# Chapter 1

**Studies on Functional Oxide Systems**

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**References**
1.1. Introduction:

Functional oxides are recognized for their stunningly rich physics and for their potential as next-generation electronic materials. Their properties include high Tc superconductivity, colossal magneto-resistance (CMR), high dielectric/ferroelectric/piezoelectric performance, multiferroicity behavior, resistive switching behavior, giant thermoelectric and magnetocaloric effects, giant ionic conduction, and catalytic behavior. Due to their intrinsic chemical and crystal similarities, functional oxides can be stacked in multilayer heterostructures exhibiting an astonishing degree of epitaxial perfection. Such artificial systems not only allow one to combine in a single device the functionalities of their individual layers, but often reveal an even wider range of emergent novel properties that can be surprisingly different from those of the single building blocks.

Functional oxides have attracted intense research interest especially from the condensed matter physics and materials science communities during the last couple of decades. A broad range of interesting functionalities such as high temperature superconductivity, CMR (anti-) ferromagnetic, (anti-) ferroelectric, piezoelectric and more recently multiferroic properties have been presented by them. The rich spectrum of materials physics involved has triggered extensive studies to understand the fundamental nature of existing systems, so as to control/design novel materials for applications. These materials are characterized by a strong interplay between the fundamental degrees of freedom, namely the electronic spin, charge, orbital and their interplay with the lattice (Figure 1.1). New states of matter have emerged as a consequence of competition/cooperation between these degrees of freedom. Second, nanoscale complexity, driven by chemical/ionic/electronic inhomogeneities is a key feature that which have large physical responses (for example, piezoelectric/dielectric responses in relaxors, CMR in doped manganites, high temperature superconductivity in cuprates), as illustrated schematically in Figure 1.2. Finally, the use of state-of-art thin film deposition tools, such as RHEED assisted pulsed laser deposition (also known as laser MBE), conventional MBE and chemical vapour deposition has driven the synthesis of atomically sharp, artificial hetero-structures that have exhibited novel physical phenomena, especially at the hetero-interfaces.
Figure 1.1: (a) A schematic of the ABO$_3$ perovskite crystal structure, with electronic structure of 3d transition metal ion shown on the right site. (b) The left side is a schematic illustration of a prototypical epitaxial oxide interface, wherein the fundamental degree of a freedom interact leading to new states of matter.
1.2. Types of Mixed Oxide Functional Materials:

1.2.1. High \( T_C \) superconductors:

Till 1987, superconductors necessarily involved cooling with liquid Helium with \( T_C \) below 77K. Maximum transition temperature reported was 23.2K in \( \text{Nb}_3 \text{Ge} \). In 1986, Allex Muller and George Bendorz discovered copper oxide based compound \( \text{La}_2-x(\text{Ba/Sr})_x\text{BaCu}_4\text{O}_z \) which exhibited Superconductivity at 35K [1]. This \( T_C \) was highest at that time for superconductors and material was named as High Temperature Superconductor (HTSC).

Paul Chu of Houston University, USA discovered a mixed oxide superconductor \( \text{YBa}_2\text{Cu}_3\text{O}_z \) known as 123 superconductor with \( T_C \sim 90\text{K} \) (1987) [2]. This \( T_C \) is greater than boiling temperature of liquid nitrogen (77.4K). In 1988, Japanese researchers H. Maeda and his co-workers synthesized for the first time a Bi based high temperature superconductor with \( T \sim 105\text{K} \) and zero resistance at around 85K [3]. Following this discovery Z. Z. Sheng and A. Hermann discovered a new Ti based system Ti-Ba-Ca-Cu-O (TiBCCO) with a superconducting transition at about 125K and zero resistance at about 110K [4]. In 1992, Record value of \( T_C \sim 147-160\text{K} \) in Hg based copper based (Hg-Ba-Ca-Cu-O) superconductor synthesized under high pressure were reported [5]. Figure 1.2 shows the pictorial representation of the rise in \( T_C \) in various oxide superconductors.

1.2.2. CMR Manganites:

The magnetoresistance (MR) as large as \( \sim 100\% \) was observed in manganites [6-8]. This was an extraordinarily large MR as compared to previously observed Giant magneto resistance (GMR). Therefore, to give emphasis to the strength of MR in these compounds, a new term called “colossal magnetoresistance (CMR)” was coined [6]. The origin of MR in manganites is quite different than the origin of other forms of MR discussed above. The CMR is an intrinsic property of crystal structure and has its origin in the spin disorder of conduction electron, which can be suppressed by the application of the magnetic field resulting in large MR [6-8].
Figure 1.2: The pictorial presentation of the rise in $T_c$ in various oxide superconductors.

The discovery of CMR in manganites and its relation to various electronic and magnetic properties recharged the research interest in these compounds. Since manganites appear promising candidates both from basic research and applications point of view, a major fraction of materials scientist has contributed to the better understanding of these materials. This thesis is dedicated to the understanding of various physical properties of complex manganite systems and some efforts to evaluate the application potentiality of them.

1.2.2.1. Doping studies in Manganites:

In the mixed valent manganese, one can modify the material properties by variety of ways, out of which, doping effects are one of the major method for achieving desired
properties in bulk as well as thin film forms. The doping of metal ions in $\text{ABO}_3$ structured manganites can be achieved by either hole doping or electron doping [9, 10].

