Chapter 6

A study on the magnetic properties of Gd-Sr based low bandwidth manganites in their bulk and thin film forms

This chapter deals with the magnetic properties of both bulk and thin film forms of charge ordered Gd-Sr manganites belonging to the series Gd$_{1-x}$Sr$_x$MnO$_3$ (x = 0.3, 0.5, 0.6). In the case of bulk, it is found that the Gd moments order anti parallel to the manganese spins giving rise to a ferrimagnetic behaviour. A spin glass transition due to the competing ferromagnetic (FM) and antiferromagnetic (AFM) phases of manganese is observed at around 42K. Bulk form of Gd$_{0.7}$Sr$_{0.3}$MnO$_3$ exhibits magnetization reversal for applied fields of 25 Oe and 50 Oe at very low temperatures. In the two dimensional thin film forms of Gd$_{1-x}$Sr$_x$MnO$_3$, coercivity is different when compared to their bulk counterparts, moreover, the spin reversal and magnetic behaviour exhibited by thin films are at variance with respect to their bulk. An overview of structural and compositional analysis of films will be presented. Surface morphology of the films was examined from SEM and AFM images.

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6.1 Introduction

The magnetic properties of mixed valent perovskite manganites strongly depend on the degree of substitution of trivalent elements by divalent cations [1]. The other factors that influence the nature of different magnetic interactions in these compounds are ionic radii of rare earth and dopant cations, small changes in Mn-O-Mn bond length and bond angles induced by tolerance factor [2-3]. There are very few literature reports dealing with heavy rare earth elements (Eu, Gd, Tb, Dy) based manganites, since their magnetization, conductivity and magnetic ordering temperatures are lower when compared to manganites based on lighter rare earths [4-6]. The replacement of lighter rare earth elements in mixed valent manganites by heavier rare earth elements induce lattice distortion associated with modification of tolerance factor which in turn influence the double exchange mechanism and hence influence magnetic interactions [2]. Due to smaller ionic radii of heavier rare earth R atom, Mn-O-Mn bond distribution is maximum and hence a weak double exchange results [7]. Since heavy rare earth elements exhibit largest magnetic moments of all the series, their intrinsic magnetism affects the magnetic response of the Mn sub lattice and thus the overall manganite system. Thus a diverse magnetic response of the overall manganite system is expected by incorporating heavier rare earth ions instead of lighter ones. It is reported that compounds with larger ionic radii such as La, Pr and Nd are ferromagnetic (FM), whereas compounds with smaller ionic radii such as Sm, Eu and Gd exhibit properties of spin glass [8]. Large difference in the ionic radii of R and A ions results in the Mn-O-Mn bond angle variation which in turn leads to spin glass state [9].

There have been reports on Gd and Dy based perovskites showing specific magnetic features including a reversal of magnetization at low temperatures [10]. The magnetization curves of perovskite manganites based
on smaller rare earth ions such as Dy, Tb, Gd show anomalies below 10K [10]. In GdMnO₃, besides Mn³⁺ ordering observed at 42K, due to the magnetization of Gd ions, spin ordering due to Gd spins were observed at around 7K [10-11]. Earlier Troyanchuk et. al reported that Gd ions magnetic moments were aligned opposite to the magnetic moments of Mn ions [12]. Spin reversal and ferrimagnetism have been observed in both bulk and thin film forms of Gd₀.₆₇Ca₀.₃₃MnO₃ [7, 13]. G. J. Snyder et al. explained the existence of a ferrimagnetic phase in Gd₀.₆₇Ca₀.₃₃MnO₃ by the antiferromagnetic interaction between Mn sub lattice with Gd sub lattice [4]. This ferrimagnetic interaction results into magnetic reversal and this depends on the applied field. Yanwei Ma et al. has studied the effect of application of magnetic field on the spin reversal of calcium doped GdMnO₃ [13]. The intrinsic magnetic nature of Gd ion plays an important role in the overall magnetic behaviour of the system. Due to the ionic radii mismatch of Gd and Sr, it is interesting to study the effect of Strontium doping on the magnetism in GdMnO₃ system. Since the mean size radius of Gd is smaller when compared to Sr, Gd₁₋ₓSrₓMnO₃ belonging to low bandwidth manganites and there exists a stable charge ordered phase over a wide range of doping (x=0.3 - 0.7) [14]. Earlier Garcia Landa et. al has reported the co-existence of charge ordered state and spin glass state in bulk form of Gd₀.₅Sr₀.₃MnO₃ [15]. The cluster glass like behaviour due to co-existence of ferromagnetic (FM) – antiferromagnetic (AFM) phases and ferrimagnetic interaction introduced by Gd substitution suggests an AFM exchange coupling between Gd³⁺ and Mn³⁺/Mn⁴⁺ sub lattice.

