Study on the properties of piezoelectric materials and manganese-based oxide perovskites

by

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Abstract

Perovskite type piezoelectric and manganese oxide materials have gained a lot of attention in the field of device engineering. Lead zirconium titananium oxide (PbZr$_{1-x}$Ti$_x$O$_3$ or PZT) is a piezoelectric material widely used as sensors and actuators. Miniaturization of PZT-based devices will not only perfect many existing products, but also opens doors to new applications. Lanthanum manganese oxides La$_{1-x}$A$_x$MnO$_3$ (A-divalent alkaline earth such as Sr, Ca or Ba) have been intensively studied for their colossal magnetoresistance (CMR) properties that make them applicable in memory cells, magnetic and pressure sensors. In this study, we fabricate PZT and LSMO(LCMO) heterostructures on SrTiO$_3$ substrates and investigate their temperature dependency of resistivity and magnetization as a function of the thickness of LSMO(LCMO) layer. The microstructure of the samples is analysed through TEM. In another set of samples, we study the effect of application of an electric field across the PZT layer that acts as an external pressure on the manganite layer. This verifies the correlation of lattice distortion with transport and magnetic properties of the CMR materials.
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Chapter 1

Introduction

Manganese based oxide perovskites, $T_{1-x}D_x\text{MnO}_3$ (where $T$ is a trivalent rare-earth ion and $D$ a divalent ion such as Ca, Sr, Ba or Pb) have long been known for their unique electrical and magnetic properties. The Curie and charge ordering transition temperatures of these materials depend on the kind of dopant and the value of $x$, the pressure and magnetic field. An external magnetic field and pressure, as well as internal pressure (ion size mismatch) change the Mn-Mn electronic transfer integral and lead to a change of the magnetic and transport properties of doped manganese perovskites [1]. Recent studies on thin films, ceramics, and single crystals with carefully controlled compositions of these compounds have revealed an enormous magnetoresistance (MR) phenomena [2]. A large negative MR is usually observed around $T_c$ by applying an external magnetic field, and a resistivity change of orders of magnitude is induced (the so-called colossal magnetoresistance (CMR) effect), associated with a ferromagnetic to paramagnetic phase transition [3]. The CMR property in these materials makes them applicable in magnetic recording and making of memory devices and transistors.

Among a number of perovskite type manganese oxides with various combinations of $(T,D)$, $La_{1-x}Sr_x\text{MnO}_3$ and $La_{1-x}Ca_x\text{MnO}_3$ are considered to be prototypical and reference materials. The parent compound $La\text{MnO}_3$ is an antiferromagnetic insulator but the substitution of a trivalent $La^{3+}$ by a divalent ion (such as $Sr^{2+}$ or $Ca^{2+}$ in this study) causes the coexistence of $Mn^{3+}$ and $Mn^{4+}$ and the Lanthanum manganite becomes a conductive ferromagnet. For $La_{1-x}Sr_x\text{MnO}_3$ (LSMO) crystals, the FM state appears below $T_c$ and above a critical doping $x_c \approx 0.17$ (compositional I-M phase boundary) and increases up to $T_c \approx 380$
K at the doping level of x=0.3-0.5 [2]. Based on previous research, the transport properties of LCMO are optimized for a doping value of x=0.3. For this value, the compound’s structure has the most proper value of ferromagnetic spin mixture of Mn$^{3+}$(3d$^4$) and Mn$^{4+}$(3d$^3$) ions [4], and as a result, resistivity is minimized and the compound’s sensitivity to magnetic field and pressure is increased. This composition yielded the highest reported Curie temperature and the lowest resistivity when the conduction becomes metallic like.

The transport properties of these materials is explained by the double exchange effect. According to the double exchange interaction, the transfer of an itinerant $e_g$ electron between neighboring Mn ions (local $t_{2g}$ spins) through the O$^{2-}$ ion results in ferromagnetic interaction due to on site Hund coupling. An external magnetic field forces the local $t_{2g}$ spins to align. It reduces spin scattering, therefore causes decrease in resistivity, enlarges the ferromagnetic phase, and results in increase of $T_c$ [1]. An applied external pressure has a similar effect on resistivity and Curie temperature. By applying external pressure, the Mn-O-Mn bond angle increases toward 180° and the Mn-O bond length increases. This results in a more effective transfer of the $e_g$ electrons and causes the resistivity to drop and $T_c$ to increase [4].

The main aim of this research is to study heterostructures of La$_{1-x}$Sr$_x$MnO$_3$ (LSMO), La$_{1-x}$Ca$_x$MnO$_3$ (LCMO) and piezoelectric perovskite oxide PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) on SrTiO$_3$ (STO) substrates to investigate the effect of applied pressure provided by the PZT layer on the electronic and magnetic properties of the manganite layer, as a function of the applied bias voltage across the PZT layer and the thickness of LSMO/LCMO layer. It is the property of piezoelectric materials to become strained when placed in an electric field, and conversely, become electrically polarized when put under mechanical stress [5]. Application of a bias voltage across the PZT layer causes the PZT structure to either stretch or compress, thus affecting its lattice parameters [6]. This acts as an external pressure on the manganite layer, affecting its transport properties by altering its lattice parameters.

When an electric voltage is applied to a piezoelectric material, the Weiss domains increase their alignment proportional to the voltage. The result is a change of dimensions (expansion
or contraction) of the material [6].

Some piezoelectric materials also exhibit ferroelectric behavior. Ferro-electric thin films can be applied to wide range of devices, from non-volatile memory applications to sensors and actuators due to their ferro-electricity, pyro-electricity and piezo-electricity. Lead Zirconate Titanate (PZT) is one of the most thoroughly investigated ferro-electric materials [7] and is an important material for manufacturing ultrasonic transducers and actuators. Currently, PZT films are extensively investigated for device miniaturization, enhanced device performance, and integration with semiconductor circuitry.

Because PZT, LSMO and LCMO belong to the perovskite family of oxides and are thus structurally very similar, it is possible to realize such heterostructures in epitaxial, single crystalline form [8]. Another reason for studying these heterostructures is the small lattice mismatch between the two structures compared to other perovskite oxides.

In chapter 2, a detailed theoretical review of the properties of piezoelectric and manganite oxide materials is presented. In this research, four different types of multilayer thin-film samples were studied. Heterostructures of LSMO on PZT (PZT-LSMO) were ablated on STO substrates using pulsed laser deposition (PLD) technique, in nearly same experimental conditions, except with different thicknesses of LSMO in order to examine whether LSMO retains its thickness dependent properties in the presence of PZT. The other type of thin-film studied was the heterostructure of PZT on LSMO (LSMO-PZT), grown on Nb doped STO substrate. The heterostructures of LCMO and PZT with similar growth techniques as above samples were also fabricated.