**Doping at La (A) site:**

It is well reported and understood fact that doping of divalent cations (A) at A site of the type La$_{1-x}$A$_x$MnO$_3$ modifies the structural, transport and magnetotransport properties of these compounds which has been found to depend on various parameters such as average A site cation radius (ionic radii), size variance ($\sigma^2$), tolerance factor (t), etc. The amount of doping x, also decides the structural, transport and magnetic phase modification [11, 12].

The doping of metal ions at A-site in the antiferromagnetic insulating LaMnO$_3$, PrMnO$_3$, NdMnO$_3$, etc, results in the modifications in their transport and magnetic behaviors [13]. The hole doping at A-site results in the formation of Mn$^{4+}$ ions at the cost of Mn$^{3+}$ ions, thereby suppressing the cooperative Jahn-Teller distortion resulting in the insulator-metal transition in cocomitment with ferromagnetic-paramagnetic transition along with the concomitant suppression in resistance under applied field [14].

**Doping at Mn (B) site:**

Several reports exist on the effect of Mn site doping in mixed valent manganites on transport, magnetotransport and magnetic behavior of these compounds [15, 16]. It is reported that the substitution of non-magnetic Zn$^{2+}$, Al$^{3+}$, In$^{3+}$, Ga$^{3+}$, Ti$^{4+}$, Gr$^{4+}$ etc., and magnetic Fe$^{3+}$, Ru$^{3+}$,Mo$^{6+}$, etc. modify the transport and magneto transport by way of affecting the Mn-O-Mn mode angles and hoping of charge carriers in Mn-site doped mixed valence manganites [17, 18]. Unlike the systematic effect of A-site doping, on the magnetic and transport properties of manganites, the substitution at Mn site, lead to a mixture of effects, caused by changes such as, crystal structure, charge carrier concentration, and more importantly the interaction between Mn and the substitutional ion. It is interesting to studies on the effect of the change in the distance between Mn ions in the manganites as well as the Mn$^{3+}$/Mn$^{4+}$ ratio and to introduce disorder in the Mn
lattice. This can be done by the substitution of magnetic/non-magnetic ions at the Mn site.

1.2.2.2. Salient Features of mixed valent Manganites:

Ionic Radius ($r_A$):

Ionic radius $r_{ion}$ is a measure of the size of an ion in a crystal lattice. It is measured either in picometers (pm) or Å with $1\,\text{Å} = 100\,\text{pm}$. X-ray crystallography can readily give the length of side of the unit cell of a crystal, but it is much more difficult to distinguish between boundaries between two ions. The ionic radius is not a fixed property of a given ion, but varies with co-ordination number, spin state, and other parameters. Nevertheless, ionic radius values are sufficiently transferable to allow periodic trends to be recognized.

Ionic size (from the same ion) also increases with increasing coordination number, and an ion in a high-spin state will be larger than the same ion in a low-spin state. Anions (negative charged ions) are mostly larger than cations (positive charged ions). In general, ionic radius decreases with increases positive charge and increases with increasing negative charge.

Tolerance Factor ($t$):

Perovskite based structures occasionally show lattice distortion as modification from the Cubic structure due to doping. One of the possible origin in the lattice distortion is the deformation of the MnO$_6$ Octahedron arising from the Jahn-Teller effect that is inherent to high-spin ($S=2$) Mn$^{3+}$ with double degeneracy of e$_g$ orbitals. Another lattice distortion arises from the MnO$_6$ Octahedra in the perovskite structure, forming rhombohedral or orthorhombic lattices. In these distorted perovskite, the MnO$_6$ octahedra show alternate buckling and tilting of the structure [19, 20, 21].

Such a lattice distortion and stability of the perovskite AMnO$_3$ [where, A=RE$_{1-x}$AE$_x$] structure is governed by the Goldsmith tolerance factor ‘t’ which measures the deviations from perfect cubic symmetry ($t=1$) and is defined as,

$$t = \frac{d_{A-0}}{\sqrt{2}d_{Mn-0}} = \frac{\langle r_A \rangle + r_0}{\sqrt{2}(\langle r_{Mn} \rangle + r_0)}$$
where, \(d_{A-O}\) is the distance between the A-site, wherein the lanthanide or alkaline earth ions are located, to the nearest oxygen ion i.e., \((<r_A>+ r_0)\) and \(d_{mn-o}\) is the shortest distance which are calculated from the sum of the ionic radii for 12 coordinated A-site cations and 6 coordinated Mn ions [22]. However, the tolerance factor is dependent on both temperature and pressure. A-O bond has a larger thermal expansion coefficient and is normally more compressible than the Mn-O bond of an AMnO\(_3\) perovskite. Since, for an undistorted cube the Mn-O-Mn bond is straight \((d_{A-O} = \sqrt{2}d_{Mn-o})\) that makes \(t=1\), which is known as an ideal perovskite or the perfect cubic closely packed structure.

Sometimes, A-ions are too small to fill the space in the cubic centers and due to that the oxygen tend to move towards that center, reducing \(d_{A-O}\) [\(d_{Mn-o}\) also changes at the same time.] For this reason, the tolerance factor becomes smaller than one, \(t<1\), as the A-site radius is reduced, and the Mn-O-Mn angle gets smaller than 180°. So, that for \(t<1\), the cubic structure transforms to the orthorhombic structure, which leads to deviation in the Mn-O-Mn bond angle from 180°, resulting in the distortion in MnO\(_6\) Octahedral.