Magnetic reversal was also reported in the thin film forms of Gd₀.₆₇Ca₀.₃₃MnO₃ [4, 13]. To fabricate a rich variety of electronic and magnetic devices, thin film form of these manganites with unique physical properties is necessary. Magnetization reversal is found to be an important
A study on the technology in magnetism used in magnetic data storage processes. A systematic study of both the spin reversal and spin glass existence in the charge ordered region of both bulk and thin film form of Gd$_{1-x}$Sr$_x$MnO$_3$ assume significance and less investigated. So it is in this context that a thorough investigation on thin film forms of Gd$_{1-x}$Sr$_x$MnO$_3$ is relevant.

It is presumed that in two dimensional thin film form of Gd$_{1-x}$Sr$_x$MnO$_3$, due to grain size effect, coercivity could be different when compared to bulk. Hence the magnetic behaviour exhibited by thin films will also be different. Also it is necessary to study the dependence of both coercivity and external applied field of thin films on the glassy behaviour, which was already reported in the bulk form of Gd$_{1-x}$Sr$_x$MnO$_3$ (x=0.3, 0.5 and 0.6) due to competing FM and AFM phases of manganese. To understand the nature of magnetic behaviour, polycrystalline thin film form of Gd$_{1-x}$Sr$_x$MnO$_3$ were prepared by pulsed laser deposition of polycrystalline bulk materials as targets which were synthesized by solid state reaction methods. As an initial investigation, these compositions were deposited on a silicon substrate by pulsed laser ablation. FC-ZFC magnetization measurements were carried out which could lead to the understanding of the interaction of Gd - Mn moments in bulk as well as thin films.

6.2 Experimental

6.2.1 Preparation of thin films

Bulk samples of Gd-Sr manganites belonging to the series Gd$_{1-x}$Sr$_x$MnO$_3$ (x = 0.3, 0.5, 0.6) were prepared by wet solid state reaction and compacted form of these compositions were employed as targets. For the synthesis of bulk samples, stoichiometric amounts of precursor materials namely, Gd$_2$O$_3$, SrCO$_3$ and MnO$_2$ were mixed in concentrated nitric acid. The solution was heated and excess nitric acid was boiled off. They were then calcined in air at 900°C for 12 hours. After pre sintering, the black
powder were ground and pressed into pellets and sintered at 1200°C in air for 72 hours. This sintered pellets were used as targets for depositing Gd$_{1-x}$Sr$_x$MnO$_3$ (x= 0.3, 0.5, 0.6) thin films on silicon substrates using pulsed laser deposition. A KrF excimer laser with 248 nm wavelength was employed for ablation and the estimated fluence was kept at about 2.91J/cm$^2$. To avoid the formation of native oxide layers on the surface of substrate, the substrates were pre-treated with HF solution before deposition. The substrate temperature was kept at 800°C during film growth and the deposition was carried out under an oxygen pressure of about 2 mTorr.

6.2.2 Characterization

The crystal structure of both the bulk and thin films were analysed using X-ray diffractometer (Bruker D8 Discover) with an incident Cu K$_\alpha$ radiation source. Microstructural analysis and surface morphology of the films were carried out using Zeiss Ultra 55 Field Emission-Scanning Electron Microscopy (FE-SEM) and Veeco Dimension 3000 atomic force microscope (AFM). Composition of the film was confirmed using Rutherford Back Scattering spectroscopy (RBS) using He$^{++}$ ions having energy of 1.7 MeV. Thickness of the film was determined by cross sectional SEM. To understand the nature of magnetic behaviour of thin films, Field Cooled (FC) – Zero Field Cooled (ZFC) and magnetic hysteresis (MH) measurements of magnetization were carried out using a Quantum Design superconducting quantum interference device.