The experimental methods used to prepare the ablation targets and the thin-film samples are described in chapter 3. The resistivity of the samples mentioned above was measured as a function of the temperature. For the LSMO-PZT, LCMO-PZT and PZT-LSMO samples, the resistivity was measured as a function of the bias voltage applied between the PZT layer and the substrate. Also, the magnetization measurements on the samples were carried out as a function of temperature. The XRD profiles, microstructural analysis, the details of
experimental procedures and the results are presented in chapter 4.

The final conclusions are discussed in chapter 5.
Chapter 2

Properties of the parent materials

2.1 Properties of PbZr$_{1-x}$Ti$_x$O$_3$

2.1.1 Piezoelectricity and the perovskite structure

Piezoelectricity stems from the Greek word *piezo* that means pressure. It is a linear effect that is related to the microscopic structure of the solid. Some ceramic materials become electrically polarized when they are strained. This linear and reversible phenomenon is regarded as the direct piezoelectric effect. The direct piezoelectric effect is always accompanied by the converse piezoelectric effect where a solid becomes strained when placed in an electric field [5]. The microscopic origin of the piezoelectric effect is the displacement of ionic charges within a crystal structure. In the absence of external strain, the charge distribution within the crystal is symmetric and the net dipole moment is zero. However when an external stress is applied, the charges are displaced and the charge distribution is no longer symmetric. A net polarization develops and results in an internal electric field. A material can only be piezoelectric if the unit cell has no center of inversion [5].

During World War II, research in piezoelectric materials expanded to the US, the Soviet Union and Japan. Barium titanate and lead zirconate titanate (PZT) were discovered in the 1940’s and 1950’s. These families of materials exhibited very high dielectric and piezoelectric properties. Presently, PZT is one of the most widely used piezoelectric materials. It is the basis of practically all transducers, actuators and other piezoelectric devices [5].

The lattice structure of PZT ceramic is based on the perovskite structure. As shown in figure 2.1, the perovskite structure (ABO$_3$) is the simplest arrangement, described as
Chapter 2. Properties of the parent materials

a simple cubic unit cell with a large cation (Pb) on the corners, a smaller cation (Ti,Zr) in the body center and oxygens in the center of the faces. The structure is a network of corner-linked oxygen octahedra, with the smaller cation filling the octahedral holes [9], and the larger cations filling the very small spaces between the octahedra in the larger A-site. This structure also allows for multiple substitutions on the A-site and B-site resulting in a number of useful though more complex compounds such as (Ba,Sr)TiO₃, (Pb,Sr)(Zr,Ti)O₃, Pb(Fe,Ta)O₃ and (K,Bi)TiO₃ [5].

Some piezoelectric materials are also ferroelectric. A ferroelectric material possesses a spontaneous polarization that can be reversed in direction by application of an electric field over some temperature range. Most ferroelectric materials have a Curie Temperature, Tc, below which they are polar and above which they are not [5].

The ferroelectric nature of PZT material was established in Japan early in the 1950’s [9]. Since then, intensive work has been done on these materials whose results have shown to be very promising for several applications such as nonvolatile memory elements, infrared sensors, surface acoustic wave devices and actuators [10].

2.1.2 Phase Transitions in PbZr₁₋ₓTiₓO₃

The solid solution system PbZr₁₋ₓTiₓO₃ has a complex phase diagram containing a number of materials which exhibit useful ferroelectric and piezoelectric properties(figure 2.2). This solid solution is cubic at high temperatures but becomes slightly distorted at lower temperatures, where it is ferroelectric [11]. Except for a narrow region close to PbZrO₃, the ferroelectric phase is divided in two regions of different symmetry, rhombohedral for Zr-rich compositions and tetragonal for Ti-rich compositions. The highest piezoelectric response in this system is found at the boundary between these two phases, at x=0.47, the so-called morphotropic phase boundary (MPB) [11]. The phase boundary is considered as that composition where the two phases are present in equal quantity [9]. However, it is usually assumed to mean nearly vertical, i.e., composition independent. Recent studies [11] have shown that a monoclinic
Figure 2.1: Perovskite structure [5]
phase exists between the rhombohedral and tetragonal PZT phases. The discovery of this phase around the MPB in PZT answers many of the questions raised by previous investigators about the nature of the MPB and the reason for the special physical properties of PZT in this region of the phase diagram, especially about the co-existence of rhombohedral and tetragonal phases [11].

2.1.3 Electromechanical response of PbZr$_{1-x}$Ti$_x$O$_3$

A set of equations that describe the behavior of a piezoelectric material subjected to a small stress or a weak electric field is as follows:

$$D_i = \varepsilon_{ij}^T E_j + d_{im} T_m$$

$$S_k = d_{jk} E_j + s_{km} E_m$$

where $E$, $D$, $T$ and $S$ are the electric field, electric displacement, stress and strain, respectively. The constants $s^E$, $\varepsilon^T$ and $d$ are the elastic compliance at constant electric field, the dielectric permittivity under constant stress, and the piezoelectric coefficient, respectively [12]. The latter constants can be written as a sum of two terms,

$$s = s_{ex} + s_{in}$$

$$\varepsilon = \varepsilon_{ex} + \varepsilon_{in}$$

$$d = d_{ex} + d_{in}$$

where subscript $ex$ denotes extrinsic and $in$ denotes intrinsic contributions [13]. The piezoelectric response consists of the sum of extrinsic and intrinsic effects [12]. The intrinsic effect results from the response of a single domain crystal under the application of an electric field. The extrinsic effect is caused by the elastic deformation as a result of the motion of domain walls [12]. The existence of domain walls plays an important role in the properties of PZT ceramics. When an electric field is applied, the domain wall moves to minimize the
Chapter 2. Properties of the parent materials

\[ \text{PbZr}_{1-x}\text{Ti}_x\text{O}_3 \]

\[ \text{Figure 2.2: Phase diagram of PbTiO}_3-\text{PbZrO}_3 \text{[11]. C stands for cubic phase, T for tetragonal, R}_{HT}\text{ for high temperature rhombohedral, R}_{LT}\text{ for low temperature rhombohedral, M for monoclinic and M+T for co-existence of monoclinic and tetragonal phases.} \]
domain energy. Contributions from the electrostatic and domain wall energies act against each other and the domain structure involving size, shape and population, changes. In this process, some of the domains cover other domains or change shape, all of which changes the net strain and polarization [12].

