La$_{1-x}$Sr$_x$MnO$_3$ as a candidate for a room temperature pressure sensor

by

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Perovskite manganite compounds, $La_{1-x}D_xMnO_3$ ($D$-divalent alkaline earth $Ca$, $Sr$ or $Ba$), whose electrical and magnetic properties were first investigated nearly a half century ago, have attracted a great deal of attention due to their rich phase diagram. From the point of view of designing a future application, the strong pressure dependence of the resistivity and the accompanying effects in thin films have potential for application in pressure sensing and electronic devices. In this study we report our experimental investigations of pressure dependence of the resistivity of $La_{0.84}Sr_{0.16}MnO_3$ and $La_{1-x}Sr_xMnO_3$ (LSMO) epitaxial films with $x = 0.15$, 0.20, 0.25, 0.30, 0.35, on $SrTiO_3$ substrates.
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Chapter 1

Introduction

Perovskite manganites with mixed manganese valence $La_{1-x}D_xMnO_3$, where $D=Ca, Sr, Ba$ have attracted a great deal of attention due to their unusual and potentially useful magnetic properties and their very large negative magnetoresistance (MR) in the vicinity of the magnetic phase transition temperature $T_c[1]$.

These perovskites exhibit a rich magnetic phase diagram. At high temperature they are paramagnetic, at low temperature, both antiferromagnetic and ferromagnetic phase have been observed. The ferromagnetic phases can be both insulating for $x \leq 0.2$, or metallic for, $0.2 \leq x \leq 0.45$. At higher concentration of $D$, $0.45 \leq x \leq 1$, the ground state is antiferromagnetic and nonmetallic[21].

Structurally, starting from $x = 0$, the resistivity drops with increased doping. Substitution of a trivalent ion $La^{3+}$ by a divalent ion $Sr^{2+}$ causes coexistence of $Mn^{3+}$ and $Mn^{4+}$ ions in the appropriate ratio. The double exchange (DE) interaction consists of transfer of the extra electron between neighboring Mn ions through the $O^{-2}$ ions, which results in an effective ferromagnetic interaction [3]. It also gives rise to a progressive change from planar antiferromagnetic to ferromagnetic order. By the strong Hund’s rule coupling, ferromagnetism is induced via the parallel orientation of both the travelling spins and magnetic moment of the $Mn^{3+}$ and $Mn^{4+}$ ions. Then Henderson and Hasegawa [4] formulated this mechanism and it was applied to the $La_{1-x}Sr_xMnO_3$ system by de Gennes[5].

Recently Millis [6], realized that the basic double exchange interaction itself is not sufficient to explain such large negative magnetoresistance MR. The importance of lattice degrees of freedom and electron-phonon coupling originating from Jahn-Teller distortion leads to several theories[7] [8] [9] of CMR. Besides the strong interaction between spin, charge and lattice, there appear to be further critical parameters: the average ionic radius of the A site atoms, the Goldschmidt tolerance factor [12], and the $Mn^{3+}$ to $Mn^{4+}$ ratio. Based on work done previously [10], it has been observed that for a thin film
with low $T_c$ ($T_c$ Transition temperature from the insulator antiferromagnetic to metallic ferromagnetic state) the application of hydrostatic pressure moves $T_c$ to a higher temperature at a faster rate compared with a film with higher $T_c$. It also has been observed that applied pressure lowers the electrical resistivity in the paramagnetic phase due to the anisotropic compressibility of the two-dimensional Mn - O - Mn networks[11].

One can use the strong pressure dependence of the resistivity in thin films of manganite for application in pressure sensing and electronic devices. In this study, we attempted to find out whether or not thin films of $La_{1-x}Sr_x MnO_3$ can be used as a pressure sensor.

For this purpose, we have synthesized and characterized bulk samples of $La_{1-x}Sr_x MnO_3$, where $(0.15 \leq x \leq 0.35)$. We then fabricated epitaxial thin films of these materials from bulk samples using pulsed laser deposition (PLD) technique. The effect of pressures on resistivity of these films were also investigated at room temperature.

In chapter 2, a short review of properties of manganites are discussed. Experimental methods is given in chapter 3. Finally in chapter 4 results are discussed and short conclusion is given in chapter 5.
Chapter 2

Review of Theoretical work and discussion

The compound under study, $A^{3+}_{1-x}B^{2+}_xMn^{4+}_{1-x}Mn^{4+}_xO^{2-}_3$, where A is a trivalent rare earth and B is a divalent alkaline earth ion has attracted great deal of attention due its rich phase diagram[2].