**Figure 1.3:** Distortion of MnO\(_6\)Octahedra

The hopping amplitude for carriers to move from Mn to Mn naturally decreases as \(\theta\) reduces from 180° [23]. Thus, as the tolerance factor decreases, the tendencies of charge localization increases due to the reduction in the carrier mobility. This has been
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observed experimentally and proved theoretically in doped manganites. For the ideal cubic structure, \( t=1 \), but the stable perovskite structure occurs over a range of \( 0.8 < t < 1.1 \). For lower values of ‘\( t \)’, the cubic structure is distorted to optimize the A-O bond lengths. For values of ‘\( t \)’ between 0.75 and 0.9, the MnO\(_6\) Octahedra tilts cooperatively to give an enlarged orthorhombic unit cell. This distortion (reduction of Mn-O-Mn angle from 180\(^\circ\)), affects the conduction band which appears as hybridization of the p-level of the oxygen and the \( e_g \) levels of the Mn. The orbitals overlap decreases with decrease in tolerance factor and the relation between the bandwidth \( W \) and \( \theta \) has been estimated as, \( W \propto \cos^2 \theta \) [24]. Zhou et al. (1999) [25] have investigated the influence of the tolerance factor ‘\( t \)’ and differences in the ionic radii of the A-site cations on curie temperature, resistivity, coercive field and MR. They observed that large differences between the ionic radii of the A-site cations are harmful for the magneto transport properties. Undoped LaMnO\(_3\) is an anti / Ferro / magnetic charge transfer insulator, wherein Mn is in +3 valence state only. If any divalent atom (such as Ca, Sr, Ba, Pb, etc.) is doped at the La site, for instance La\(_{1-x}\)Ca\(_x\)MnO\(_3\), it converts Mn\(^{3+}\) to Mn\(^{4+}\) state in equal proportion to the doping concentration. This is equivalent to the hole-doping in the system. The hole doping illustrates several dramatic changes in electric and magnetic properties from the parent LaMnO\(_3\) compound, such as insulator-metal transition, Paramagnetic-Ferromagnetic transition, CMR, charge-ordered state, phase separation, etc. In the light of these rich physical properties, hole-doped LaMnO\(_3\) has a potential for promising device applications such as magnetic sensors, magnetic valves, read head technology, bolometric applications etc. However, these properties strongly depend on ionic radii of the MnO\(_6\) Octahedra. Zener’s double exchange model and Jahn-Teller’s distortions of MnO\(_6\) Octahedra attempt to explain the diversity of the electrical and magnetic properties of doped LaMnO\(_3\).

**Size variance at A – site:**

There are various cations which are occupying A-site in ABO\(_3\) perovskite structure and possess certain mismatch in their ionic sizes. The size variance is significant when there is multiple cation substitution at A-site. A factor, which quantifies the extent of mismatch, is called the size-variance \( (\sigma^2) \) [26, 27] and is given by relation,
where, \( x_i \) is the fractional occupancy and \( r_i \) is the ionic radius of \( i^{th} \) cation at A-site \( <r_A> \) is the average A-site cation radius. A detailed study on the effect of size variance on the electrical and magnetic properties by Martinez et al \[28\]. He studied the manganite systems having different size-variance but constant tolerance factor and carrier density. There are consistent reports of decrease in \( T_C \) and \( T_P \) with increasing size disorder. The large size variance cause local structural distortion via random displacement of oxygen anions and therefore, decreasing the ZDE interaction. A model for random displacement of oxygen ions was proposed on the evidences of detailed neutron diffraction study.

**Crystal Field Splitting and Jahn-Teller distortion:**

The physical properties of doped perovskite manganites (LaMnO\(_3\)) involve a complex interplay between the spin, charge and orbital degree of freedom, which strongly depends on the site of the occupancy of the d-orbitals. In the cubic environment of the MnO\(_6\) octahedron, hybridization and electrostatic interaction with oxygen 2p electrons will create a crystal field for the outer 3d electrons in Mn\(^{3+}\). The d-orbitals are five-fold degenerate, and so this crystal field lifts the five-fold degeneracy of d-electrons, which are present in free Mn\(^{3+}\) ions by splitting the energy level and forming three lower-lying triple degenerate t\(_{2g}\) state, and two higher doublet of e\(_g\) state \[29\]. The low-lying t\(_{2g}\) triplet consists of the d\(_{xy}\), d\(_{yz}\) and d\(_{zx}\) orbitals. The lobes of these orbitals had been oriented between the O\(^{2-}\) ions. The higher energy e\(_g\) doublet consists of the d\(_{x^2-y^2}\) and d\(_{3z^2-r^2}\) orbitals. Their lobes point in the direction of the O\(^{2-}\) ions, which raises their energy because of the stronger cumblic repulsion of the MnO\(_6\) octahedra in doped LaMnO\(_3\).

The energy difference due to crystal field splitting (CFS) between t\(_{2g}\) and e\(_g\) levels for LaMnO\(_3\) is \(-1.5\text{ev}\) \[30\]. Due to strong inter-atomic Hund’s coupling, all electrons of Mn\(^{3+}\) and Mn\(^{4+}\) are aligned parallel in the ground state, leading to a total spin of \( S=2 \) in Mn\(^{3+}\) and \( S=3/2 \) in Mn\(^{4+}\), respectively. All the three outer electrons of Mn\(^{4+}\) occupy the t\(_{2g}\) sites, while the extra electron of Mn\(^{3+}\) is situated in one of the e\(_g\) levels. The t\(_{2g}\) orbitals overlap relatively little with the p-orbitals of nearby oxygen atoms. Thus, t\(_{2g}\) electrons can be considered as forming a localized core spin (\( S=3/2 \)). On the other hand, e\(_g\) orbitals
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overlap with the p-orbitals of neighboring oxygen atoms. Although the \( e_g \) electrons are strongly coupled ferromagnetically to the \( t_{2g} \) spin, and can hop between different Mn ions. Thus the partial degeneracy of the 3d orbitals has been removed by CFS. The lattice motion usually breaks the remaining degeneracy. In this distortion the energy of Mn\(^{4+}\) remains unchanged but the energy of Mn\(^{3+}\) is lowered.