2.2 Properties of Lanthanum Manganites

Manganese-based oxide perovskites, $T^{3+}_{1-x}D^{2+}_xMn^{3+}_{1-x}Mn^{4+}_xO_2^-$, where $T$ is a trivalent rare earth and $D$ is a divalent alkaline earth ion such as Ca, Sr, Ba, or Pb, have recently been intensively studied due to their interesting electrical and magnetic properties and potential device applications.

The undoped parent compound $ABO_3$ is an insulating anti-ferromagnet. The ideal perovskite structure for $ABO_3$ compounds is 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. The structure of this compound can be characterized by the Goldschmidt tolerance factor $t$, where $t=\frac{(R_O+R_A)}{\sqrt{2}(R_O+R_B)}$. $R_O$, $R_A$ and $R_B$ are the ionic radii of Oxygen, $T(D)$ and Mn ions, respectively. The tolerance factor measures the deviation from perfect cubic structure ($t=1$)[3]. Structures with $0.8\leq t \leq 0.9$ are orthorhombic, those with $0.9\leq t \leq 0.97$ are cubic, and those with $0.97\leq t \leq 1.02$ have tetragonal structure [4].

The parent compound $LaMnO_3$ has an orthorhombic structure with $t=0.89$. Therefore a very slight increase in $t$ induced by substituting larger ions like $Ba^{2+}$ or $Sr^{2+}$ for $La^{3+}$ is needed for transition to a cubic structure. Among a number of perovskite type manganese oxides with various combinations of $(T,D)$, $La_{1-x}Sr_xMnO_3$ (LSMO) and $La_{1-x}Ca_xMnO_3$ (LCMO) are considered to be prototypical and reference materials. Substituting $Sr^{2+}$ or $Ca^{2+}$ for $La^{3+}$ ions reduces the average value of $R_B$ and consequently increases the tolerance factor to a value above 0.96 which would lead to a rhombohedral perovskite structure [14]. As a result of this substitution, the volume of the unit cell decreases, thus creates distortions in the
structure. These distortions contribute to the electronic and magnetic properties in this compound [14].

In the last ten years, an overwhelming interest in the manganite perovskites arose primarily due to the observation of a negative colossal magnetoresistance (which is magnetoresistance associated with a ferromagnetic to paramagnetic phase transition) close to $x=0.3$[15]. The insulator-metal transition at low temperatures is an orthorhombic to rhombohedral transition. The LSMO compounds with doping level $0.175 \leq x \leq 0.4$ and LCMO compounds [4] with $0.2 \leq x \leq 0.5$ become conducting ferromagnets when cooled down to some critical temperature $T_c$ and are metallic in low temperatures [3].

The electrical conductivity in these oxides was explained in terms of double exchange (DE) interaction, introduced by Zener [16] with transfer of an electron from the $e_g$ state of an Mn$^{3+}$ ion to a vacant $e_g$ state of an adjacent Mn$^{4+}$ ion across an O$^{2-}$ ion. The strength of the DE interaction is measured through the transfer integral $t_{\text{eff}} = t_0 \cos(\Theta/2)$ [1] where $\Theta$ is the relative angle between two neighboring local spins and $t_0$ is proportional to Mn-O-Mn bond angle and bond length. In Zener's picture, considering a Mn$^{3+}$-O$^{2-}$-Mn$^{4+}$ chain, an electron hops from the oxygen ion onto the Mn$^{4+}$ ion, at the same time with an electron hopping onto the oxygen ion from the Mn$^{3+}$ ion. The result is a positive exchange coupling induced by the carriers, called the "Double Exchange" interaction. In a double hopping event, it is required that both electrons have the same spin, which must also be the same as the spin on the Oxygen ion. The electron spins in Mn$^{4+}$ and Mn$^{3+}$ should be aligned so that the parallel alignment of Mn moments is achieved [14]. The angle between Mn spins, $\Theta$, is sensitive to magnetic field. An external magnetic field forces the local $t_{2g}$ spins to align ($\Theta \rightarrow 0$). The electrical resistivity $\rho$ is then a minimum when the spins are parallel. This mechanism gives rise to a negative magnetoresistance for a disordered spin system. The change due to a magnetic field in this spin disorder resistivity is expected to be largest at the Curie temperature $T_c$ because the parallel susceptibility is a maximum at this point [17].

In case of LSMO, for $x \geq 0.25$ crystals with $T_c \geq 340$K sharp MR peaks occur above 320K
as one can guess from a strong decrease in magnetoresistance at lower temperatures. Thus, the observation of huge MR below the magnetic transition in a wide range of temperatures is explained by the forced alignment of spins in the field direction [17].

Application of external pressure has same effects on the transport properties and resistivity of manganite perovskites. While $\Theta$ in the transfer integral is sensitively dependent on applied magnetic field, $t_0$ is strongly pressure dependent. By applying external pressure, the Mn-O-Mn bond angle should increase toward 180° and the Mn-O bond length should increase. This results in an increase in $t_0$ and consequently $t_{eff}$. The more effective transfer of the $e_g$ electrons upon application of pressure causes the resistivity to drop and $T_c$ to increase [4].

Figure 2.3 shows a schematic diagram of the crystal structure of LSMO(LCMO). A large cation La$^{3+}$ or smaller Sr$^{2+}$ (Ca$^{2+}$) cation sits at the center of the cube, a Mn$^{3+}$ or Mn$^{4+}$ at each corner, and the O$^{2-}$ ions are at the midpoint of the cube edges [4].

The crystal in figure 2.3 appears to be cubic, but in reality the unit cell has a distorted shape. Two different distortions characterize the crystal’s structure. One distortion is related to the MnO$_6$ octahedra, which is affected by the free space created by the substitution of a Sr(Ca) ion for La. This free space affects the bending of Mn-O-Mn bond and thus influences the strength of electron transfer through the Mn$^{3+}$-O$^{2-}$-Mn$^{4+}$ chain.

The second distortion is due to Jahn-Teller effect which is related to distortion of highly symmetrical molecules. According to Jahn-Teller theorem, for a non-linear molecule in an electronically degenerate state, distortion must occur to lower symmetry, remove the degeneracy and lower the energy [18]. The Mn$^{3+}$ ions have three localized electrons in $t_{2g}$ orbitals (xy, yz and zx symmetry) and one electron in $e_g$ orbital ($z^2$ and $x^2-y^2$ symmetry). The $z^2$-state band is occupied by the electron that mediates the ferromagnetic interaction coupling in the Mn-O-Mn chain. Its band-width is sensitive to pressure, i.e. increases with pressure and so increases the chance for the electron to delocalize [19].