The undoped parent compound $ABO_3$ are insulating antiferromagnet. Here A represents a large ion such as $La^{3+}$, $Ca^{2+}$, $Ba^{2+}$, $Sr^{2+}$ and B is $Mn^{3+}$, $Mn^{4+}$, or other ions. The ideal perovskite structure for compounds of the $ABO_3$ may be described as cubic, with 12-fold coordinate A ions at the corners, 6-fold coordinated B ions at the body centers, and 6-fold coordinated O ions at the face centers of the unit cubes[12].

Such a compound structure can be characterized by the Goldschmidt[12] tolerance factor $t$, where $(R_o+R_A) = (\sqrt{2}) * t (R_o+R_B)$ where $R_o$, $R_A$, $R_B$ are theoretical ionic radii of Oxygen, and A an B ions, respectively. Megaw[13] has found that the different possible distortions of the perovskite structures from cubic symmetry occurs for separate ranges of values of the tolerance factor. Thus, with $0.8 \leq t \leq 0.9$ should lead to orthorhombic structure, whereas $0.9 \leq t \leq 0.97$ should lead to cubic symmetry and $0.97 \leq t \leq 1.02$ to tetragonal symmetry.

At finite doping charge balance is maintained by a fraction, x of Mn ions assuming a tetravalent, $Mn^{4+}(d^3)$ configuration in a random fashion throughout the crystal, with the reminder in the $Mn^{3+}(d^4)$ state. The parent compound LaMn$O_3$ ( with $Mn^{3+}$) $t = 0.89$ has an orthorhombic structure [14].

Therefore, LaMn$O_3$ with the t value of 0.89, only a slight increase in t induced by substituting larger ions Ba or Sr for La, is needed for a transition to a cubic structure. Alternatively substituting $La^{3+}$ ions with ions such as $Sr^{2+}$ reduces the average value of $R_A$ and consequently increases, the tolerance factor (t) to a value above 0.96 which would lead to a rhombohedral perovskite structure [15]. However, there are some differences in the phase
Chapter 2. Review of Theoretical work and discussion

4

diagram for the case of Sr doping compare to Ca doping, owing mainly to the size difference between Ca and Sr ions[2]. One of the key issues in understanding the microscopic origin of the CMR in this kinds of perovskites is the possible coupling among structural, electronic, and magnetic phase transitions. Recent work [2],[16] has demonstrated a direct linkage between the magnetic structural properties and the average ionic radius of the La site $<R_A>$ in $La_{1-x}Sr_xMnO_3$.

The insulator - metal transition at low temperature is an orthorhombic ($x \leq 0.175$) to rhombohedral ($x \geq 0.175$) transition[2]. These magnetic compounds are insulating and antiferromagnetic at the end points values of $x=0$ and $x=1$, where $0.175 \leq x \leq 0.4$ they conduct and become ferromagnetic when cooled to some critical temperature $T_c$ and at low temperature are described as metallic [2].

As a consequence of this substitution, the $La_{1-x}Sr_xMnO_3$ system would experience a continuous linear decrease of lattice volume and increase of $Mn^{+4}$ density. The decrease in volume creates distortion in its structure, these distortion are known to contribute to the electrical and magnetic properties in this compound [14].

In the parent compound LaMnO$_3$, the octahedrally coordinated $Mn^{+3}$ ions have a $t^3_2e^1_g$ configuration[17]. Where the $t^3_2e^1_g$ electrons can be viewed as localized, the $e^1_g$ orbitals are strongly mixed with the 2p oxygen orbitals. $Sr^{+2}$ doping introduces holes in the $e^1_g$ 2p band and the material becomes metallic. In perovskite manganites the active orbitals are Mn - d orbitals. While three of the d electrons are tightly bound to form a core spin $S^c$, the outer shell electron may hop from Mn site to Mn site via the intermediate closed shell oxygen. The itinerancy of these electrons is represented by the hopping integral $t$. The spin of hopping electron tends to be aligned to $S^c$ on each site due to the strong Hund coupling $j_H$ [17]. In this structure, if we take La (Sr) ions at the origin of the unit cell, the Mn ions occupy the corners of the cube and surrounding each Mn ion there are six $O^{-2}$ ions forming a octahedron. At and around $x=1/3$, the compound orders ferromagnetically. Zener [3] proposed the double-exchange interaction (DE) as the mechanism responsible for the alignment of the Mn magnetic moments. Substitution of a trivalent ion $La^{+3}$ by a divalent ion $Sr^{+2}$ causes coexistence of $Mn^{+3}$ and $Mn^{+4}$ ions in the appropriate ratio. The DE interaction consists of the transfer of the extra electron between neighboring Mn ions through the $O^{-2}$ ions, which results in an effective ferromagnetic interaction due to the strong on-site Hund’s coupling[17]. The hopping integral is given by $t=t_0\cos\theta/2$
where \( t_0 \) denotes the bare value and \( \theta \) is the angle between neighboring core spins [18]. The large \( j_H \) means that the hopping of an outer-shell electron between two Mn sites is affected by the relative alignment of the core spins, being maximal when the core spins are parallel and minimal when they are antiparallel. Also, electron hopping promotes ferromagnetic order. This phenomenon has been widely regarded as the only significant physics in the regime \( 0.2 < x < 0.5 \).