The oxygen ions surrounding the Mn\(^{3+}\) ions can slightly readjust their locations, and create an asymmetry between the different directions, which can effectively, removes the degeneracy. This lifting of degeneracy due to the orbital-lattice interaction is pronounced as the Jahn-Teller cooperative effect. This effect tends to occur spontaneously because the energy penalization of the lattice distortion grows as the square of that distortion, while the energy splitting of the other degenerate orbitals is linear.

![Jahn-Teller distortion](image)

Figure 1.4: Jahn-Teller distortion

Due to this reason, it is energetically favorable to spontaneously distort the lattice, thus removing the degeneracy. Thus, the Jahn-Teller distortion is rather effective in the
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lightly doped manganites, i.e., with a large concentration, 1-x of Mn\(^{3+}\) site to another. On increasing the Mn\(^{4+}\) content, the Jahn-Teller distortion is reduced and the stabilization of the 3z\(^2\)-r\(^2\)e\(_g\) orbitals become less effective. Nevertheless, in a large number of manganites, the eg orbitals of two types, 3z\(^2\)-r\(^2\) and x\(^2\)-y\(^2\) are not occupied by the e\(_g\) electrons of Mn\(^{3+}\) at random and thus an orbital order is achieved.

However, Mn\(^{4+}\) or Mn\(^{2+}\) ion is not a Jahn-Teller ion because there is no occupancy of an electron in the e\(_g\) level, or there are two electrons in the e\(_g\) levels, respectively; and hence for these ions, the MnO\(_6\) octahedra is not distorted. LaMnO\(_3\) is an orbital ordered antiferromagnetic insulator due to the presence of all Mn\(^{3+}\) ions. This compound undergoes anti ferro magnetic transition at 120K.

In La\(_{1-x}\)A\(_x\)MnO\(_3\) compounds, due to hole doping, the static Jahn-Teller distortion decreases with an increase in the doping level due to a decrease in the number of Mn\(^{3+}\) species. It has been observed that in a certain range of doping (x ~ 0.2-0.4), the ground state becomes Ferro magnetic. This is recognized as the creation of Mn\(^{4+}\) ions that tends to delocalize the e\(_g\) electron of Mn\(^{3+}\) ion under the influence of double exchange interaction. Thus, in this range of doping, a paramagnetic to ferromagnetic phase transition takes place, which is accompanied by a sharp drop in resistivity.

1.2.2.3. Zener Double Exchange Mechanism:

In the mixed valent manganites, the conduction process between two Mn ions was explained by C. Zener [31, 32] and therefore, called “Zener-Double Exchange (ZDE)”. The knowledge of the electronic structure of these mixed valent manganites materials, gives us the necessary insight for understanding the ZDE conduction in manganites. The ZDE is responsible for the transformation from paramagnetic insulating state to ferromagnetic metallic state. The conduction takes place between the adjacent Mn\(^{3+}\) and Mn\(^{4+}\) ions. Mn\(^{3+}\) has an e\(_g\) electron on d\(_{z^2}\) orbital whereas Mn\(^{4+}\) has vacant e\(_g\) electron. The e\(_g\) electron of Mn\(^{3+}\) experiences a net potential difference with respect to vacant site of Mn\(^{4+}\) and hence it has a tendency to hop to the vacant site.

This hopping process of electron is possible only due to the ligand oxygen ions. Oxygen has two 2p, spin up and spin down electrons in its outermost orbital. The e\(_g\)
electron of Mn^{3+} hops to spin up orbital of oxygen ion. According to Hund’s rule, an orbital can occupy only one electron, the oxygen ion accepts the $e_g$ electron of Mn^{3+} ion by giving its own spin up electron to Mn^{4+} ion. Since, the conduction process was hypothesized by C. Zener, who explained the conduction of electron between two Mn ions takes via ligand oxygen ion and therefore this process was termed as ‘Zener Double Exchange’. The itinerant $e_g$ electron retains its spin up state due to Hund’s rule coupling. An important aspect for the ZDE is that it is spin-polarized conduction and occurs only when the spins of the adjacent Mn ions are aligned parallel or are ferro magnetically ordered.