LCMO has a similar structure to that of LSMO. A great deal of study and research has
Figure 2.3: The ideal antiferromagnetic perovskite structure for LaMnO$_3$. In real structure, the Oxygen octahedron is distorted with a combination of basal plane distortion mode, the octahedral stretching mode and a rotation [4].
been carried out on both materials. CMR, with appropriate doping level of \( x \) is observed in both materials. There are some differences between the phase diagrams of LSMO and LCMO, mainly due to the size difference of \( \text{Sr}^{2+} \) and \( \text{Ca}^{2+} \) cations. Most of the experiments have been carried out for concentrations \( x < 0.5 \), because CMR effects are best observable around \( x \approx 0.3 \).

A schematic temperature-doping phase diagram for LSMO system is shown in figure 2.4. At zero temperature, undoped LMO is a canted antiferromagnetic insulator (CI). When doped with holes via Sr substitution, transitions to ferromagnetic insulator (FI) occurs at \( x \approx 0.09 \) [8]. On further increasing \( x \), another transition to ferromagnetic metal is observed. The CMR effect is most pronounced near \( T_c \), where for doping levels \( x \) between 0.15 and 0.25 holes/unit cell, LSMO undergoes a simultaneous magnetic and metal-insulator phase transition, from a paramagnetic insulating state (PI) to a ferromagnetic metallic state (FM) upon cooling [8]. The FM regime reveals a rhombohedral structure and shows CMR. At high temperature two distinct phases appear, PI and PM. For \( x > 0.5 \) a tetragonal phase occurs which is ferromagnetic metal.
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Figure 2.4: Temperature-doping phase diagram for $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. PI denotes the paramagnetic insulator, CI the spin canted antiferromagnetic insulator, FI the ferroelectric insulator, PM the paramagnetic metal, and FM the ferromagnetic metal [8]
Chapter 3

Experimental Methods

3.1 Preparation of La$_{1-x}$Sr$_x$MnO$_3$ ceramic targets

Generally, La$_{1-x}$Sr$_x$MnO$_3$ is prepared from oxide powders by a number of solid state reactions, with several times of grinding in between. The oxide powders are mixed with right proportions. The powders usually used are Lanthanum oxide (La$_2$O$_3$), Manganese IV oxide (MnO$_2$), and Strontium Carbonate (SrCO$_3$).

La$_2$O$_3$ is first heated in 600°C for 24 hours and weighed again immediately after annealing. The purpose for doing this is that Lanthanum oxide loses water in the heating process and therefore about 8% of its original mass is reduced. Thus it is wise to raise the desired mass of the oxide powder by 10% and then anneal it in the furnace. After drying, the Lanthanum oxide powder is mixed with the rest of the oxides and placed in shaker to be ball-milled for an hour. The fine mixture of powders is then pressed to a tablet and calcinated in 950°C for 24 hours. It is then crushed, reground, pressed into tablet and sintered at 1450°C for another 24 hours.

The above procedure results in a compact ceramic, free from impurities such as La$_2$O$_3$ and SrCO$_3$. Extensive and repeated grinding increases the homogeneity of the material and helps obtain particles of appreciably small size. However, this is a time consuming process to produce single phased powder and also, extensive grinding is believed to severely restrain the solid state reaction [4].

An alternate, more efficient method for preparing ceramic targets is the citrate synthesis and pyrolysis process, or the solgel method. The powder obtained by this method is ultra
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<td>dissolved in 9.5cc</td>
<td>13.63gr</td>
<td>Balance pH with</td>
</tr>
<tr>
<td></td>
<td>2.5116gr. MnO$_2$</td>
<td>HNO$_3$, diluted</td>
<td>citric acid</td>
<td>NH$_4$OH</td>
</tr>
<tr>
<td></td>
<td>0.7688gr. SrCO$_3$</td>
<td>with 20cc H$_2$O</td>
<td>added</td>
<td>pH=6.8</td>
</tr>
</tbody>
</table>

Table 3.1: Recipe for citrate synthesis of La$_{0.65}$Sr$_{0.35}$MnO$_3$

fine and already has the correct stochiometric values. The ceramic target tablets 13 mm in diameter and about 3 mm thick were produced according to the following procedure:

First, La$_2$O$_3$, MnO$_2$, and SrCO$_3$ powders of proper molar ratios are dissolved in nitric acid. Little amount of distilled water is added to avoid violent reaction. The solution is diluted with 20cc distilled water.

Citric acid is added while the solution is being stirred and heated, and brought to boil. At this stage, the solution changes its color from black to green to yellow and finally becomes clear. It’s left overnight to be continuously stirred.

The next day, ammonium hydroxide is diluted in distilled water with equal volumes and is added drop by drop to the solution to raise its pH up to 6.8. The solution gradually thickens and turns milky white. It is covered and left to be continuously stirred overnight.

The solution is finally transferred to an oversized quartz beaker and is heated, without being stirred. Most of the solution is allowed to evaporate. The remaining turns to a black and thick compound. A spontaneous combustion is initiated and produces a very fine powder.

The powder is then collected and pressed into tablets. The tablets are sintered at 1450°C for 24 hours and then cooled at a rate of 2°C per minute. Table 3.1 illustrates the recipe for making a La$_{0.65}$Sr$_{0.35}$MnO$_3$ tablet.

Other LSMO ceramic samples with stochiometry values of $x$=0.15, 0.18 and 0.2 were also prepared but according to the phase diagram in figure 2.4, the mentioned values were very close to the insulating region, and so did not reveal a satisfactorily metallic behavior
once they were ablated on STO substrates. As a result they were not used in fabrication of PZT-LSMO heterostructures.

### 3.2 Pulsed Laser Deposition of thin films

Thin film samples were grown using the pulsed laser deposition (PLD) technique, using a XeCl laser working at 308 nm. The laser was usually re-charged after growing every two samples by being evacuated, flushed with Helium gas, and re-filled with proper ratio of gases. The thin film growth was carried out in a high-vacuum chamber illustrated in figure 3.1.

The growth process is roughly shown in figure 3.1. Laser beam shines on mirror D and is reflected at an angle of 45°, passes through a quartz lens to window F and is focused on the spinning target. Upon hitting the target’s surface, the laser pulses form a plume of ejected particulates that would deposit on a pre-polished surface of a SrTiO$_3$ single crystal substrate with dimensions 5x5x2 mm.

