,
shows that, the LPMO manganite films grown by simple and cost effective CSD technique are suitable for applications.

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