On any deviation from this magnetic order between the spins of adjacent Mn ions, the ZDE decreases and after certain critical spin disorder, ZDE vanishes. For instance, if the spins of adjacent Mn ions are in antiferromagnetic order, there will be no ZDE. In such a case super exchange will be favored. The probability of electron transfer is maximum when all spins are aligned parallel and favored at low temperature due to a decrease in thermal fluctuation of spins at temperatures (T<Tc). As the temperature is increased, the alignment of spins is disturbed, which causes a simultaneous decrease in the hopping probability of electrons, enhancing the resistivity. However, the application of the magnetic field can align spins, which results in a decrease in resistivity. Thereafter a maximum change in resistivity due to external applied magnetic field is observed near Tc.
Figure 1.5: Zener Double Exchange Mechanism

The relation of ZDE with spin magnetic order of Mn ions was given by Anderson and Hasegawa [33] in 1955, who had defined the transfer integral depending on the angle between the spin moments of adjacent Mn ions. The transfer integral is created when spins are parallel and annihilated for antiparallel spins. In case of the strong Hund’s rule coupling, coupling constant $J_\text{H}$ tends to $\alpha$ and the hopping amplitude of electron is defined by the transfer integral, $t_{ij}$, which is given by,

$$t_{ij} = t_0 \left[ \cos \theta_{ij} / 2 \right]$$

where $\theta_{ij}$ is the angle between the neighboring spins. The transfer electron and Hamiltonian explains the concomitant occurrence of $T_p$ and $T_C$. Also resistivity may be related to Curie temperature $T_C$, which is given by the relation,

$$\rho = \left( ah / x_e^2 \right) \left( T / T_C \right)$$
where, x is the fraction of Mn$^{4+}$ and a is lattice parameter. This relation indicates concomitant occurrence of $T_c$ and insulator-metal transition.

### 1.2.3. Introduction to Multiferroics:

Electricity and magnetism were combined into one common discipline in the 19th century, culminating in the Maxwell equations. But electric and magnetic ordering are mostly separately in solids. The electric charges of electrons and ions are responsible for the charge effects, whereas electron spins responsible for magnetic properties.

Multiferroic is Phenomena where-linear coupling between magnetic and electric fields which would cause, a magnetization proportional to an electric field. (i.e., the appearance of magnetization $M$ on an electric field $E$, or the inverse effect of electric polarization $P$ generated by the application of magnetic field $H$). The coupling between electric and magnetic field is known as magneto electric (ME) effect.

\[
\text{ME effect} = \frac{\text{electrical}}{\text{mechanical}} \times \frac{\text{mechanical}}{\text{magnetic}}
\]

By definition, a single phase Multiferroic [34] is a material that simultaneously possesses two or more of called ‘ferroic’ order parameters-ferroelectricity, ferromagnetism, ferroelasticity and ferrotoroidocity. Magnetoelectric coupling typically refers to the linear magneto electric effect or the induction of magnetization by an electric field or polarization by a magnetic field [35].
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**Figure 1.6:** The coupling between charge and spin ordering.

### 1.2.3.1. Types of Ferroicity:

**Ferroelectric** materials possess a spontaneous polarization that is stable and can be switched hysteretically by an applied electric field; antiferroelectric materials possess ordered dipole moments that cancel each other completely within each crystallographic unit cell.

**Ferromagnetic** materials possess a spontaneous magnetization that is stable and can be switched hysteretically by an applied magnetic field; antiferromagnetic materials possess ordered magnetic moments that cancel each other completely within each magnetic unit cell.

**Ferroelastic** materials display a spontaneous deformation that is stable and can be switched hysteretically by an applied stress.

**Ferrotoroidic** materials possess a stable and spontaneous order parameter that is taken to be the curl of a magnetization or polarization.
Multiferroism describes materials in which two or all three of the properties ferroelectricity, ferromagnetism, and ferroelasticity occur in the same phase. The overlap required of ferroic materials to be classified as Multiferroics is shown schematically in figure 1.8(a). Only a small subgroup of all magnetically and electrically polarizable materials are either ferromagnetic or ferroelectric and few are still simultaneously exhibit both order parameters. In these select materials, there is the possibility that electric fields cannot only reorient the polarization but also control magnetization; similarly, a magnetic field can change electric polarization. This functionality offers an extra degree of freedom – called magnetoelectrics [Figure 1.8(b)].
Figure 1.8: (a) Relationship between Multiferroics and magneto electric materials (from [3]). (b) Different types of coupling present in materials.

1.2.3.2. Magnetoelectric Multiferroics:

By definition, magneto / electric Multiferroics must be simultaneously both ferromagnetic and ferroelectric [36].

Figure 1.9: ABO$_3$ crystal structure

Magnetoelectric multiferroics can be understood by investigating a number of factors including symmetry, electronic properties, and chemistry. It has been proposed that multiferroic properties can be governed by chemically controlling the functionality

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on a site-by-site basis. Many researchers have focused on model systems, such as the perovskites with chemical formula ABO$_3$, as a pathway for the creation of multiferroics behavior. Single phase multiferroism has been identified in only a few perovskite oxides and is typically achieved by making use of the stereochemical activity of the lone pair on large (A-site) cations to provide ferroelectricity while retaining magnetism on the smaller (B-site) cations.

Multiferroic materials lie in the possibility of strong magnetoelectric coupling and the possibility to create new functionalities in materials. The magneto electric effect in its most general definition delineates the coupling between electric and magnetic fields in matter. A better understanding of magneto electric coupling arises from expansion of the free energy functional, i.e.