#### 3.2.1 PLD of PZT-LSMO heterostructures

Originally, the laser was programmed to ablate single layered thin-films. But in order to grow multilayer thin-films with different targets, the laser program was modified to rotate the stepping motor M to bring a target to position H as shown in figure 3.1, and start the ablation for a certain number of pulses. After the ablation is over, the next target to be ablated is substituted for the previous target by the stepping motor and the ablation starts again, and this continues for upto a maximum of four targets.

Several thin-film samples were fabricated in different temperatures with different LSMO stochiometries, and finally the growth conditions were optimized for doping level $x=0.35$, PZT ablation temperature 580°C and LSMO ablation temperature 680°C.

The LSMO and PZT ceramic targets surfaces are smoothed with soft sand paper and pasted on target holders with silver paste. The substrate is ultrasonic washed in alchohol and
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, O-spiral of heating element, and P-thermometer [4]
acetone and dried with Argon gas. The chamber has to be absolutely clean from any dust or soot so it is flushed with Argon gas before starting each growth. After placing the substrate in location N, the chamber is evacuated down to a pressure of the order of $10^{-5}$ Torr and the substrate is heated up to 580°C. The temperature is stabilized by the temperature controller shown in figure 3.1. Once the chamber is evacuated and the temperature is stabilized, oxygen gas is allowed inside the chamber to a pressure of 0.4 mbars. The targets are arranged by the laser program such that each is brought to position H by the stepping motor at the time of its layer deposition. First, the PZT target is placed at H and the deposition starts at 580°C. Once the deposition is over, the stepping motor rotates and substitutes the LSMO target for PZT at H. The temperature is then increased to 680°C for deposition of the LSMO layer. After growing the LSMO layer on PZT, the sample is annealed at 730°C in Oxygen atmosphere (1 Barr) for an hour. The temperature is lowered fast to maintain the structure adapted by the film. Previous studies have shown that cooling the samples at a slow rate impedes the crystal phase transition and results in poor crystalization.

To obtain an epitaxially grown crystalline film, it is mandatory to anneal the film in Oxygen atmosphere at high temperature. Oxygen interacts with the target material and undergoes photon and electron impact dissociation during the ablation process between the target and the substrate by producing a highly active atomic oxygen gas. High temperature increases adatom surface mobility and improves the film surface morphology [4].

All PZT-LSMO heterostructures were grown in almost same physical conditions. The thickness of the PZT layer was the same (4000 Å) in all samples, while the LSMO layer was grown with different thicknesses, from 1000 Å to 500 Å in order to investigate whether the PZT layer had any effect on the LSMO transport properties as a function of the LSMO thickness. The list of samples produced and studied appear in table 3.2. The notation PZT-LSMO specifies the order of ablation for the targets; first the PZT layer is ablated on STO substrate, and then LSMO is ablated on top of PZT.

Due to technical difficulties, multilayer films of LSMO-PZT (PZT on LSMO) and LCMO-
### Table 3.2: List of PZT-LSMO thin-film samples produced.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Substrate</th>
<th>Thickness of LSMO</th>
<th>Thickness of PZT</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZT-LSMO-TH-09</td>
<td>SrTiO₃</td>
<td>1000 Å</td>
<td>4000 Å</td>
</tr>
<tr>
<td>PZT-LSMO-TH-11</td>
<td>SrTiO₃</td>
<td>800 Å</td>
<td>4000 Å</td>
</tr>
<tr>
<td>PZT-LSMO-TH-12</td>
<td>SrTiO₃</td>
<td>500 Å</td>
<td>4000 Å</td>
</tr>
</tbody>
</table>

### Table 3.3: List of the thin-film samples studied

PZT (PZT on LCMO) could not be fabricated. We needed to grow the thin-films on 10x10 mm Niobium doped STO (which is a conducting substrate). The PZT layer had to be grown on LSMO(LCMO) using a mask, such that it would only cover the central area of about 5x5 mm on LSMO(LCMO). Also, for the growth of the manganite layer on Nb-STO another mask was needed to leave the near-edge surface of the substrate uncovered in order to setup contacts between the PZT layer and the substrate. We also needed to use lithography to pattern the films for the contacts. Therefore the rest of the samples studied in this research were provided by the technology group at Max Planck Institute in collaboration with Professor H. U. Habermeier. They are listed in table 3.3.
Chapter 4

Results

4.1 X-ray profiles

Four different heterostructures of PZT and LSMO(LCMO) samples were grown on (001) SrTiO₃ substrates. The diffraction patterns of PZT-LCMO, LCMO-PZT, PZT-LSMO and LSMO-PZT thin-films grown on SrTiO₃ substrates were determined by X-ray diffraction (XRD) performed at Max Planck Institute.

All the samples were fabricated with similar growth conditions. The PZT layer was ablated at 550°C with thickness of 2000Å and the manganite layer at 650°C with thickness of 1000Å in a pressure of 0.4 mbar Oxygen gas. The samples were finally annealed at 680°C for 30 minutes in 1 bar Oxygen atmosphere. Cooling rate affects the degree of crystallization. Annealing conditions the surface of the sample by repairing the damage caused to the film surface during deposition. When the annealed films are cooled slowly, the grains are given a longer time to re-orient themselves into their most preferred orientation, thus resulting in a more random structure. In fast cooling process, a more periodic form is achieved [4]. The samples were all produced by fast cooling after being annealed.

The X-ray wavelengths used were $K_\alpha_1=1.540\text{Å}$, $K_\alpha_2=1.544\text{Å}$ and $K_\beta=1.392\text{Å}$. As seen in the XRD patterns, the dominant wavelength is $K_\alpha$. The intensity ratio of $K_\alpha_2$ to $K_\alpha_1$ is 0.5. The double (00l) peaks for STO are due to diffraction of these two wavelengths. The resolution of the peaks increases as the angle increases. The XRD raw data confirm that the intensity of $K_\alpha_1$ peaks are twice that of $K_\alpha_2$ peaks for STO. The (00l) peaks in the diffraction patterns reveal c-axis-oriented growth of PZT and LSMO(LCMO) layers on
<table>
<thead>
<tr>
<th>Samples</th>
<th>PZT-LSMO</th>
<th>LSMO-PZT</th>
<th>PZT-LCMO</th>
<th>LCMO-PZT</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZT (Å)</td>
<td>5.747</td>
<td>5.804</td>
<td>5.754</td>
<td>5.753</td>
</tr>
<tr>
<td>LSMO(Å)</td>
<td>5.399</td>
<td>5.392</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LCMO(Å)</td>
<td></td>
<td></td>
<td>5.382</td>
<td>5.383</td>
</tr>
<tr>
<td>STO (Å)</td>
<td>3.9042</td>
<td>3.9037</td>
<td>3.9037</td>
<td>3.9047</td>
</tr>
</tbody>
</table>

