Chapter 3

Investigation on the Magnetolectric Transport Properties of Gadolinium Based Manganites

3.1 Introduction

Manganites and Cobaltites belong to the perovskite class of materials. They exhibit interesting magnetic, electrical and structural properties. These class of materials have been in the forefront of material research for three decades or so. Among them, manganites occupy a special position because of its application potential as catalysts, as electrode materials and in various other applications like bolometer etc. [1 - 4]. Since the discovery of CMR in manganites research on these class of materials is on the rise. They exhibit simultaneous phase transitions namely from ferromagnetic to paramagnetic and metal to insulator. They also display electronic and structural peculiarities including orbital and charge ordering, formation of local moments and Jahn Teller distortions [5, 6]. Such richness combined with their relatively simple structure make them ideal for investigating the general principles that govern these properties.

Charge ordering has a prominent role in the transport properties of manganites. Charge ordered state exists for a wide doping range for low bandwidth manganites. Metal to insulator (M-I) transition is observed in the case of Lanthanum (high and intermediate bandwidth) manganites at near room temperatures. However manganites doped with smaller rare earth ions like Gd, Pr (low bandwidth manganites) exhibited metal insulator transition only at very low temperatures [3, 7]. At the same time when the M-I transition is attained for low average radius A-site cation perovskites, higher magnetoresistance ratio is obtained. This makes rare earth based manganites very attractive for further investigation. Relatively, fewer studies are reported on perovskites based on heavy
rare earths. This is because it was presumed that smaller radius cation in the A site
does not result in M-I transition at near room temperature. Reports on heavy rare
earth doped manganite are scarce in literature. Compositions x=0.3 to 0.7 exhibit
charge ordering and hence was chosen for magnetoresistance study.

The evaluation of conducting properties in the paramagnetic regime will
help probe the mechanism of conduction in these compounds. The conduction
mechanism in the paramagnetic phase is a matter of controversy as different
schools of thought propose different models for conduction. For example, data on
certain compounds were fitted with purely activated law by R. M. Kusters et al.,
G. C. Xiong et al. and M. F. Hundley et al. [8 -10]. While some authors proposed
small polaron hopping conduction mechanism (SPH) over an extended
temperature ranges [11-15]. At the same time N. F. Mott and E. A. Davies used
the Variable Range Hopping mechanism (VRH) for the whole temperature range
[16, 17]. The electrical conductivity studies in the low temperature regime will
enable to propose a plausible mechanism for conduction in manganites. This
chapter deals with the structural, dc conductivity, magnetisation and
magnetoresistance studies of Gd$_{1-x}$Sr$_x$MnO$_3$ (x=0.3, x=0.4 and x=0.5), which was
prepared by wet solid state reaction method.

3.2 Sample preparation and structural characterization

Gd$_{1-x}$Sr$_x$MnO$_3$ (x=0.3, x=0.4 and x=0.5) samples are prepared using wet
solid state reaction method. Stochiometric amounts of Gd$_2$O$_3$, SrCO$_3$ and MnO$_2$
were mixed in concentrated nitric acid. The solution was heated, boiling off the
excess nitric acid. This precursor was calcinated in air at 900°C overnight. The
remaining black powder was pressed into pellets and sintered at 1200°C in air for
3 days [7, 18]. The sample was analyzed by means of X-Ray Powder
Diffractometer (Rigaku Dmax - C) using Cu-K$_\alpha$ radiation ($\lambda$ =1.5414Å). The X-
ray diffraction pattern of the samples is shown in figure 3.1. From the XRD
pattern it is clear that the sample Gd$_{0.5}$Sr$_{0.5}$MnO$_3$ is single phasic with an
orthorhombically distorted perovskite structure. The scanning electron microscopy studies were carried out using a field emission scanning electron microscope JSM 6335 FESEM at 50 kV. The SEM pictures of GSMO sample are shown as figures 3.2(a) to 3.2(c). The SEM images indicate that the size of particles is in the micron regime. From atomic absorption spectroscopy (AAS) and energy dispersive spectroscopy (EDS), the stoichiometry of the elements in the sample was evaluated and is in good agreement with theoretical values.