$$F(E,H) = m^S_i H_i - \frac{1}{2} \varepsilon_{ij} E_i E_j - \frac{1}{2} \mu_{ij} H_i H_j - \frac{1}{2} \beta_{ijk} E_i H_j H_k - \frac{1}{2} \gamma_{ijk} H_i E_j E_k - \cdots$$

with $E$ and $H$ as the electric field and magnetic field respectively. Differentiation leads to the constitutive order parameters polarization

$$P_i(E,H) = -\frac{\partial F}{\partial E_i} = m^S_i + \varepsilon_{ij} E_j + \alpha_{ij} H_j + \beta_{ijk} H_j H_k + \gamma_{ijk} H_i E_j + \cdots$$

and magnetization,

$$M_i(E,H) = -\frac{\partial F}{\partial H_i} = m^S_i + \mu_{ij} H_j + \alpha_{ij} E_i + \beta_{ijk} E_i E_j + \gamma_{ijk} E_j E_k + \cdots$$

where $\varepsilon$ and $\mu$ are the electric and magnetic susceptibilities, respectively and $\alpha$ represents the induction of polarization by a magnetic field or magnetization by electric field and is known as the linear magneto electric effect. It should be noted that higher order magneto electric effects such as $\beta$ and $\gamma$ are possible, however, they are much smaller in magnitude then the lower order terms. Furthermore, the magneto electric response is limited by the
relation $\alpha_i^2 < \chi_i^s \chi_i^m$ where $\chi^s$ and $\chi^m$ are the electric and magnetic susceptibilities, respectively. This means that the magneto electric effect can only be large in ferroelectric and/or ferromagnetic materials.

1.2.3.3. Types of Multiferroics:

The origin of magnetism is basically the same in all magnets: it is the presence of localized electrons, mostly in the partially filled $d$ or $f$ shells of transition-metal or rare-earth ions, which have a corresponding localized spin, or magnetic moment. Exchange interactions between the localized moments lead to magnetic order. The situation with ferroelectrics is quite different. There are several different microscopic sources of ferroelectricity, and accordingly one can have different types of Multiferroics.

Generally there are two groups of multiferroics. The first group, which can be called type-I Multiferroics, contains those materials in which ferroelectricity and magnetism have different sources and appear largely independently of one another, though there is some coupling between them. In these materials, ferroelectricity typically appears at higher temperatures than magnetism, and the spontaneous polarization $P$ is often rather large (of order $10 - 100 \mu C/cm^2$).

The second group, which we can call type-II Multiferroics, is the materials [37, 38], in which magnetism causes ferroelectricity, implying a strong coupling between the two. However, the polarization in these materials is usually much smaller ($\sim 10^{-2} \mu C/cm^2$).

[i] Type-I Multiferroics:

Type-I multiferroics are “older” and more numerous. These are good ferroelectrics, and the critical temperatures of the magnetic and ferroelectric transitions can be well above room temperature. The coupling between magnetism and ferroelectricity in these materials is weak. Type I Multiferroics have four major subclasses.

Multiferroic perovskites:
There are many magnetic materials among perovskites [39], and also many ferroelectrics [40]. Ferroelectrics are the perovskites like BaTiO$_3$ or Pb(ZrTi)O$_3$ (PZT). But comparing these materials demonstrates that there seems to be mutual exclusion of magnetism and ferroelectricity in perovskites: there is practically no overlap of these two material of a transition metal, practically all ferroelectric perovskites contain transition metal ions with an empty $d$ shell, such as Ti$^{4+}$, Ta$^{5+}$, W$^{6+}$. Ferroelectricity in these systems is caused by the off-center shifts of the transition metal ion, which forms strong covalent bonds with one (or three) oxygens, using their empty $d$ states. The presence of real $d$ electrons in $d^n$ configurations of magnetic transition metals suppresses this process, preventing ferroelectricity in magnetic perovskites. In most cases a magnetic $d^n$ ion is stable in the center of its O$_6$ octahedra. One possible way that, there may be making”mixed” perovskites with $d^0$ and $d^n$ ions. Unfortunately the coupling of magnetic and ferroelectric subsystems in mixed perovskites is rather weak.

**Figure 1.10:** In “mixed” perovskites with ferroelectrically active $d^0$ ions (green circles) and magnetic $d^n$ ions (red), shifts of $d0$ ions from the centers of O$_6$ octahedra (yellow plaquettes) lead to polarization (green arrows), coexisting with magnetic order (red arrows).

**Ferroelectricity due to lone pairs:**

In BiFeO$_3$, and PbVO$_3$, Bi$^{3+}$ and Pb$^{2+}$ play the major role in the origin of ferroelectricity. In these ions, there are two outer 6s electrons that do not participate in chemical bonds. They are called lone pairs. They have a high polarizability—the condition required for ferroelectricity. The origin of ferroelectricity in these compounds
by ordering of these lone pairs (with certain admixture of \( p \) orbitals) in one direction [Figure: 1.11].

**Figure 1.11:** In materials like BiFeO\(_3\) and PbVO\(_3\), the ordering of lone pairs (yellow "lobes") of Bi\(^{3+}\) and Pb\(^{2+}\) ions (orange), contributes to the polarization (green arrow).

**Ferroelectricity due to charge ordering:**

One more mechanism for multiferroics that can lead to ferroelectricity is charge ordering. Such an order observed in transition metal compounds, especially those formally containing transition metal ions with different valence. If, after charge ordering, both sites and bonds turn out to be inequivalent, this can lead to ferroelectricity [Figure: 1.12] [41]. But more often we observed that there exist ions with different charge (often because they are different elements), but on top of that there occurs dimerization. TbMn\(_2\)O\(_5\) belongs to this class [38], as does the newly discovered multiferroic Ca\(_3\)CoMnO\(_6\) [42].