Table 4.1: Average lattice parameters of PZT, LSMO and LCMO films grown on STO substrates

STO substrates. However, K\textsubscript{β} peaks of the substrate and PZT layer are visible in all of the patterns. No impurity phases are detected. In all samples, the PZT peaks appear in smaller angles than STO, and the LSMO or LCMO peaks appear in larger angles. This is due to the lattice mismatch between the three structures. Considering the heterostructures to have a pseudo-cubic structure, the lattice parameters of PZT, LSMO, LCMO and STO were determined using the Bragg law \(2d\sin\theta = n\lambda\) and the equation for \(d\) spacing between planes \(1/d^2 = h^2/a^2 + k^2/b^2 + l^2/c^2\) and are listed in table 4.1. The lattice parameters obtained are in good agreement with the corresponding bulk values.

### 4.2 TEM imaging of the thin-film samples

Although the XRD patterns confirmed that the PZT and LSMO(LCMO) layers had grown epitaxially on the STO substrates, the microstructure of the films had to be inspected carefully to detect any imperfections that could affect the conductivity and transport properties of the thin-film samples.

In multilayer perovskite oxide thin films grown on single crystal substrates, the stress induced on the films due to the misfit with the substrate and the adjacent layers affects their structure. Their lattice spacing and interatomic distances can be significantly different from the bulk equivalent. Therefore, also the electronic structure and the physical and chemical
Figure 4.1: $\theta$-2$\theta$ x-ray diffraction scan taken on LCMO-PZT thin-film
Figure 4.2: $\theta$-2$\theta$ x-ray diffraction scan taken on PZT-LCMO film
Figure 4.3: $\theta$-$2\theta$ x-ray diffraction scan taken on LSMO-PZT film
Figure 4.4: $\theta$-2$\theta$ x-ray diffraction scan taken on PZT-LSMO film
properties can be very different [20].

We observed the microstructure of our samples by using transmission electron microscopy (TEM). TEM is shining a high energy electron beam on a very thin sample, in order to obtain high resolution imaging of thin films in cross-section or plan view for microstructural and compositional analysis [21].

For our samples, TEM was carried out at the University of Antwerp in Belgium in collaboration with Prof. G. Van Tendeloo and Dr. O. I. Lebedev. We are thankful to be able to use their results in this study, before their publication.

TEM sample preparation of powder or ceramic materials is very straightforward. The samples are crushed, dispersed in alcohol and deposited on a carbon grid before introduction to the microscope. Preparing TEM samples from thin-film material on their substrates is more complex. Plan-view and also cross-section samples are prepared by first mechanically polishing the samples, followed by ion milling. The cross section samples are usually cut parallel to a cubic plane of the substrate, perpendicular to the contact plane. The plan-view samples are thinned from the substrate side. Therefore, some regions show overlap of film and substrate, while other areas contain only film material. The selected piece of material is deposited on a carbon grid and transferred to TEM for further inspection [20].

After the samples are prepared for TEM, they cannot be used for measurements. Therefore, another set of samples, identical to the ones used in TEM were produced under same experimental conditions (table 3.3), and the resistivity and magnetization measurements were performed on them.

Figure 4.5 exhibits the cross-section TEM image of the four typical samples studied. Figure 4.6 reveals the magnified interface of PZT/STO of sample PZT-LCMO. In this sample and also in PZT-LSMO, some inclusions and misfit dislocations are observable along the PZT/STO interface. For both samples, the interface looks similar. It is suggested that the dislocations and inclusions coexist, and one is the reason of another [22]. The bright contrast inclusions seen within the PZT layer indicate Ti-rich regions. In the LSMO-PZT
sample (fig 4.7), the LSMO/STO interface looks perfect. LSMO has a pseudo-cubic structure and no dislocations, amorphous or secondary phases exist. The LCMO/STO interface also does not have any inclusions, and LCMO has an orthorhombic structure [22].

The PZT/LSMO and LCMO/PZT interfaces, as seen in figure 4.8 and figure 4.9 respectively, mainly contain misfit dislocations. LSMO and LCMO have a larger lattice mismatch with PZT compared to STO. This fact is also deducible from table 4.1. As seen in figure 4.5, in LSMO-PZT, LCMO-PZT and also PZT-LSMO samples, the Ti-rich inclusions in the PZT layer form vertical columns, that extend to the PZT/LSMO(LCMO) interface. The destructive effect of these Ti-columns on the piezoelectricity of PZT layer will be explained in the next section.

4.3 Resistivity

The resistivity of the thin-film samples was measured by the four point contact technique using the Van der Pauw method [23]. Gold was deposited on four corners of the film’s surface to enhance electrical contact. As roughly shown in figure 4.10, a thin gold wire was soldered at one end to each gold spot with indium and soldered to a copper wire at the other end. The four corners were labeled A, B, C, and D. The system was evacuated to a pressure of $10^{-6}$ Torrs and the temperature was reduced to 12 K using a closed cycle Helium Cryostat. As the temperature decreased, a current in the order of microamperes was applied between the contacts A and B, and the voltage between C and D was measured. To eliminate thermoelectric effects, the direction of the current would be reversed, and another reading would be recorded and the results were averaged. The resistance $R_1$ was calculated using the average value of the two voltages and applied current. The resistance $R_2$ was calculated the same way, across A and D. The resistivity of the thin film sample was determined by substitution of resistances $R_1$ and $R_2$ into the equation [23]

$$\rho = \frac{\pi d}{ln2} \cdot \frac{(R_1 + R_2)}{2} f\left(\frac{R_1}{R_2}\right)$$  \hspace{1cm} (4.1)
Figure 4.5: Cross-section TEM image of four different thin-film samples
Figure 4.6: Cross-section TEM image of the PZT/STO intersection in PZT-LCMO thin-film
Figure 4.7: Cross-section TEM image of the LSMO/STO intersection in LSMO-PZT thin-film
Figure 4.8: Cross-section TEM image of the LSMO/PZT intersection in PZT-LSMO thin-film
Figure 4.9: Cross-section TEM image of the PZT/LCMO intersection in LCMO-PZT thin-film
where the Van der Pauw function $f$ of the argument $R_1/R_2$ satisfies

$$\cosh \left[ \frac{\ln 2}{f} \cdot \left( \frac{R_1}{R_2} \right) - 1 \right] = \frac{1}{2} \exp \left[ \frac{\ln 2}{f} \right]$$

(4.2)

After reaching the desired vacuum pressure, the cryostat was turned on. The measurement started at room temperature, and continued as the temperature decreased to 12 K. The cryostat was turned off at that temperature, and the measurement went on as the temperature slowly increased back to room temperature, in order to investigate the reproducibility of the data. For those samples whose $T_{MI}$ (Metal-Insulator transition temperature) appeared above room temperature, a heater was used to warm the sample up to 350 K, and let to cool down to 300 K again.