6.3 Results and Discussions

6.3.1 Structural characterization using XRD

Figure 6.1 shows the X-ray diffraction pattern of thin films of GSOMO. No impurity phase was found in any of the thin films. GSOMO film grown on Si substrate exhibited the same structure as that of its bulk counterparts which is orthorhombic and with a space group of Pbnm. This is in agreement
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with previous reports [14-15]. The XRD data have been analysed by refining the experimental data using a standard Rietveld refinement techniques using Full PROF program. The Rietveld refined XRD pattern of Gd$_{0.5}$Sr$_{0.5}$MnO$_3$ is shown in figure 6.2. Figure 6.3(a) and (b) shows Rietveld refinement for Gd$_{0.7}$Sr$_{0.3}$MnO$_3$ and Gd$_{0.4}$Sr$_{0.6}$MnO$_3$ thin films.

![Figure 6.1: XRD pattern of Gd$_{1-x}$Sr$_x$MnO$_3$ (x = 0.3, 0.5, and 0.6) thin films.](image1)

![Figure 6.2: Rietveld refined XRD pattern of Gd$_{0.5}$Sr$_{0.5}$MnO$_3$ thin film.](image2)

The refined lattice parameters of all films are shown in table 6.1. A systematic decrease in lattice parameters is observed with increasing strontium substitution. An increase in lattice parameter with decreasing Strontium substitution is expected as in the case of bulk due to the larger
ionic radii of Sr\(^{2+}\) ions (0.144 nm) compared to that of Gd\(^{3+}\) ions (0.107 nm). The lattice parameters and hence the cell volume of thin film samples are found to be slightly smaller than the bulk samples. This indicates that the unit cell of the film samples are compressed as compared to their bulk counterparts. XRD of bulk GSMO is already shown in figure 4.1.a and the refined lattice parameters are included in table 4.1. For convenience, the refined lattice parameters and crystallite size of bulk GSMO is reproduced in table 6.1. The average crystallite size estimated from XRD data using Scherrer’s formula and also cell volume of both bulk and thin films of Gd\(_{1-x}\)Sr\(_x\)MnO\(_3\) (x = 0.3, 0.5, 0.6) are estimated and shown in table 6.1. It is found that the average crystallite size of thin films is less than that of bulk. Earlier it was reported that the unit cell parameter decreases as the average crystallite size decreases [16]. The grain size of the film is dependent on deposition parameters. The best stoichiometry as well as the single phase nature is retained in the films too.

**Table 6.1. Structural parameters of GSMO bulk and thin films.**

<table>
<thead>
<tr>
<th>Sample codes</th>
<th>Bulk a Å</th>
<th>b Å</th>
<th>c Å</th>
<th>Crystallite size nm</th>
<th>Cell Volume (Å(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>GSMO3 Bulk</td>
<td>5.41±0.0</td>
<td>5.42±0.0</td>
<td>7.69±0.0</td>
<td>43</td>
<td>225.27</td>
</tr>
<tr>
<td>GSMO5 Bulk</td>
<td>5.40±0.0</td>
<td>5.41±0.0</td>
<td>7.68±0.0</td>
<td>41</td>
<td>224.27</td>
</tr>
<tr>
<td>GSMO6 Bulk</td>
<td>5.359±0.001</td>
<td>5.407±0.002</td>
<td>7.68±0.003</td>
<td>34</td>
<td>222.54</td>
</tr>
<tr>
<td>GSMO3 Thin film</td>
<td>5.402±0.001</td>
<td>5.42±0.002</td>
<td>7.68±0.004</td>
<td>37</td>
<td>224.92</td>
</tr>
<tr>
<td>GSMO5 Thin film</td>
<td>5.39±0.001</td>
<td>5.41±0.001</td>
<td>7.67±0.002</td>
<td>32</td>
<td>223.65</td>
</tr>
<tr>
<td>GSMO6 Thin film</td>
<td>5.357±0.003</td>
<td>5.407±0.002</td>
<td>7.666±0.004</td>
<td>25</td>
<td>222.05</td>
</tr>
</tbody>
</table>
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Figure 6.3: Rietveld refined XRD pattern of (a) Gd$_{0.7}$Sr$_{0.3}$MnO$_3$ (b) Gd$_{0.4}$Sr$_{0.6}$MnO$_3$ thin films.