Moreover, accompanying the change of the transport properties, the overall magnetic order among the \( Mn^{+3}, Mn^{+4}, \) ions also change from antiferromagnetic into ferromagnetic.

The crystal structure of \( La_{1-x}Sr_xMnO_3 \) is shown in Figure 2.1.

A large \( La^{+2} \), or a smaller \( Sr^{+2} \), ion sits at the cube center, a manganese \((3+ \text{ or } 4+)\) ion at each corner and the oxygen atom are the midpoints of the cube edges. For simplicity, the atoms in the unit cell in Figure 2.1 are shown to be located at 90 degree angles to each other, but in reality, the unit cell has a distorted shape. The distorted is due to the replacement of the larger \( La^{+3} \) ion with a smaller \( Sr^{+2} \) ion. This substitution creates an extra free space in the lattice, which is filled and hence shifting the Mn-O-Mn arrangement away from forming a 180 degree chain[19].

Two different distortions are known to characterize the structure of (LSMO)[20]. The first distortion, is related to the MnO\(_6\) octahedra, which is effected by the free space that is created by substituting of La by a smaller atom such as Sr. The free space effects the bending of the Mn-O-Mn bond and hence influences the strength of the hopping of the free electrons through the \( Mn^{+3} - O^{-2} - Mn^{+4} \) chain, and influencing the electronic properties of the system. The second distortion is due to the Jahn-Teller effect which is related to distortion of highly symmetrical molecules [17].

The \( Mn^{+3} \) ions have three localized electrons in \( t_{2g}^3 \) and one electron in \( e_g^1 \) states. The width of the band, which hosts the electron, which mediates the ferromagnetic interaction coupling in the Mn-O-Mn chain, is susceptible to pressure[17],[21]. The band width increases with pressure and hence increases the chance for the electron to delocalize. The bandwidth for a polaron is given by \( j_B \sim \exp(-\alpha R) \) where \( \alpha \) is a constant and \( R \) is the distance between two neighboring polarons [21]. Pressure decreases \( R \) and has a strong positive effect on \( j_B \) thereby increasing the charge carrier mobility and decreasing \( \rho \). According to double exchange model, transfer of charge carrier from site to site mediates the ferromagnetic exchange. The transfer integral
Figure 2.1: The ideal antiferromagnetic cubic perovskite structure for $LaMnO_3$. In the actual structure, the Oxygen octahedron is distorted with a combination of the basal-plane distortion mode, the octahedral stretching mode and a rotation [32].
for electrical conduction between neighboring Mn site as mentioned before is defined by $t = t_0 \cos \theta / 2$ the broadening of the bandwidth, increases charge carrier mobility and decreases $\rho$. The pressure -induces increase of charge carrier mobility would increase $t_0$ and is partly responsible for enhancing the double exchange ferromagnetic coupling strength, which increase $T_c$.\[21\]

Recently, Millis[6] has shown that a Hamiltonian incorporating only the DE interaction can not explain, the FM transition. He [6] and Roder [8] proposed, in addition to DE, an electron-phonon coupling term. Such an interaction is not unexpected in a picture where transport is via hopping among $Mn^{+3}$ and $Mn^{+4}$ ions. Here, the hole, corresponding to an $Mn^{+4}$ ($d^3$ ) ion must replace a $Mn^{+3}$ ($d^4$ ion which, in the dilute limit, can be associated with a large Jahn - Teller coupling.

Most of the recent work has focused on Ca and Sr substituted compound and the Colossal magnetoresistance, with appropriate concentration of x are observed for both cases.

There are some differences in the phase diagram for the two cases, owing mainly to the size difference between Ca and Sr ions, and the phase boundary is a little bit different.

The complex phase diagram has been studied by many groups and a more or less coherent picture can be deduced from the variety of experimental results reported \[22\], \[23\], \[24\], \[25\].

In $La_{1-x}Sr_xMnO_3$ the main body of experimental investigations has been carried out for Sr concentration $x < 0.5$. This partly has been due to the fact that colossal magnetoresistance effects show up around $x = 0.3$ \[31\]. However, for $x > 0.5$ much less experimental information is available[26].