4.3.1 Resistance measurement on PZT-LSMO-1 and PZT-LCMO-1

Resistance measurement was carried out using the four point measurement technique on PZT-LSMO-1 and PZT-LCMO-1 samples, with doping level of $x=0.3$ for both LSMO and LCMO layers. For each sample, the PZT layer was grown on SrTiO$_3$ substrate at 550°C and the manganite layer was ablated on top of the PZT layer at 650°C in a pressure of 0.4 mbar Oxygen gas. The samples were finally annealed at 680°C for 30 minutes.

Figure 4.11 and figure 4.12 illustrate the plot of resistance versus temperature for PZT-LCMO-1 and PZT-LSMO-1 respectively. As the temperature increases, the resistance also increases because the carriers are increasingly being scattered by phonons. At high temperatures, higher than $T_c$, the carrier mean free path becomes comparable with the distance between the ions, polaron hopping dominates, and the resistance drops. This indicates a transition from a ferromagnetic metal to a paramagnetic insulator.

The Curie temperature is very close to $T_{MI}$, which is taken as the temperature of the maximum in the $\rho$-T curves.
Figure 4.10: (a) Schematic view from above of a PZT-LSMO heterostructure grown on a SrTiO$_3$ substrate with the gold wire contacts; (b) cross section view of the same sample. Gold is deposited for electrical transport measurements.
Figure 4.11: Resistance vs. Temperature for PZT-LCMO-1
Figure 4.12: Resistance vs. Temperature for PZT-LSMO-1
Figure 4.13: (a) Schematic view from above of LCMO-PZT-3 heterostructure grown on Nb doped SrTiO$_3$ substrate with the gold wire contacts to the bias voltage and Van der Pauw configuration; (b) cross section view of the same sample.

For PZT-LCMO-1, a sharper drop in resistance is observed near $T_{MI}$, compared to PZT-LSMO-1. However, $T_{MI}$ in PZT-LSMO-1 appeared at 350 K, while PZT-LCMO-1 revealed an insulator to metal transition at a lower temperature of 210 K.

### 4.3.2 Resistivity measurement on LCMO-PZT-3

Another sample studied was LCMO-PZT-3 where the LCMO layer was grown on SrTiO$_3$ substrate at 650°C and the PZT layer was ablated on top of the LCMO layer at 550°C in a pressure of 0.4 mbar Oxygen gas. The sample was finally annealed at 680°C for 30 minutes. A rough sketch of the contacts on this sample is shown in figure 4.13.
Figure 4.14: Resistivity vs. Temperature for LCMO-PZT-3
Figure 4.15: $R_1$ vs. Temperature for LCMO-PZT-3
Figure 4.16: $R_2$ vs. Temperature for LCMO-PZT-3
Figure 4.17: Injecting current vs. Temperature for LCMO-PZT-3
In order to investigate the isotropy in the sample, $R_1$ and $R_2$ were plotted versus temperature separately, as illustrated in figure 4.15 and figure 4.16 respectively. In figure 4.15 there is a slight shift towards higher temperature for the data obtained with bias voltage, below 100K and resistance drops to an order of 2000 ohms. A more significant drop in resistivity is evident in the plot of $R_2$ versus temperature. The difference in the behavior of resistivity in the two graphs suggest that there is anisotropy in the thin-film sample.

### 4.3.3 Resistivity measurement on PZT-LSMO and PZT-LCMO samples

We fabricated several thin-films of LSMO on PZT with different stochiometries for LSMO and different ablation temperatures for the LSMO and PZT targets. Among twenty two samples, three samples with doping level $x=0.35$ and thicknesses 1000Å, 800Åand 500Årevealed satisfactory conducting behavior.

The PZT-LCMO samples were provided by Max Planck Institut and their growth process was similar to the PZT-LCMO-1 sample.

The plots of resistivity versus temperature for three different thicknesses of PZT-LSMO and PZT-LCMO samples are illustrated in figure 4.18 and figure 4.19 respectively.

In both cases resistivity increases and $T_{MI}$ decreases as the thickness is reduced. In figure 4.18, for the thinnest sample, $T_{MI}$ decreases to 297K. The increase in resistivity is due to the effect of the PZT layer underneath, that causes strain and distorts the thin layer of LSMO structure ablated on top of it. The effect becomes stronger as a thinner layer of LSMO is ablated on top of PZT. All other samples grown with LSMO layers thinner than 500Åbecame insulators.

Overall thicker films have a higher $T_{MI}$ because they are less strained by the PZT surface. In the layers away from the PZT, the MnO$_6$ octahedra are in more relaxed form, electron transfer is more effective, and thus leads to a higher $T_{MI}$.

In the case of PZT-LCMO thin-films, a much sharper drop in resistivity is observed
Figure 4.18: Resistivity vs. Temperature for three different thicknesses of PZT-LSMO thin-films just below $T_{MI}$ and the transitions occur in lower temperatures compared to PZT-LSMO samples. The 100Å sample became an insulator, due to the strain effects the PZT layer had on LCMO’s structure.

4.4 Magnetization

The magnetic properties of the thin-film samples were investigated by DC magnetometry, using the Superconducting Quantum Interference Device (SQUID) detection system (model MPMS/MPMS2-Quantum Design).
Figure 4.19: Resistivity vs. Temperature for PZT-LCMO thin-film samples
DC magnetic measurements determine the equilibrium value of the magnetization in a sample. The sample is magnetized by a constant magnetic field and the magnetic moment of the sample is measured, producing a DC magnetization curve $M(H)$. In modern instruments, the moment is measured by induction techniques. Inductive measurements are performed by moving the sample relative to a set of pickup coils, either by vibration or one-shot extraction. In conventional inductive magnetometers, the voltage induced by the moving magnetic moment of the sample in a set of copper pickup coils is measured. A much more sensitive technique uses a set of superconducting pickup coils and a SQUID to measure the current induced in superconducting pickup coils, yielding high sensitivity that is independent of sample speed during extraction[24].