Another similar possibility is when the bonds are inequivalent because of the structure of the material, the site-centered charge order appearing on top of that. This is the case in the multiferroic LuFe\(_2\)O\(_4\) [43], which shows improper ferroelectricity below 330 K. The arrangements of the electrons arise from the charge frustration on a triangular lattice with the mixed valence state of Fe\(^{2+}\) and Fe\(^{3+}\) ions. Ferrimagnetic behavior occurs

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Studies on Functional Oxide Systems below 240 K. In addition, charge ordered ferroelectricity is suggested in Fe$_3$O$_4$ and (Pr, Ca) MnO$_3$ \cite{44}.

![Figure 1.12](image)

**Figure 1.12:** (a) Site-centered charge ordering in half-doped manganites like Pr$_{0.5}$Ca$_{0.5}$MnO$_3$, (b) bond-centred ordering, (c) combined ordering, giving ferroelectricity.

**Geometric ferroelectricity:**

Ferroelectricity in YMnO$_3$ has nothing to do with the magnetic Mn$^{3+}$, but is caused by the tilting of the practically rigid MnO$_2$ block. This tilting occurs just to provide closer packing, and as a result the oxygen ions move closer to the rather small Y ions [Figure: 1.14].

The “geometric” mechanism of generation of polarization in YMnO$_3$ \cite{45} describes the tilting of a rigid MnO$_2$ block with a magnetic Mn remaining at the center. Because of the tilting, the Y-O bonds form dipoles (green arrows), and there appears two “down” dipoles per one “up” dipole so that the system becomes ferroelectric and multiferroic when Mn spins order at lower temperatures.
Figure 1.13: The “geometric” mechanism of generation of polarization in YMnO$_3$

[ii] Type-II Multiferroics:

Magnetic Multiferroics:

Type-II Multiferroics in which ferroelectricity exists only in a magnetically ordered state and is caused by a particular type of magnetism [37, 38]. In TbMnO$_3$ magnetic ordering appears at $T_{N1} = 41$K, and at a lower temperature, $T_{N2} = 28$ K, the magnetic structure changes and electric polarization appears. In TbMnO$_3$ magnetic field can strongly influence the electric polarization: e.g. In TbMnO$_3$ the polarization rotates (or “flops”) by 90 degrees when a critical magnetic field is applied along a certain direction [37]. In TbMn$_2$O$_5$ [38] the influence of an external field is even stronger: the polarization changes sign with field, and a field alternating between $+1.5$ and $-1.5$ Tesla leads to corresponding oscillations in the polarization. Since the discovery of these materials, a number of other type-II multiferroics with strong magnetoelectric coupling have been discovered and studied.

Mechanism point of view of multiferroic behavior, type-II multiferroics divided into two groups: those in which ferroelectricity is caused by a particular type of magnetic spiral and those in which ferroelectricity appears even for collinear magnetic structures.
Spiral type-II Multiferroics:

Most of the type-II Multiferroics belong to this subgroup. Ferroelectricity appears in conjunction with a spiraling magnetic phase, mostly of the cycloid type. This is the case in TbMnO$_3$, NiV$_2$O$_6$, and MnWO$_4$. In TbMnO$_3$ below $T_{N1} = 41$ K the magnetic structure is a sinusoidal spin-density wave, where all spins point in one direction, but the size of the local moment varies periodically in space [Figure: 1.14]. Below $T_{N2} = 28$ K, the Mn spins order so that the tip of the spins sweep out a cycloid [Figure: 1.14]. Katsura, Nagaosa, and Balatsky [46], using a microscopic approach, and Mostovoy [47], using a phenomenological approach, showed that in a cycloidal spiral a polarization $P$, appears, that is given by:

$$P \sim r_{ij} \times [S_i \times S_j] \sim [Q \times e]$$

where $r_{ij}$ is the vector connecting neighboring spins $S_i$ and $S_j$, $Q$ is the wave vector describing the spiral, and $e \sim [S_i \times S_j]$ is the spin rotation axis [Figure. 1.14]. The microscopic mechanism of this polarization is connected with the spin-orbit interaction [46, 48].

(a) Sinusoidal spin density wave, in which spins point along one direction but vary in magnitude. (b) The cycloidal spiral with the wave vector $Q = Q_x$ and spins rotating in the (x, z)-plane. (c) Figure called “proper screw” the spins rotate in a plane perpendicular to $Q$. 

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Magnetic frustration is the source of spiral magnetic ordering in an insulator. So, type-II Multiferroics are usually found in frustrated systems. From these ideas and above Eq., one can understand the role of a magnetic field. The effect of an external field $H$ on a cycloid is analogous to the well-known spin-flop transition in an antiferromagnet: in a magnetic field, the sublattice moments prefer to lie in a plane perpendicular to the field so they can’t in the direction of the field with less cost in exchange energy between neighboring spins.

Consequently, when a magnetic field forces the plane of a magnetic cycloid to flop by 90 degrees, the polarization $P$ also flops: according to Eq., $P$ lies in the plane of spins but perpendicular to $Q$. One word of caution about Eq.: Its derivation assumes particular crystal symmetry, such as simple cubic or tetragonal. In these cases, Eq. is indeed valid, and, for example, the polarization of a proper screw indicated in Figure 1.14, in which spins rotate in the plane perpendicular to the wave vector of a spiral $Q$, would be zero.
However, as recently shown by Arima [49], this may not be the case for other symmetries, in which case there may appear a nonzero polarization even for a proper screw spiral. Experimentally, this was observed in RbFe(MoO₄)₃ [50] and more recently in other layered triangular systems such as CuFeO₂ and ACrO₂ (A= Cu, Ag, Li, Na) [51].