In figure 2.2 the phase diagram for the concentration regime $0 < x < 0.25$ where mixed single crystals can be grown[26] is shown. We included the results from earlier work \[27\](0 < x < 0.3). The complex sequence of magnetic phase at low concentrations is highly influenced by the cooperative Jahn - Teller distortion of the $O'$ (Jahn - Teller distorted orthorhombic) phase and by the orbital order of the $O''$ (orbital ordered orthorhombic) phase \[28\]. In $La_{1-x}Sr_xMnO_3$ around $x \simeq 0.12$, the temperature dependence of electrical resistivity shows metallic behavior below $T_c$ consistent with double exchange picture. On further increasing x (0.1 < x < 0.17), it seems clear that a new type of orbital order, probably connected with charge order, determines the low- temperature insulating ferromagnetic phase around $x=0.125$ \[22\][28]. Finally, for Sr concentrations x < 0.17 the long - range Jahn -Teller distortion become superpressed and a ferromagnetic metal evolves below the
Figure 2.2: Phase diagram of $La_{1-x}Sr_xMnO_3$ for the complete concentration regime [26]
ferromagnetic phase transition [26]. In a certain range of doping, x = 0.2 - 0.4, the ground state is ferromagnetic, and a large FM regime evolves which reveals a rhombohedral structure and shows Colossal Magnetoresistance Resistance effects throughout [2]. At high temperature there appear to be two distinct phases, paramagnetic insulator (PI) and paramagnetic metal (PM). For x > 0.5 a tetragonal phase appears which is a ferromagnetic metal [26].
Chapter 3

Experimental Methods

3.1 Preparation of the ceramic target.

In this study, ceramic target tablets of $La_{1-x}Sr_xMnO_3$ tablets were prepared in the following way:

- Appropriate high purity amounts of MnO$_3$, SrCO$_3$, $La_2O_3$, powder were dissolved in Nitric Acid individually.
- Distilled water was added to MnO$_3$ and $La_2O_3$ in order to be dissolved in the Nitric Acid. The solution were preheated for dissolving completely in Nitric Acid. The three solution were mixed together and stirred completely.
- In this stage, an appropriate amount of Citric Acid was added to the solution gradually. The solution turns transparent from brownish opaque, (color is light yellow).
- By slowly adding ammonia ($NH_4OH$)to the solution, the pH of the solution was increased to the value of 6.8. This solution was left over night and the pH was rechecked, then ammonia was added again to reach to the pH value of 6.8 (during this process, the solution was stirred continuously ).
- The solution was transferred to the tall beaker and put on a hot plate. Upon heating the brown solution became more transparent and yellow while boiling slowly. Most of the solution was allowed to evaporate, the remaining solution turns into a black and thick compound. At a higher temperature a spontaneous combustion is initiated which produces a very fine powder, which fills the oversized beaker.
- The powder was sintered at 1100°C for 16 hours. The powder was reground with Acetone, pelletized into tablets by press (13 mm in diameter) and again sintered at 1350°C for 24 hours. With this method we made five ceramic samples of $La_{1-x}Sr_xMnO_3$ with different concentration of Sr, $x=$ 0.15, 0.20, 0.25,0.30, 0.35. To make one or two tablets of $La_{1-x}Sr_xMnO_3$ we followed the recipe in Table 3.1.
Table 3.1: Recipe for the Citrate synthesis of $La_{1-x}Sr_xMnO_3$,
I) $La_2O_3$ gr, II) $SrCO_3$ gr, III) $MnO_3$ gr, IV) Nitric Acid cc,
V) Citric Acid gr, VI) pH

<table>
<thead>
<tr>
<th>$La_{1-x}Sr_xMnO_3$</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
</tr>
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<tbody>
<tr>
<td>$La_{0.85}Sr_{0.15}MnO_3$</td>
<td>2.77</td>
<td>0.44</td>
<td>1.73</td>
<td>5.7</td>
<td>0.5</td>
<td>7.3</td>
</tr>
<tr>
<td>$La_{0.80}Sr_{0.20}MnO_3$</td>
<td>2.60</td>
<td>0.59</td>
<td>1.73</td>
<td>4.5</td>
<td>0.5</td>
<td>7.3</td>
</tr>
<tr>
<td>$La_{0.75}Sr_{0.25}MnO_3$</td>
<td>2.44</td>
<td>0.73</td>
<td>1.73</td>
<td>4.1</td>
<td>0.9</td>
<td>7.3</td>
</tr>
<tr>
<td>$La_{0.70}Sr_{0.30}MnO_3$</td>
<td>4.56</td>
<td>1.77</td>
<td>3.47</td>
<td>7.7</td>
<td>2.2</td>
<td>14.6</td>
</tr>
<tr>
<td>$La_{0.65}Sr_{0.35}MnO_3$</td>
<td>4.62</td>
<td>1.77</td>
<td>3.47</td>
<td>7.1</td>
<td>2.2</td>
<td>14.6</td>
</tr>
</tbody>
</table>

3.1.1 Pulsed Laser Deposition (PLD) of $La_{1-x}Sr_xMnO_3$, thin films.

All Thin Films were fabricated by the pulsed laser deposition, PLD method. An Excimer laser, operates at 308 nm with a pulse width 5ms and 0.6 s repetition period.

