Electronic and magneto transport property of $\text{Pr}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ system in nanometric gran size modulation

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Abstract. Grain size effect on electronic- and magneto-transport properties of hole doped manganite $\text{Pr}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (PSMO) in nanometric dimension has been thoroughly investigated under external magnetic field range from zero to $\pm$ 8 Tesla down to 4 K. Metal-insulator transition temperature ($T_P$) which is observed for all the PSMO nanometric samples, differs from the ferromagnetic to paramagnetic transition temperature ($T_C$) in the nanometric regime compare to its reported bulk counterpart mainly due to the enhanced surface disorder effect. Temperature dependent low field complex magneto-impedance (LFMI) behaviour has also been studied in presence of external magnetic field range of 0 - 800 Oe down to 77 K.

1. Introduction

The perovskite manganites with generic formula $\text{Re}_{1-x}\text{R}_x\text{MnO}_3$, where Re is trivalent rare earth cation (e.g. La, Pr, Nd etc.) and R is divalent alkaline earth cation (e.g. Ca, Sr, Ba, Pb etc.) have drawn considerable attention, especially following the discovery of their negative colossal magnetoresistance (CMR) [1-3] effect. In these materials subtle balance between charge, spin, lattice and orbital degrees of freedom leads to a variety of phases with fascinating properties like charge ordering (CO) and orbital ordering (OO) [4,5], metal - insulator (M-I) transition [6,7], ferromagnetic insulator (FMI), canted anti-ferromagnetic insulator (CAFI) [8] etc. In the bulk polycrystalline or single crystal manganite system the double exchange mechanism strongly correlates the electronic transport property with its magnetic property. In nanometric grain size modulation, a drastic change in physical properties mainly arises due to finite size effect. A number of reports have already been published [9-11], but there is no such details systematic study on PSMO system in nanometric size modualtion. Investigation on electronic- and magneto-transport properties of a series of chemically synthesized PSMO nanoparticles is the main focus of this paper.

2. Experimental details

A series of nanometric PSMO samples with different particle size ($\Phi$) were synthesized by chemical ‘pyrophoric’ reaction process [12] making solution of $\text{Pr}_6\text{O}_{11}$, $\text{Sr(NO}_3)_2$ and $\text{Mn(CH}_3\text{COO)}_2$ in required stoichiometric ratios. The burnt ash like powder was calcined at 850°C for 5 hours followed by three different sintering temperatures (850°C, 950°C and 1050°C) to obtain samples with different particle size. X-ray diffraction (Philips PW1710) study was carried out with Cu-K$\alpha$ radiation ($\lambda = 1.5418$ Å) to investigate the proper phase formation in the samples. High field magneto-transport and electronic-transport study of PSMO samples were carried out (down to 2 K) by a standard four
probe contact method using a high field low temperature facilities (8 T CFM VTI, CRYOGENIC Ltd., U.K.). The low-field (up to 5000 Oe) magneto-transport (down to 77 K) measurement was also carried out using a homemade set up. Temperature and frequency dependent (down to 77 K) low field magneto impedance (LFMI) measurements were studied using a 1000 Oe solenoid coil magnet along with a high frequency HIOKI 3532-50 LCR Hi-TESTER meter. A high precision temperature controller (model 331, Lakeshore) was used to measure and control the temperature (within ± 10 mK resolution) for all the measurements.

3. Results and Discussions

The XRD patterns in Fig. 1(a) including its inset confirm the single phase of PSMO sample with orthorhombic structure (Pbnm space group). The average crystallite sizes of the samples are found to be 28 nm (PSMO 850), 37 nm (PSMO 950), and 42 nm (PSMO 1050). The log-normal distribution of particle size of PSMO 850 sample gives an average particle size of 28 nm. From the high resolution TEM (HRTEM) micrograph the estimated inter planer lattice spacing (d) is ~ (3.501 ±0.001) Å, which corresponds to the (111) plane of the crystal. From the field dependent MR study of various temperatures under 8 Tesla magnetic field, we have observed maximum 85% change in MR for PSMO 850 sample, 83.5% change in MR for PSMO 950 (as shown in Fig. 1(b)) near $T_p$, and a 82.27% change in MR for PSMO 1050 at 150 K (not shown here), respectively. Almost ~ 44% change in MR has been found with respect to the MR value obtained at lowest temperature (4 K) for all of PSMO nanometric samples at 8 Tesla. To find out the spin polarized tunnelling contribution (MR_{SPT}) over total magneto-resistance (MR = MR_{SPT} + MR_{INT}) for the PSMO polycrystalline nanoparticles, we have used a generic model proposed by the Raychoudhuri et al. [13].

![Figure 1](image_url) (a) Rietveld refinement of HRXRD of PSMO 1050 sample. The inset shows normal XRD of PSMO 850, 950, 1050 samples; (b) HFMR and LFMR variation of PSMO 950 sample at different temperatures in the magnetic field range of 0 to ± 8 Tesla.