![X-ray diffraction pattern](image1)

**Figure 3.1** X-ray diffraction pattern of Gd$_{1-x}$Sr$_x$MnO$_3$ (x=0.3, x=0.4 and x=0.5)

(a) ![SEM micrograph](image2)  (b) ![SEM micrograph](image3)  (c) ![SEM micrograph](image4)

**Figure 3.2** SEM micrograph of Gd$_{1-x}$Sr$_x$MnO$_3$ [(a) x=0.3, (b) x=0.4 and (c) x=0.5]
3.3 D. C Conductivity and Magnetisation Studies of GSMO samples

3.3.1 D. C Conductivity studies

The low temperature dc conductivity measurements of the GSMO samples were carried out by using source measuring unit (Keithley 236) and by cooling the sample using CTI-CRYOGENICS Model 22C cryodyne cryocooler, in a temperature range of 20K - 300K. This system uses helium as the refrigerant and can be interfaced with many instruments that require cryogenic temperatures. The pressure maintained in the compressor is 400 PSIG/2758 kPa. The temperature was controlled using Lake Shore Model 321 auto tuning temperature controller, which has a stability of ±0.1K. The pressure inside the cryo cooler was maintained at 10^-5mB with the help of INDO VISION vacuum Pumping System Model VPS-100. The dc conductivity system is fully automated by using proprietary software called ICS.

The temperature variation of resistivity for the GSMO samples is depicted in figure 3.3. From the figure it is clear that all the three compositions show insulating nature in the measured temperature range. But careful observation reveals a slope change near 40 K. which is an indication of metal insulator transition. The behaviour is common to low band width manganites, and a very high magnetic field is needed to make a metal insulator transition [7]. The variation of resistivity with composition is in accordance with double exchange (DE) mechanism. According to DE mechanism the hopping amplitude is maximum when the value of Mn^4+/Mn^3+ ratio is 0.5. The hopping amplitude is optimum for the doping x = 1/3. As amount of strontium doping increases, more Mn^3+ ions are produced and hence the Mn^4+/Mn^3+ ratio recedes away from the optimum 0.5 value and consequently resistivity value decreases.
The exact conduction mechanism in the paramagnetic phase of the GSMO samples can be ascertained by analyzing the resistivity data with equations of different conduction mechanisms. In paramagnetic insulating regime, mainly three types of mechanism have been found to be ruling the conduction process in these compounds. They are (1) thermal activation or band gap model, (2) variable range hopping model (VRH) and (3) small polaron hopping model (SPH). Band gap model is widely employed in most of the semiconductors and insulators [8 - 10]. There is an energy gap between conduction band and valence band. If the thermal energy is sufficient to overcome the band gap the electron becomes free to conduct. The expression for resistivity can be written in the following form

$$\rho = \rho_0 \exp\left(\frac{E_A}{k_B T}\right)$$  \hspace{1cm} (3.1)

where T is the absolute temperature, $\rho_0$ is the value of resistivity at infinite temperature, $E_A$ is the activation energy and $k_B$ is the Boltzmann’s constant. From equation (3.1) it is clear that the resistivity data should exhibit Arrhenius temperature dependence (i.e. straight line behaviour between log $\rho$ and 1/T). The variation of log $\rho$ with reciprocal of temperature for the three GSMO samples in
the temperature range 50K - 300K (the resistivity data below 50K is avoided to make sure that the region is purely paramagnetic) is given in figure 3.4.

![Graph showing resistivity vs reciprocal temperature for x=0.3, x=0.4, x=0.5](image)

**Figure 3.4** Temperature variation of resistivity with reciprocal temperature of Gd$_{1-x}$Sr$_x$MnO$_3$ (x=0.3, x=0.4 and x=0.5)

However from figure 3.4, it is clear that all the variations are non linear and hence we conclude that the band gap model is insufficient to explain the conduction process in these class of material. The second possibility is small polaron hopping model (SPH) [11-15]. In the case of small polarons (deeply trapped electrons), the thermal energy is not sufficient to overcome the deep potential well and to hop out of its site. Then the hopping is possible by a multiphonon assisted process [19]. That is, the electron is activated to an intermediate state first, which is still a localized state with higher energy. Then the thermal energy acquired from the second phonon is sufficient for hoping out from the intermediate state to its nearest neighbour. The expression for resistivity is

$$\rho = AT \exp\left(\frac{E_A}{k_BT}\right)$$  \hspace{1cm} (3.2)

where $T$ is absolute temperature and $E_A$ is activation energy and $A$ is a constant. The value of $A$ is given by
\[ A = \frac{k_B}{\nu_{ph} N e^3 R^2 c (1 - c) \exp(2\alpha R)} \] (3.3)

where \( N \) is the number of ion sites per unit volume, \( R \) average inter site spacing, \( c \) is the fraction of sites occupied by polaron, \( \alpha \) is the electron wave function decay constant, \( \nu_{ph} \) is optical phonon frequency and \( k_B \) is the Boltzmann's constant. Further, in order to check whether the conduction process obeys SPH a graph is plotted with \( \log(\rho/T) \) on the Y-axis and \( 1/T \) on the X-axis (figure 3.5). The graph is linear at the high temperature side but there is deviation from linearity at the low temperature side. So it can be concluded that SPH model alone can not account for the conduction process.