In order to maintain the laser power constant, the laser was regularly re-charged, evacuated, flushed with He gas, and re-filled with proper ratio of Ne, HCl, Xe and $H_2$ to a 55 psi pressure. The growth was carried out in a high - vacuum chamber similar to the one illustrated in Figure 3.1. The laser beam is reflected by a 45 degree mirror through a quartz lens ( $f=$ 30 cm) and through window F onto the spinning target in the high vacume ( $6.5 \times 10^{-6}$) Torr.

The bulks were fixed on the target spinning holder H, by silver paste. Films were deposited to the surface of a SrTiO$_3$ (100) crystal substrate (5×5×0.5 mm). For preperation of the substrate we followed the following procedure:

All substrates have been cleaned in Ultrasound bath with Acetone and then in absolute Ethanol, for 30 minutes, and have been dried with Argon gas. The SrTiO$_3$ (100 ) substrates were placed on a holder, (N).

The chamber was evacuated to the high vacuum ( $5.5 \times 10^{-6}$ Torr). The substrate was heated to 750°C or 800°C by transferring heat through spiral heating elements (O). Oxygen pressure of 0.4 mbar were held during deposition. For growing all thin films 10000 laser pulses were used. Pulses of laser beam generate a plume of ejected particulates prependicular to the target.
Figure 3.1: Schematic drawing of the growth chamber, Legend: A, B-pumps, D-mirror, E-lens, F-quartz window, H-spinning target, J-plume of particles ablated from target, S-substrate, N-substrate holder in the heater, O-spiral of resistive heating element, and P-thermometer[32]
surface regardless of the angle of incident.

The deposited film was postannealed at 850°C or 900°C in one atmosphere of Oxygen and subsequently cooled down to room temperature in one hour.

3.1.2 Characterization of films

The electrical resistivity was measured by the standard four-contact methods. Before the measurement four parallel strips of gold layer were evaporated on the film. Then four gold wires were attached to the strips by using indium solder to achieve ohmic contacts.

The SQUID detection system was used for susceptibility measurement. The MPMS system consist of a Helium dewar with a superconducting magnet SQUID detection system and probe assembly connected to control systems. Automatic control and data acquisition are provided by a PC computer and subsystem controllers for the control of gas, temperature, magnetic field and sample transport. The design of the system allows the probe to be refit for various type of measurement.

3.1.3 Measurement of resistivity under external pressure

Pressure effects were measured by increasing the pressure up to 15 kbar using a self - clamping type pressure cell as shown in Fig. 3.2 and Fig. 3.3

The pushing force which was applied to the cell at room temperature by a conventional press, was transmitted to the sample region by the Tungsten - carbide push rod. The sample was placed in a high pressure region inside nylon cup filled with a 1:1 2-Methylbutane 3-Methyl-1-butanol ratio. The pressure in the cell was determinate by using the pressure dependence of the resistance of lead as an internal pressure manometer. For achieving good contacts the lead strip was spot-welded to copper wires, and a thin gold wire is soldered to each of the four corners of the film using indium. The four corners were labed as 1, 2, 3, 4. A current of 10 (µ) A is applied between contacts 1, 4 and the voltage was measured between 2, 3. The nylon cup is sealed at one end by a hardened steel piston through which electrical leads (4 for lead, 4 for sample ) were brought out of the high pressure region. The pressure cell was placed inside a cryostat, as is shown in Fig. 3.2 and Fig. 3.3. The resistivity of thin films was measured by applying force ( The range of 1 to 20 tons ) at room temperature.
Figure 3.2: Schematic drawing of the pressure cell. 1. Piston rod (WC), 2. tightening nuts, 3. springs(CuBe), 4. body of cell(CuBe), 5. Plug(CuBe/WC), 6. protecting washer(CuBe/Teflon), 7. sample area, 8. obturator(hardened steel), 9. wires [33].
For every half ton (10-15) interval the resistance of the sample and lead were measured. The pressure inside the cell (kbar), estimated with the experimental equation of

$$P = 358.36 - 919.639X + 842.46X^2 - 281.209X^3$$

(3.1)

Where $X = \frac{R}{R_0}$, $R$ and $R_0$ is the lead resistance at finite and zero pressure respectively [29].

A complete measurement has been done on thin film of $La_{0.84}Sr_{0.16}MnO_3$. For this experiment the same system as was described before has been used. The outer dewar evacuated, the middle and inner dewar filled with liquid Nitrogen, and the pressure cell is allowed to cool down to around 77 K, then measurements were taken as the system slowly warms up. Measurements were carried out first at ambient pressure. The other measurements were taken following the subsequence application of different forces and different temperatures.