6.3.2 Surface analysis by SEM

Figure 6.4: (a) Cross sectional SEM image of Gd$_{0.5}$Sr$_{0.5}$MnO$_3$ thin film, FE-SEM images of thin film forms of (b) Gd$_{0.7}$Sr$_{0.3}$MnO$_3$ (c) Gd$_{0.5}$Sr$_{0.5}$MnO$_3$ (d) Gd$_{0.4}$Sr$_{0.6}$MnO$_3$.

The average value of thickness calculated from cross sectional SEM of Gd$_{0.5}$Sr$_{0.5}$MnO$_3$ thin films is shown in figure 6.3.a and is found to be ~ 300 nm for all the films. Surface morphology of the films by SEM shows that the film surfaces are dense, compact and is uniform in nature. Films exhibit a well-defined structure with a visible grain boundary indicating the crystalline
nature. It is seen that the microstructure is quite homogeneous with an average grain size of nearly 37nm. Crystallite size estimated from XRD and grain size evaluated from SEM is found to be matching. Also the grain growth and crystallisation is observed with decreasing Strontium substitution. SEM images of GSMO3, GSMO5 and GSMO6 are respectively shown in figures 6.4.b, 6.4.c and 6.4.d. Grain size distribution of Gd$_{0.5}$Sr$_{0.5}$MnO$_3$ thin film is shown in figure 6.5.

![Figure 6.5: Representative grain size distribution of GSMO5 thin film.](image)

**6.3.3 Surface analysis by AFM**

Topography and roughness of the films were analysed using an Atomic Force Microscope. AFM images of polycrystalline microstructures of Gd$_{1-x}$Sr$_x$MnO$_3$ (x = 0.3, 0.5, 0.6) films deposited on Si substrate is shown in figure 6.6.

From AFM images it is evident that the surface has a granular structure similar to that observed in the SEM. The morphology of the films shows a very dense structure having a very low roughness. Low value of roughness indicates that the structural features are homogeneous. This structure is observed to be similar to Zone II/ Zone T structures of “microstructure zones model” suggested by Thornton [17-18]. Hence both
AFM and SEM give a dense, closely packed morphology with a smooth surface. Root mean square roughnesses (RMS) of GS MO thin films on an area of 5µm x 5µm are also calculated. With decreasing strontium percentage the surface roughness and average grain size increases. The progressive morphological evolution of grain growth upon decreasing percentage of Strontium is clearly visible from the nature of surface by both SEM and AFM analysis.

![AFM images of thin film forms of Gd0.7Sr0.3MnO3, Gd0.5Sr0.5MnO3, Gd0.4Sr0.6MnO3.](image)

6.3.4 Rutherford Back Scattering Analysis

Figure 6.7 shows RBS analysis of Gd1-xSr_xMnO3 (x = 0.3, 0.5, 0.6) thin films. The chemical composition of thin films was found out by RBS elemental analysis. The RBS spectra were fitted with the SIMNRA software and the results are summarized in table 6.2. As far as the composition of the films are concerned there is one to one correspondence with their bulk
targets. From the RBS data it is found that the samples synthesised were stoichiometric with respect to the oxygen content.

### Table 6.2. Stoichiometry of GSMO thin films.

<table>
<thead>
<tr>
<th>Film Name</th>
<th>Stoichiometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>GSMO3</td>
<td>Gd$<em>{0.71}$Sr$</em>{0.31}$MnO$_3$</td>
</tr>
<tr>
<td>GSMO5</td>
<td>Gd$<em>{0.51}$Sr$</em>{0.50}$MnO$_3$</td>
</tr>
<tr>
<td>GSMO6</td>
<td>Gd$<em>{0.41}$Sr$</em>{0.60}$MnO$_3$</td>
</tr>
</tbody>
</table>

Figure 6.7: RBS spectrum of GSMO thin films.