Figure 3.5 Temperature variation of \( \log(\rho/T) \) with reciprocal temperature of Gd\(_{1-x}\)Sr\(_x\)MnO\(_3\) (x=0.3, x=0.4 and x=0.5)

Now the next alternative is to check whether the VRH model can be applied to account for the observed conduction process. According to the variable range hopping (VRH) model [20-25] if the electron is not deeply trapped (that is a large polaron) it can hop from one site to another with phonon assistance. At low
temperature the thermal energy is not sufficient to allow electrons to hop to their nearest neighbours, but the possibility to hop further to find a site with a smaller potential difference exists. Since the hopping range is variable, it is called variable range hopping. In three dimensional VRH model, resistivity can be expressed as

$$\rho = \rho_0 \exp\left(\frac{T_0}{T}\right)^{1/4}$$  \hspace{1cm} (3.4)

Here the straight line behaviour is between log $\rho$ and $T^{-1/4}$. The constant $T_0$ is given by

$$T_0 = \frac{18\alpha^3}{k_B N(E_F)}$$  \hspace{1cm} (3.5)

where $\alpha$ is the electron wave function decay constant, $N(E_F)$ density of states at Fermi level and $k_B$ is Boltzmann’s constant. VRH theory was developed to explain electron transport in doped semiconductors. There is a competition between the potential difference and electron hopping distance [16, 17]. That is reflected in the expression for hopping rate to a site at a distance $R$, with higher energy $\Delta E$ than the origin.

$$\gamma = \gamma_0 \exp\left(-2\alpha R - \Delta E / k_B T\right)$$ \hspace{1cm} (3.6)

For this VRH model the graph plotted between log $\rho$ and $T^{-1/4}$ should be a straight line. From figure 3.6, it is clear that there is a linear behaviour in the temperature range 50K – 170K. Thus for a wide temperature range the conduction mechanism in the paramagnetic phase of the material obeys VRH. Above 170K the conduction is SPH assisted. This could be verified by plotting a graph between log ($\rho / T$) and $1/T$, above 170K [figure 3.7(a)] and log $\rho$ vs $T^{-1/4}$ in the temperature range 40K – 170K [figure 3.7(b)]. From the figure it is clear that the two variations are straight lines. Sayani Bhattacharya et al. reported the same
behaviour for manganite $La_{1-x}Ca_xNa_yMn_3O_3$ [26] and Mollah et al. reported the same for manganite $Pr_{0.65}Ca_{0.35-x}Sr_xMnO_3$ [27].

*Figure 3.6* Variation of $\log (\rho)$ with $T^{-1/4}$ of $Gd_{1-x}Sr_xMnO_3$ ($x=0.3, x=0.4$ and $x=0.5$)

*Figure 3.7* (a) Variation of $\log (\rho/T)$ with reciprocal temperature (b) Variation of $\log (\rho)$ with $T^{-1/4}$ of $Gd_{1-x}Sr_xMnO_3$ ($x=0.3, x=0.4$ and $x=0.5$)
3.3.2 Magnetisation studies

In order to understand the metal insulator transition in manganites in the scenario of double exchange mechanism the magnetisation studies of the samples are necessary. The magnetisation studies of the GSMO samples were carried out using vibration sample magnetometer (model EG & G Par 4500) in the temperature range 10K – 300K. The magnetisation curves FC and ZFC for Gd$_{0.5}$Sr$_{0.5}$MnO$_3$ at two different magnetic fields [(a) 50 Oe and (b) 200 Oe] are presented in figure 3.8.

![Magnetisation curves for Gd$_{0.5}$Sr$_{0.5}$MnO$_3$](image)

**Figure 3.8** Temperature variations of magnetisation of Gd$_{0.5}$Sr$_{0.5}$MnO$_3$ at (a) 50 Oe and (b) 200 Oe.

As temperature decreases from room temperature the magnetisation increases showing a transition from paramagnetic to ferromagnetic. But at very low temperatures the sample shows an irreversible thermomagnetisation process. Under a magnetic field of 50 Oe the splitting between ZFC and FC magnetisation is observed at 125 K and when the field is increased to 200 Oe, the splitting becomes narrower and the splitting temperature ($T_{\text{split}}$) shifts to 70 K. This splitting is one of the characteristics of spin glass like behaviour and the shift in the splitting temperature with different magnetic fields is a consequence of the balance between the competing magnetic and thermal energies. These results suggest that this compound is in a spin glass like state at temperatures lower than
This spin glass like behaviour was already reported in Gd$_{0.5}$Sr$_{0.5}$MnO$_3$ by Garcia-Landa et al. [7].