The magnetization $M$ depends on the magnetic anisotropy and on the relative field direction[17]. The magnetic anisotropy in these Mn oxides is uniaxial as found in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ oxides[25]. The highest magnetization along the direction parallel to the sample surface implies that this direction is closest to the easy axis. However, $T_c$ is independent of the field orientation. [17]. For each sample, field cooled (FC) and zero field cooled (ZFC) measurements were performed, and the magnetic moment was measured as a function of temperature in the presence of magnetic field with magnitude 100G and 50000G for PZT-LSMO samples. As explained in the theoretical discussion chapter, in CMR materials, the application of external magnetic field shifts the metal-insulator transition to higher temperatures, i.e increases $T_c$ and reduces the resistivity of the material. We measured the magnetization of PZT-LSMO samples in $H=50000G$ to see this effect.

4.4.1 Magnetic properties of the thin-film samples

The response of the PZT layer and the SrTiO$_3$ substrate had to be taken into account in order to observe the correct response of the Lanthanum manganite layer to the magnetic field. For this purpose, a 4000Å thick thin-film of PZT on STO was fabricated, and its magnetic moment was compared to a STO substrate in the same fields the other PZT-LSMO films
were measured. Insulating STO shows a magnetic moment which is partly diamagnetic and partly paramagnetic [26]. PZT reveals a weak paramagnetic response [27], which was also deduced by the comparison of the temperature dependency of magnetic moment of STO and STO-PZT. The magnetic moment of STO-PZT was subtracted from the moment of PZT-LSMO samples to yield the magnetic response of LSMO layer only. It was noticed that the STO-PZT film had a very weak response in H=100G, but its response became significantly strong in H=50000G. Figures 4.20 and 4.21 show the temperature dependency of the magnetization ratio for PZT-LSMO samples in 100G and 50000G fields respectively, and figure 4.22 illustrates the behavior of magnetization ratio versus temperature for the PZT-LCMO samples in H=100G.

As illustrated in fig 4.21, in a much stronger field of 50000G, the FC and ZFC measurements become significantly close, which means strong fields are required to align the moments in the samples. Although the magnetic response of STO substrate and the PZT layer were eliminated, a diamagnetic response was observed above 300K which might be due to the strong influence of the STO substrate on very thin layers of LSMO, since this effect is more pronounced in thinner films and in strong fields. Also, T_c has moved to temperature higher than 375K. In figure 4.22, the leap in the magnetization curve for the 100Å thick sample is due to very low signals and error in measurement. In both fields, thicker films reveal a higher magnetization, which means that thinner films respond less to the magnetic field. This is due to the nature of their domain walls. In thicker films a smaller field is needed to align the moments since Bloch walls are formed which force the neighboring domain moments to align.

In thick films (> 900Å) or bulk matter, lots of domains exist within which the spins are all aligned by very strong exchange forces. The domain walls are of the Bloch type walls. The spin orientation changes from one domain to that in a neighboring domain by rotating around an axis perpendicular to the plane of the wall. In thin films (< 450Å), the domain walls are of the Neel type, and the spin direction changes from a given domain to that in a
Figure 4.20: Magnetization ratio vs. Temperature for three different thicknesses of PZT-LSMO samples in H=100G
Figure 4.21: Magnetization ratio vs. Temperature for three different thicknesses of PZT-LSMO samples in H=50000G
Figure 4.22: Magnetization ratio vs. Temperature for three different thicknesses of PZT-LCMO samples with $H=100\text{G}$

neighboring domain by rotating around an axis in the plane of the wall. Bloch walls behave as three dimensional structure, while Neel walls as two dimensional. In a Bloch wall, when a magnetic field is applied, all the domains force each other to align either by each domain aligning itself with the field or by moving the domain wall. Moving a domain wall means that a domain grows as another adjacent domain shrinks. In thin films, the same thing happens, but the reinforcement from other domains is limited to immediate in-plane domains [28].
Chapter 5

Conclusions

$\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ceramic tablets were prepared using the solgel technique. Epitaxial thin films of PZT-LSMO were fabricated using the pulsed laser deposition technique, with different doping levels for $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. We could not grow LSMO thin-films at the ideal temperature (750°C) because the PZT layer would decompose at temperatures higher than 700°C. Therefore, with low doping levels of LSMO targets, the PZT-LSMO thin-films became insulators. It was observed that for $x=0.35$, the thin film samples revealed the desired metallic behavior. Therefore, $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$-$\text{La}_{0.65}\text{Sr}_{0.35}\text{MnO}_3$ thin film samples were grown on SrTiO$_3$ substrates (001) with different thicknesses of LSMO. The temperature dependency of resistivity and magnetization as a function of thickness carried out on PZT-LSMO as well as PZT-LCMO samples deduced similar results as in reference [4].

Thickness had an important role on the transport properties of the manganite layers. Thinner samples had higher resistivity and lower transition temperatures. This is because of the strain affecting the structure of the manganite layer due to its lattice mismatch with the PZT layer. Also, lower concentration of Oxygen in thinner films reduces the number of carriers within the material.

On the other hand, thicker films developed higher magnetization, or in other words responded more to the magnetic field. This is due to the difference in the nature of their domain walls. PZT had a very weak response to the magnetic field, so the magnetization data were very similar to those of STO-LSMO(LCMO) samples. However, for PZT-LSMO samples in high field, the substrate response became so strong that the saturation of magnetization was not observable.
The main aim of this study was to investigate the effect of an applied bias voltage across PZT layer as an external pressure on the manganite layer. The resistivity measurements on LCMO-PZT sample showed a drop in resistivity by applying bias voltages upto 1V. Application of bias voltage created an electric field across the PZT layer, causing mechanical distortion in its lattice structure. This affected the LCMO structure, causing contraction and alignment of Mn-O-Mn bonds that influence the electron transfer between Mn ions.

As seen in the TEM images, the defects in the growth of the PZT layer gave rise to a leakage current that increased drastically with voltage. Same measurements were performed on LSMO-PZT and PZT-LSMO heterostructures but due to growth defects in the PZT layer, this effect was not observable.

The results of this research show that in the studied heterostructures, the Lanthanum Manganite materials maintained their transport properties in the presence of PZT. LSMO seems to be a better candidate than LCMO in engineering piezoelectric and manganite heterostructures for device purposes such as miniaturized transistors and pressure sensors, due to its higher transition temperature and broader metallic phase. The thickness of the manganite layer must be taken into account, and growth conditions for such heterostructures must be optimized to yield defectless structures.
Bibliography