6.3.5 Magnetization Measurements

#### 6.3.5.1 MH measurements

Magnetization as a function of applied field at 10K of Gd$_{1-x}$Sr$_x$MnO$_3$ ($x = 0.3$, $0.5$, $0.6$) in bulk form is shown in figure 6.8. The magnetic hysteresis loops for thin films of Gd$_{1-x}$Sr$_x$MnO$_3$ ($x = 0.3$, $0.5$, $0.6$) measured up to 80 kOe at 10K and 300K are shown in figure 6.9. Coercivity of both bulk and thin film form of Gd$_{1-x}$Sr$_x$MnO$_3$ ($x = 0.3$, $0.5$, $0.6$) are noted separately in their corresponding MH loops. It is to be noted that coercivity in thin films is very much lesser when compared to their bulk target. This can be due to their lower crystallinity and smaller grain size when compared to their bulk target. It is found that at 10K the loop is not saturated even in an
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applied field of 70 kOe. Unsaturated increase of magnetization is indicative of a ferrimagnetic like state in both thin films and bulk.

Figure 6.8: Magnetic hysteresis loops of Gd$_{1-x}$Sr$_x$MnO$_3$ bulk at 10K (a) $x=0.3$, (b) $x=0.5$ and (c) $x=0.6$.

Figure 6.9: Magnetic hysteresis loops of Gd$_{1-x}$Sr$_x$MnO$_3$ thin film at 10K (a) $x=0.3$, (b) $x=0.5$ (c) $x=0.6$ (d) Magnetic hysteresis loops of Gd$_{1-x}$Sr$_x$MnO$_3$ ($x=0.3, 0.5, 0.6$) thin film at 300K.
There are several reports highlighting a magnetic phase change exhibited by manganites [7, 10, 19-22]. It has been reported that a metamagnetic FM phase can be formed by the partial transformation of CO/AFM phases under high field. As Gd$_{1-x}$Sr$_x$MnO$_3$ belonging to small bandwidth manganites, range of compositions showing charge ordering is wide rather than usual single composition at x= 0.5 as in other manganites. Hence samples with x= 0.3, 0.5, 0.6 are charge ordered. In charge ordering, both FM and AFM phases co-exist and this may results in competitive magnetic interactions.

6.3.5.2 FC - ZFC magnetic measurements

FC - ZFC measurements carried out on bulk form of Gd$_{1-x}$Sr$_x$MnO$_3$ (x = 0.3, 0.5, 0.6) under a magnetic field of 200 Oe is shown in figure 6.10. The substitution of trivalent Gadolinium by divalent Strontium converts Mn$^{3+}$ into Mn$^{4+}$. Going from x = 0.3 to x = 0.6, it is found that effective magnetic moment decreases. This is because for the composition corresponding to x=0.3, the double exchange effect is maximum as seen in the case of Lanthanum compounds.

Temperature dependent magnetization studies under applied fields of 25 Oe and 50 Oe of bulk Gd$_{0.7}$Sr$_{0.3}$MnO$_3$ (GSMO3) is shown in figure 6.11. When a magnetic field of 25 Oe, which is very much less than their coercive field (H$_c$ = 770 Oe), is applied on GSMO3, ZFC magnetization first decreases with increasing temperature and then rapidly increases to a maximum, T$_{cusp}$ and finally reaches the reversible state at T$_{irr}$. While FC magnetization increases with decreasing temperature, it reaches a maximum and then sharply decreases to zero and goes to negative values on further cooling. The temperature at which magnetization decreases to zero is called compensation temperature and the phenomenon of attaining negative values is called magnetic reversal [4]. Here FC curve crosses the temperature axis at
the compensation temperature $T_{\text{comp}}=11\text{K}$ and goes to a negative value for a field (25 Oe) lower than its coercive field. Earlier Snyder et al. also found a similar type of magnetic reversal in Calcium substituted GdMnO$_3$ [4]. They explained this anomaly by attributing it to the interaction of Gd sub lattice with Mn sub lattice.

![Graph](image)

**Figure 6.10:** ZFC and FC magnetization measurements of bulk Gd$_{1-x}$Sr$_x$MnO$_3$ ($x=0.3, 0.5, 0.6$) under a magnetic field of 200 Oe.