Figure 3.9 shows the field dependence of magnetisation up to 3 T of Gd$_{0.5}$Sr$_{0.5}$MnO$_3$ at different temperatures. It is found that at temperatures lower than $T_{irr}$ (at 10 K and 40 K); the low field region of magnetisation becomes a nonlinear function of field and also displays hysteresis. This feature is also characteristic of a magnetic ordering and is consistent with that of the results of Terai et al. [28] in Gd$_{0.5}$Sr$_{0.5}$MnO$_3$. From temperature dependent magnetisation curves (figure 3.10) for the other two compositions (Gd$_{0.6}$Sr$_{0.4}$MnO$_3$ and Gd$_{0.7}$Sr$_{0.3}$MnO$_3$) it is evident that a paramagnetic to spin glass like transition occurs for Gd$_{1-x}$Sr$_x$MnO$_3$ (x=0.3, x=0.4 and x=0.5) at low temperatures. The magnetic transition at low temperature causes metal insulator transition via double exchange mechanism.

![Figure 3.9 Hysteresis curves of Gd$_{0.5}$Sr$_{0.5}$MnO$_3$ at different temperatures](image)
3.4 MR studies of GSMO

Magneto-resistance studies for the samples Gd$_{1-x}$Sr$_x$MnO$_3$ ($x=0.3$, $x=0.4$ and $x=0.5$) were done by taking resistivity measurements with a standard four probe technique, using Kiehley source meter and sensitive voltmeter. A detailed description of the MR experimental setup was given in chapter 2. The resistivity measurements were carried out in zero magnetic field and in applied fields of 1T, 5T and 8 T. The resistivity variations with applied field are shown in the figure 3.11. The external field causes a reduction of the resistivity in the entire temperature range for all the compositions indicating the colossal magneto-resistance (CMR) property of the manganite samples. The metal insulator (M-I) transition is obtained with the application of high magnetic filed (8T) for the sample Gd$_{0.7}$Sr$_{0.3}$MnO$_3$. For the other two compositions the M-I transition could not be obtained even for 8T field. This is because of their increased resistivity at low temperatures ($>10^6 \Omega \text{Cm}$) is out of the range of the measuring MR set up and therefore undergone cutoff at low temperatures. The comparative reduction in resistivity for the sample Gd$_{0.7}$Sr$_{0.3}$MnO$_3$ is due to the closeness of Mn$^{4+}$/Mn$^{3+}$.
ratio to the optimum value for double exchange mechanism. Because of the reduced resistivity, a metal insulator transition (MIT) by the application of 8T field could be observed in the case of Gd0.7Sr0.3MnO3. Thus charge ordered manganites show MIT only with the application of very high magnetic field.

MR of the GSMO samples was calculated using the equation (1.1). The MR measurements of all the GSMO samples had been undertaken in the temperature range 80K-300 K and the variation of MR with temperature is shown in the figure 3.12.

Figure 3.11 Temperature variation of resistivity with temperature under different applied magnetic fields for the sample Gd1-xSr_xMnO3 [(a) x=0.3, (b) x=0.4 and (c) x=0.5]
Figure 3.12 Variation of MR with temperature for the samples Gd_x, Sr, MnO_3 [x=0.3, x=0.4 and x=0.5]

Figure 3.13 Variation of MR with applied magnetic field (zero to 8 T) for the samples Gd_x, Sr, MnO_3 [x=0.3, x=0.4 and x=0.5]
From the figure it is clear that all the samples show a linear increase of MR% with decrease in temperature. The observance of MR% peak near the transition temperature was prohibited by the limitation of the measuring device beyond $10^6 \, \Omega \, \text{cm}$. The figure 3.13 shows the variation of MR with applied magnetic field. With applied field the MR% increases for all the compositions, due to the large suppression of magnetic fluctuation caused by the high magnetic field. The MR% is more in the case of GSMO with $x=0.3$. This is due to the closeness of $Mn^{4+}/Mn^{3+}$ ratio to the optimum value for double exchange mechanism.

3.5 Conclusion

GSMO samples $\text{Gd}_x\text{Sr}_x\text{MnO}_3 \, [x=0.3, \, x=0.4 \, \text{and} \, x=0.5]$ were prepared using wet solid state reaction method. The particles were found to have orthorhombically distorted perovskite structure. In the absence of magnetic field no metal insulator transition is exhibited by all the GSMO samples, which is a common feature in the case of low bandwidth manganites. But a slope change near 40 K is an indication of metal insulator transition associated with magnetic transition. The resistivity value increases with Sr doping. This can be explained by double exchange mechanism. The temperature variation of magnetisation indicates that there is a transition from paramagnetic state to magnetically ordered state like spin glass state near 40K. The coincidence of two transition temperatures near 40 K is an indication of hopping due to double exchange mechanism in low band width manganites. The conduction mechanism in the paramagnetic phase of the sample is variable range hopping (VRH) at low temperature followed by small polaron hopping (SPH) at high temperature. Magneto resistance studies reveal that the low bandwidth manganite exhibits colossal magnetoresistance property. The MR percentage increases with increase of applied field and decrease of temperature.
References