From the fitting of experimental LFMR data, the calculated spin polarized tunnelling (SPT) contribution as well as the intrinsic contribution (INT) in magneto-resistance data (as tabulated in Table - 1) indicates that MR_{SPT} increases in PSMO 1050 sample up to 1.53% with respect to PSMO 850 sample, whereas MR_{INT} decreases up to 2.38% in PSMO 1050 sample with respect to PSMO 850 sample. The expected values of MR and calculated values of MR match very well for each nanometric samples. High field magneto-resistance is related to the contribution from spin polarized inter granular tunneling of electrons across the grain boundaries and spin dependent scattering across the grain surfaces due to field induced-depression of local magnetic disorder near the grain boundary. A strong temperature (down to 77 K) and frequency (up to 2 MHz) dependence low field complex magneto impedance (LFMI) [$= [Z (\omega, H, T) - Z (\omega, 0, T)] / Z (\omega, 0, T)$] have been observed for all PSMO nanometric samples [14]. Figure 2(a) depicts a temperature dependent MI of PSMO 1050 sample whereas inset of Fig. 2(a) shows frequency dependent MI change of PSMO 1050 sample. PSMO 1050 sample shows maximum percentage of MI change (~ - 45%) at 250 K. Figure 2(b)
shows a combined plot of % MI change for all PSMO nanometric samples as a function of magnetic field at 77 K and at a frequency of 1 MHz. Maximum -35 % MI change has been found for PSMO1050 sample and only -6% change in MI has been found for PSMO 850 sample.

**Table 1** LFMR values and estimated various contributions of MR of PSMO samples for different particle size.

| Crystallite size | MR_{SPT} (%) | MR_{INT} (%) | MR_{EXP} (%) | MR (%) |
|------------------|---------------|--------------|--------------|--------|
| PSMO 850         | -8.54         | -11.54       | -20.08       | -20.3  |
| PSMO 950         | -6.95         | -12.21       | -19.16       | -19.4  |
| PSMO 1050        | -21.63        | -2.63        | -15.85       | -16.1  |

In PSMO 950 sample, the maximum change in MI, have been found -21% at 2 MHz frequency (is not shown here) by sweeping the dc magnetic field up to 800 Oe. PSMO 850 sample depicts maximum -8% change in MI at lowest attainable temperature (77 K) at 1 MHz whereas no MI is observed at room temperature. Frequency dependent MI of PSMO 850 sample at 77 K shows maximum -15% change in MI at higher frequency (2 MHz) rather than 100 KHz. In higher frequency range, most likely the skin penetration depth becomes smaller and charge carrier conduction process along the surface region of the PSMO samples increases due to skin depth effect of electrodynamics, which can produce a moderate value of MI [15]. Figure 3(a) shows resistivity plot of PSMO 850 at different magnetic fields of zero, 1, and 8 Tesla. MR variation as a function of temperatures for samples PSMO 850 at 1, and 8 Tesla magnetic fields is shown in the inset of Fig. 3(a). We have observed the metal-insulator transition around ~ 180 K for PSMO 850 and PSMO 950 nanometric samples whereas in case of PSMO 1050 (not shown here), it was found near 250 K. The temperature dependent resistivity plots of all PSMO samples under without magnetic field is shown in Fig. 3(b). It is clear from the Fig. 3(b) that the peak resistivity value monotonically decreases (~ 13.91%) with size reduction at 0 Tesla magnetic fields. We have observed that lowest MR value of all nanometric samples appear around room temperature which corroborates the resistivity data of PSMO sample. It is clear that MIT transition temperatures are suppressed with increasing of magnetic fields. Shifting of $T_p$ towards the lower temperature with variation of particle size is most likely due to the grain surface effect on electronic transport. Low temperature resistivity upturn has been observed below 50 K for all PSMO samples. The upturn of resistivity at low temperatures regime for all the nanometric samples may
arises due to various reasons, namely Coulomb blockade charging effect, Kondo-like mechanism, high spin disorder increment of impurity scattering of electrons in magnetic inhomogeneous matrix, however it has been found that electron-electronic interaction mechanism [16] and weak localization can explain the resistivity upturn properly for these kind of hole doped PSMO nanomanganites.

4. Conclusion

In summary chemically synthesized PSMO nanoparticles exhibit a strong dependency on electronic and magneto- transport behaviors in nanometric grain size modulation. The HFMR in these nanoparticles arises mainly due to the spin polarized tunneling of conduction electrons between the adjacent ferromagnetic grains, which is enhanced with the decrease of grain size. We have observed relatively high MI values at higher frequency regime than low frequency regime. It confirms that the surface conduction increases in the PSMO manganite with decreases of the skin depth. The MIT transition temperatures ($T_P$) slightly differ with grain size variation. Nano size induced grain boundary effect is believed to be responsible for this modification of $T_P$.

5. Acknowledgement

One of the authors, Poloy T. Das wishing to acknowledge Council of Scientific and Industrial Research (CSIR) for the financial support through award no.: 09/081 (1077)/ 2010-EMR-I.

6. References

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Figure 3 (a) Resistivity plot as a function of temperature of PSMO 850 sample at 0, 1, and 8 Tesla respectively; Inset of (a), % of MR variation of PSMO 850 sample at 1 and 8 Tesla respectively, (b) Combined resistivity plot of PSMO 850, 950 and 1050 samples at 0 Tesla.