The ordering of manganese (Mn$^{3+}$ and Mn$^{4+}$) spins due to strong competition between FM phase and AFM phase results in the formation of a frustrated state, termed as spin glass, is observed at around 42K. It is noticed that FC and ZFC splitting gap is substantial under low applied fields (25 Oe and 50 Oe) unlike the splitting observed under an applied field of 200 Oe. Thus it can be concluded that irreversibility decreases at higher applied fields. This thermomagnetic irreversibility is also an indication of the existence of a glass state [22]. Garcia Landa et al. has reported the presence of a spin glass in Gd$_{0.5}$Sr$_{0.5}$MnO$_3$ at 42K [15]. There are also reports on the co- existence of CO and spin glass state at low temperatures in manganites.
At glass transition temperatures the dominating magnetization is due to the ordering of manganese spins. Below this temperature, Gd spins became more dominant and hence FC magnetization decreases and magnetic reversal is observed on further cooling under the applied field.

Thus this system behaves as a ferrimagnetic like system of two interacting magnetic sub lattices of Manganese and Gadolinium. The substitution of trivalent Gd by divalent Sr converts Mn$^{3+}$ into Mn$^{4+}$ and also generates magnetic clusters. On cooling under the presence of a small field, a field lower than the coercive field, the Mn sub lattice orders ferromagnetically, while the Gd sub lattice polarise in an opposite direction to the external field. Also at $T_{\text{cusp}}$, due to competing FM and AFM phases of manganese gives rise to an ordering of the lattice and aids in the culmination of a frustrated glass state. This accounts for the increase in magnetization and peaks at $T_{\text{cusp}}$. 

Figure 6.11: ZFC and FC magnetization measurements of bulk Gd$_{0.7}$Sr$_{0.3}$MnO$_3$ under magnetic fields of (a) 25 Oe and (b) 50 Oe.
Below spin glass transition, magnetic contributions of Gd$^{3+}$ 4f spins are prominent. Upon further cooling, Gd$^{3+}$ spins are aligned anti parallel to canted Mn$^{3+/4+}$ spins. This antiferromagnetic interaction of Gd sub lattice with Mn sub lattice reduces the net magnetization. When the temperature is lowered to compensation temperature, magnetic moments of Gd and Mn cancel exactly. Below this temperature, negative magnetization is observed. While in ZFC, the magnetization is positive in the entire temperature with a minimum dip at 24K. Curie - Weiss contribution at low temperatures in ZFC can be due to the effect of the external field on Gd sub lattice. However for a higher applied field of 200 Oe, even lower than the coercivity of GSMO3, FC magnetization no longer becomes negative. The paramagnetic contribution of Gd is more and more supporting due to the increasing field strength and it takes positive values. Earlier Yanwei Ma et al. has studied the effect of application of magnetic field on the spin reversal behaviour of calcium doped GdMnO$_3$ [13]. They reported that if the applied field is greater than the coercive field, Gd ions flip to align parallel with the external field with an increase in both FC and ZFC magnetisation. No dip in magnetization is observed at an applied field of 200 Oe, a field lower than its $H_C$.

Magnetization measurements of bulk Gd$_{1-x}$Sr$_x$MnO$_3$ (x=0.5, 0.6) under ZFC and FC conditions in a magnetic field of 25 Oe are shown in figure 6.12. With increasing strontium concentration, the transition at low temperature corresponding to Gd moments is reduced because Sr doping dilutes the magnetic Gd sub lattice. This kind of dilution of rare earth ion by Sr doping was earlier reported by S Robler et al. in Sr doped DyMnO$_3$ [26]. Hence for compositions x = 0.5 and 0.6, Curie Weiss contribution of Gd moments at lower temperatures is lesser when compared to x= 0.3.
Figure 6.12: ZFC and FC magnetization measurements of bulk (a) Gd_{0.5}Sr_{0.5}MnO_{3} (x = 0.3, 0.5, 0.6) and (b) Gd_{0.4}Sr_{0.6}MnO_{3} under a magnetic field of 25 Oe.

As the maximum external field applied is 200 Oe, which is very much less than the coercive field of bulk, increase in magnetisation by the Curie Weiss contribution of Gd ions is not seen in the case of bulk samples under study. While for thin films it is found that coercivity is very much lesser when compared to their bulk. In the case of Gd_{0.7}Sr_{0.3}MnO_{3} thin film, the paramagnetic contribution of Gd ions are more dominant and they orient along the field leading to an increase in both FC and ZFC magnetizations with a dip in the magnetization at 20K which is shown in figure 6.13.a.