Each time the cell was pressurized, two sets of data $R_{lead}(T, P)$, $R_{sample}(T, P)$ were acquired for that unknown pressure. Thereafter, by using $R_{lead}(T, 0)$, $R_{lead}(T, P)$ and equation (3.1) we were able to determine the actual pressure in the pressure cell. $R_{sample}(T, P)$ has been derived from the pressure value which has been calculated. Similarly this method has been used for all other temperature and the temperature dependence of the pressure was determined.
Figure 3.3: The sample attachment in the pressure cell, 1. sample, 2. protecting ring, 3. body of container, 4. nylon cup, 5. wires, [33]
Chapter 4

Results and Discussion

4.1 Results and Discussion

In order to study the effect of pressure on the resistivity of $La_{1-x}Sr_xMnO_3$ thin films, five bulk samples with different concentration of Sr, $x=0.15$, $x=0.20$, $x=0.25$, $x=0.30$, and $x=0.35$ were prepared.

The temperature dependence of $\rho(T)$ at ambient pressure for the above 5 bulks are presented in following Figs. 4.1 - 4.5

All bulk samples, more or less exhibit a similar pattern, and different $T_C$ as their concentration vary. Samples were cooled to about 14 K, then at ambient pressure the resistance was measured during warm up around room temperature. For samples with $T_C$ greater than 300 K, the sample was warmed up to 400K.

As the temperature is increased, the resistivity $\rho(T)$ rises as the carriers are increasingly scattered by phonons. At higher temperature ($> T_C$) the carrier mean free path becomes comparable with the distance between ions, polarons hopping are set in, and the resistivity drops. This indicates a transition from a ferromagnetic metal, $d\rho(T)/dT$ positive, to paramagnetic nonmetal, $d\rho(T)/dT$ negative. The Curie temperature is very close to $T_{MI}$, the metal -insulator transition temperature, which is taken at temperature of the maximum in the $\rho$- T curve.

In order to find $T_C$ accurately the magnetic moments of 5 bulks were measured in the magnetic field of 15 gauss with SQUID magnetometer system, as they are shown in the Fig. 4.6. The $T_C$ was determined at 5 percent change of susceptibility and the result are listed in table 4.1. These results are in good agreement with the $T_C$ reported in other works [2]. Using the sintered ceramic samples of $La_{1-x}Sr_xMnO_3$, and employing pulsed laser deposition technique we have grown several thin films of these compounds on (001) face of SrTiO$_3$ single crystal. For each film we adjusted the growth conditions in order to obtain the right stoichiometry and $T_C$.

For observing the overall behaviour of film’s resistance with pressures and
Figure 4.1: Temperature dependence of Resistance of Bulk sample $La_{0.65}Sr_{0.35}MnO_3$. 
Figure 4.2: Temperature dependence of resistance of bulk sample $La_{0.70}Sr_{0.30}MnO_3$. 
Figure 4.3: Temperature dependence of Resistance of Bulk sample $La_{0.75}Sr_{0.25}MnO_3$. 
Figure 4.4: Temperature dependence of Resistance of Bulk sample \( La_{0.80}Sr_{0.20}MnO_3 \).
Figure 4.5: Temperature dependence of Resistance of Bulk sample $La_{0.85}Sr_{0.15}MnO_3$. 
Figure 4.6: susceptibility vs temperature of Bulk samples $La_{1-x}Sr_xMnO_3$
Table 4.1: Transition temperature $T_c$ for $La_{1-x}Sr_xMnO_3$ bulk samples and thin films with different concentration of Sr

<table>
<thead>
<tr>
<th>$La_{1-x}Sr_xMnO_3$</th>
<th>$T_c$</th>
<th>$T_c$ [26]</th>
<th>$T_c$ thin film</th>
</tr>
</thead>
<tbody>
<tr>
<td>$La_{0.85}Sr_{0.15}MnO_3$</td>
<td>270K</td>
<td>270K</td>
<td>—</td>
</tr>
<tr>
<td>$La_{0.80}Sr_{0.20}MnO_3$</td>
<td>280K</td>
<td>290K</td>
<td>290K</td>
</tr>
<tr>
<td>$La_{0.75}Sr_{0.25}MnO_3$</td>
<td>330K</td>
<td>340K</td>
<td>330K</td>
</tr>
<tr>
<td>$La_{0.70}Sr_{0.30}MnO_3$</td>
<td>355K</td>
<td>360K</td>
<td>350K</td>
</tr>
<tr>
<td>$La_{0.65}Sr_{0.35}MnO_3$</td>
<td>360K</td>
<td>370K</td>
<td>360K</td>
</tr>
</tbody>
</table>

Temperature measured the temperature dependence of $R(T)$ as a function of pressure for $La_{0.84}Sr_{0.16}MnO_3$.