When a small field of 25 Oe is applied, similar to bulk due to ferrimagnetic interaction of Gd and Mn sub lattices, both FC and ZFC magnetization decreases after exhibiting their glassy transition at 40K. FC magnetization goes on decreasing with temperature while ZFC magnetization increases after a minimum at T = 20K. This is shown in figure 6.13.b.
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Figure 6.13: ZFC and FC magnetization measurements of Gd$_{0.7}$Sr$_{0.3}$MnO$_3$ thin film under a magnetic field of (a) 200 Oe and (b) 25 Oe.

The coercivity of thin films of Gd$_{1-x}$Sr$_x$MnO$_3$ decreases with increasing Sr, therefore GSMO3 exhibits higher coercivity. Hence the ferrimagnetic behaviour shown by $x = 0.3$ under an applied field of 200 Oe is absent for $x = 0.5$ and 0.6 under the same applied field (200 Oe $<< H_C$).

Temperature dependent magnetization studies in 200 Oe for field cooling and zero field cooling of Gd$_{1-x}$Sr$_x$MnO$_3$ $(x=0.5, 0.6)$ thin films is shown in figure 6.14. Unlike bulk, the magnetization variation of Gd$_{1-x}$Sr$_x$MnO$_3$ $(x=0.5, 0.6)$ thin films is paramagnetic in nature. This is due to the application of a field higher than their coercive field. When the applied field is high, the internal field produced at the Gd sites by Mn sub lattice is low and hence an applied field of 200 Oe, which is higher than coercive field, is strong enough to align Gd ions parallel to this field and leading to the superposition of Gd and Mn sub lattices. A small slope change in ZFC under 200 Oe was observed at around the glass transition temperature of 40K. Under an applied field of 500 Oe $>> H_C$, this transition vanishes. For a higher field of 500 Oe the frustrated glassy state melts resulting in a paramagnetic behaviour. This is shown in figure 6.14.b. FC-ZFC curves are almost identical at higher fields which are indicative of the melting of glass state [25].

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6.4 Conclusions

Bulk and thin film samples belonging to the series Gd$_{1-x}$Sr$_x$MnO$_3$ (x = 0.3, 0.5, 0.6) were prepared and characterized. The lower coercivity of thin films when compared to bulk is attributed to their smaller crystallinity and grain size. With strontium substitution coercivity is found to be decreasing and hence Gd$_{0.7}$Sr$_{0.3}$MnO$_3$ exhibits higher coercivity. Magnetic reversal was observed in bulk form of Gd$_{0.7}$Sr$_{0.3}$MnO$_3$ at very low temperatures in small external fields. This is due to the antiferromagnetic interaction of Gd - Mn sub lattice in Gd$_{0.7}$Sr$_{0.3}$MnO$_3$. For Gd$_{0.5}$Sr$_{0.5}$MnO$_3$ and Gd$_{0.4}$Sr$_{0.6}$MnO$_3$, the transition at low temperature corresponding to Gd moments is reduced and hence magnetic reversal is absent. Spin glass transition was observed in Gd$_{1}$. 

Figure 6.14: ZFC and FC Magnetization measurements of Gd$_{0.5}$Sr$_{0.5}$MnO$_3$ thin film under a magnetic field of (a) 200 Oe and (b) 500 Oe, (c) Gd$_{0.4}$Sr$_{0.6}$MnO$_3$ thin film under a magnetic field of 200 Oe.
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$\text{Sr}_x\text{MnO}_3$ (x = 0.3, 0.5, 0.6) at around 42K. The magnetic transitions exhibited by Gd$_{0.7}$Sr$_{0.3}$MnO$_3$ thin films under a field of 200 Oe (ZFC - FC) were quite similar to their bulk counterparts. Due to lower coercivity of thin films corresponding to higher doping (x= 0.5 and 0.6), the applied field is enough to suppress both the glassy and ferrimagnetic nature.

References

Chapter 7

Conclusion and Future Scope

The inferences drawn out of this investigation is provided in this chapter. The scope for further studies is also highlighted in this chapter. Several positives outcomes of this investigation along with some of their limitations are also dealt within this chapter. Moreover, preliminary experiments carried out on Ca$_{0.9}$Yb$_{0.1}$MnO$_3$ indicate that they exhibit appreciable Seebeck coefficient at room temperature and the initial results of this work are also briefly discussed in this chapter.