As can be seen from the Fig. 4.7, with applying external pressure, the resistance drops and $T_c$ shifts to a higher temperature.

In Fig. 4.8 we plotted $T_c$ vs pressure for this film, and we determine the $(dT_c/dP = 1.9 \text{ k/kbar})$ which is comparable with $(dT_c/dP )$ of thin films of $La_{2/3}Sr_{1/3}MnO_3$ [32]. These results can be explained by using double exchange model.

Generally, several parameters are known to contribute to the increase of $T_c$. For example, particle - size affects the metal - insulator transition temperature through change in the $Mn^{4+}$ composition by heat treatment. Another factor which could lead to an increase of $T_c$ with which would be the oxygen content in the films. The increase of the $T_c$ value upon application of pressure is a consequence of the double exchange interaction. The Strength of the DE interaction is enhanced by applying pressure which as a result, induces a higher $T_c$ and a lower resistivity. Enhancement of double exchange is measured through the transfer factor $t=t_0\cos\theta /2$. Where $t_0$ is proportional to the bond angle and the band length of Mn-O -Mn arrangement and $\theta$ is the angle between the moments on the Mn ions in the lattice structure, $t_0$ is expected to be strongly pressure dependent. By applying external pressure the Mn -O - Mn angle should increase toward 180 and the Mn - O bond length should decrease. All this should increase $t_0$ and consequently t. The more effective transfer of the $e_g$ electrons upon application of pressure causes the resistivity to drop and $T_c$ to increase[17],[30].

To see whether or not the thin films of $La_{1-x}Sr_xMnO_3$ can be used as a device for pressure sensing, we measured the pressure dependence of the room
Figure 4.7: Temperature dependence of $\rho$ (T) under various pressure for $La_{0.86}Sr_{0.14}MnO_3$ sample.
Figure 4.8: Temperature $T_c$ vs pressure for $La_{0.86}Sr_{0.14}MnO_3$ sample
Table 4.2: Variation of resistivity with temperature (294K—305K), room temperature and pressure for \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \) thin films \( 0.15 < x < 0.35 \).

<table>
<thead>
<tr>
<th>( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 )</th>
<th>( \frac{dp}{dT} ), ( \Omega\text{m K}^{-1} )</th>
<th>( \frac{dp}{dP} ), ( \Omega\text{m kbar}^{-1} )</th>
<th>ratio of slopes</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{La}<em>{0.80}\text{Sr}</em>{0.20}\text{MnO}_3 )</td>
<td>( -3.25 \times 10^{-6} )</td>
<td>( 3.14 \times 10^{-6} )</td>
<td>1.04 kbar/K</td>
</tr>
<tr>
<td>( \text{La}<em>{0.75}\text{Sr}</em>{0.25}\text{MnO}_3 )</td>
<td>( 2.11 \times 10^{-6} )</td>
<td>( 3.15 \times 10^{-6} )</td>
<td>0.69 kbar/K</td>
</tr>
<tr>
<td>( \text{La}<em>{0.70}\text{Sr}</em>{0.30}\text{MnO}_3 )</td>
<td>( 1.46 \times 10^{-6} )</td>
<td>( 3.29 \times 10^{-6} )</td>
<td>0.44 kbar/K</td>
</tr>
<tr>
<td>( \text{La}<em>{0.65}\text{Sr}</em>{0.35}\text{MnO}_3 )</td>
<td>( 2.24 \times 10^{-6} )</td>
<td>( 3.80 \times 10^{-6} )</td>
<td>0.59 kbar/K</td>
</tr>
</tbody>
</table>

temperature resistance of all films, we have fabricated from bulks samples. To determine \( (dR/dT)_{294K} \) near room temperature, first we measured resistance of these films as a function of temperature as shown in Figs. 4.9–4.12. The results of these measurements are given in Table 4.2.

As can be seen in this table, \( dp/dT \) decreases with increasing concentration of Sr up to \( x = 0.3 \) and then increases as we pass the optimum doping \( x = 1/3 \) concentration. We should mention here that the thin film of \( \text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3 \) showed semiconducting behavior at all temperatures.

The pressure dependence of resistivity as a function of pressure at room temperature for each film is given in Figs. 4.13–4.16. For all \( x \), the figures show that the applied pressure decreases the resistance at room temperature for each of these \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \) films. From the least-square fits to the data of Figs. 4.13–4.16 we calculated the slopes of \( (dp/dP)_{294K} \) shown in table 4.2.

The ratio of the slopes is seen to be of the order of 1 kbar/K. This implies that a slight change in temperature as the pressure changes will be responsible for as much of a change in resistivity, as the original change in pressure itself.

All samples with different \( T_C \) are affected differently by the external pressure. This behaviour is due to the fact that, in these samples possibly an electron-phonon interaction is involved. The double exchange interaction is increased which in turn lowers the resistivity of the films. External pressure is able to reduce the resistivity through increasing Mn–O–Mn bond angles.

Application of external pressure on the other hand, modifies both the Mn–O bond length and the Mn–O–Mn bond angle (decreasing the bond
Figure 4.9: Temperature dependence of resistivity of $La_{0.65}Sr_{0.35}MnO_3$ thin film, slope $= 2.24 \times 10^{-6} \Omega \text{m K}^{-1}$ (294k - 305k)
Figure 4.10: Temperature dependence of resistivity of $La_{0.70}Sr_{0.20}MnO_3$ thin film, slope = $1.461 \times 10^{-6} \Omega \text{m K}^{-1}$ (294k - 305k)
Figure 4.11: Temperature dependence of resistivity of $La_{0.75}Sr_{0.25}MnO_3$ thin film, slope $= 2.117 \times 10^{-6} \Omega \text{m K}^{-1}$ (294k - 305k)
Figure 4.12: Temperature dependence of resistivity of $La_{0.80}Sr_{0.20}MnO_3$ thin film, slope = $3.256 \times 10^{-6} \Omega \text{m K}^{-1}$ (294k - 305k)
Figure 4.13: Pressure dependence of resistivity $La_{0.65}Sr_{0.35}MnO_3$ thin film at room temperature, slope $= 3.80 \times 10^{-6} \Omega \text{m kbar}^{-1}$, standard error of slope $= 1.03 \times 10^{-7}$
Figure 4.14: Pressure dependence of resistivity $La_{0.70}Sr_{0.30}MnO_3$ thin film at room temperature, slope $= 3.30 \times 10^{-6}\Omega m kbar^{-1}$, standard error of slope $= 1.07 \times 10^{-7}$
Figure 4.15: Pressure dependence of resistivity $La_{0.75}Sr_{0.25}MnO_3$ thin film at room temperature, slope = $3.15 \times 10^{-6} \Omega \text{m kbar}^{-1}$, standard error of slope = $3.5 \times 10^{-8}$
Figure 4.16: Pressure dependence of resistivity $La_{0.80}Sr_{0.20}MnO_3$ thin film at room temperature, slope $= 3.14 \times 10^{-6} \Omega \text{m kbar}^{-1}$, standard error of slope $= 3.6 \times 10^{-8}$
length and increasing the bond angle). Both result cause in an increase of the effective bandwidth for $e_g$ electrons. Although effects of magnetic field and pressure are different, the final results are similar in that both help reduce the resistivity and increase $T_{MI}$.

As can be seen from Table 4.2. The error due to variation of resistance with temperature is significant at room temperature. The lowest error was found to be 44 \% of $d(\rho)/dP$ for $La_{0.70}Sr_{0.30}MnO_3$. Because the variation of the resistance with temperature is large, one can not use these films as a sensor. For any application of these films one needs to accurately measure the temperature or control the temperature. However, this might add substantial cost to the development of such a device which makes it difficult to compete with other pressure sensing devices.
Chapter 5

CONCLUSION

We have fabricated five bulks of \( La_{1-x}Sr_xMnO_3 \) with different concentrations of Sr \( X=0.15, 0.20, 0.25, 0.30, 0.35 \) by using the parameters listed in table1 3.1. By forming them into tablets and using appropriate growth parameters, we have successfully fabricated epitaxial \( La_{1-x}Sr_xMnO_3 \) films of various concentration of Sr on SrTiO\(_3\) substrate(001)by the pulsed laser deposition method.

All films, show the \( T_C \) close to expected temperature, and all graphs more or less exhibited the same pattern. In the course of this study, we have shown that the different concentration of Sr plays an important role in shifting the transition temperature, in their response to pressure. The transition temperature also increases with pressure. Furthermore, the metal -insulator transition temperature increases as concentration of Sr increases. The increase in the transition temperature with pressure can be interpreted as the consequence of pressure induced change in the alignment of the Mn - O - Mn bonds, which influence the magnetic exchange between \( Mn^{+3} \) and \( Mn^{+4} \) ions. The variation of \( d\rho/dP \) and \( d\rho/dT \) at room temperature has been derived from graphs for all thin films as shown in Table 4.2. By using this data we estimated error in \( d\rho/dP \) due to change of resistivity with temperature.

In summary thin films with the highest concentration of Sr show a greater response to pressure than do the films with lower concentration of Sr. However, the error due to variation of resistance with temperature makes it impractical to use these material as a pressure sensing devices at room temperature.
Bibliography