**Type-II Multiferroics with collinear magnetic structures:**

The second group of magnetically driven ferroelectrics are those in which ferroelectricity appears in collinear magnetic structures - that is all magnetic moments aligned along a particular axis - without the necessary involvement of the spin-orbit interaction. Polarization can appear in these materials as a consequence of exchange striction because the magnetic coupling varies with the atomic positions. The simplest example is Ca₃CoMnO₆ [42]. Ca₃CoMnO₆ consists of one-dimensional chains of alternating Co²⁺ and Mn⁴⁺ ions. At high temperature the distances between the ions along the chain are the same, the chain has inversion symmetry, and polarization is absent.

In Ca₃CoMnO₆, exchange striction arises from transition metal ions with a different valence (Co²⁺ and Mn⁴⁺) and get the same effect even for identical magnetic ions, when one takes into account that the exchange in transition metal oxides usually occurs via intermediate oxygens and depends on both the distance between the metal ions and the metal-oxygen metal bond angle.

**1.3. Recent investigation and application of functional oxides:**

In RMnO₃ perovskites where R is a small rare earth, the Mn magnetic order in the basal plane is of the type ↑↑↓↓↓. As proposed by Sergienko, Sen, and Dagotto [52], exchange striction in this case can cause the oxygen ions to shift perpendicular to the Mn-Mn bonds, which produces a polarization along the direction of the shift. This effect was observed in [53], although its value was much less than estimated theoretically [52, 54].

One more mechanism giving ferroelectricity even in a collinear magnet is the “electronic” ferroelectricity in frustrated magnets [55]. Oxide materials have become high-tech functional materials beyond their traditional role as dielectrics. They show a
rich variety of complex emergent behaviors, such as memristive effects, catalytic activity and complex multiferroic effect. At first glance ferroic effects, ionically driven modifications, and catalytic activity appear to play out in separate spheres: Ferroelectricity, ferromagnetism, -elasticity and toroidicity are properties of the ideal bulk material, ionics depend vitally on atomic scale defects, while catalytic activity is confined to surfaces. Consequently, the scientific exchange between the respective communities is limited. However, at closer examination ionics, ferroics, and catalytic activity are intimately linked. Grain boundaries, impurities and structural defects strongly influence the dynamics of ferroic domains, catalytic activity often relies on atomic scale defects, such as oxygen vacancies, and can at the same time lead to the generation of new defects. At the same time the dynamics of defects are strongly influenced by local electric fields, domain boundaries, surfaces chemical potentials and other quantities influences by ferroic properties and catalytic action.

One of the most promising emerging technologies are memristors and the devices constructed from them. Memristors are passive two-terminal electronic devices which connect the magnetic flux $\varphi$ to the charge $q$ via a relationship of the form $d\varphi = M(q,t)dq$. The memristance $M$ is a characteristic state function for the specific memristor. In the case of constant memristance the memristor is identical to an ohmic resistor $M \equiv R$. In the non-linear case I-V characteristics appear which otherwise can only be realized using active elements like transistors. This makes memristive devices technologically very interesting [56]. One particular application is the use of memristive devices as non-volatile memory. A simple, two-terminal passive element can be manufactured at much lower cost and much higher integration densities than active element based conventional memory cells. Even though the concept of memristive devices has already been developed in the 1970s from symmetry considerations of the basic equations of electronics [57], no physical manifestation could be realized for a long time. A specific class of memristors exhibits a hysteresis behavior which leads to at least two stable resistive states $R_{on} \ll R_{off}$. These can be accessed by subjecting the devices to switching currents $I_{set} \ll I_{reset}$ (where SET denotes the transition $R_{off} \rightarrow R_{on}$ and RESET the reverse). Technically, resistive switching elements have been realized as thin films of reduced oxides. A classification of models for resistive switching mechanisms is given in
[58], based on the technical requirements on the resulting memory cells, redox-chemistry related mechanisms in oxides are of particularly high interest [58].

Very recent results show that nanoscale NbO cells exhibit an S-shaped I-V curve with negative differential resistance, which can be understood as locally active memristors exploiting a metal-insulator transition. These devices have been demonstrated to enable the construction of transistorless logic circuits and neuron emulation [59]. Especially, it is possible to replace the time-dependent resistors of the Hodgkin-Huxley model of neuronal action [60] with memristors, overcoming some of the model's limitations. Other theorized applications of memristors include transistorless differential amplifiers [61], adaptive filters [62] and programmable amplifiers [63]. At the current state of the art, the understanding of the ionic scale mechanisms governing the memristive effect in oxides is still rudimentary.

More generally, conducting oxides are very promising materials for adaptive electronics applications [64]. Switching characteristics can not only be realized by nanionic effects leading to redox chemistry, but also by ferroelectric [65], ferromagnetic [66] or multiferroic materials [67]. Ferroelectrics display a hysteresis of the electrical polarization, characterized by a remanent polarization at zero electrical field and the possibility to continuously pole the material between positive and negative extrema. Fundamentally, the ferroelectric effect is well understood to be caused by a non-centrosymmetric distortion of the crystal leading to an emergent dipole moment [64]. Memoristive I-V characteristics can be obtained from ferroelectric materials in various ways, including modulating the height of Schottky barriers between metal electrodes and a ferroelectric layer [75] or ferroelectric tunnel junctions where the tunnel barrier height across an ultrathin layer of ferroelectric materials is dependent upon the polarization direction [76]. Ferroelectrics offer not only possibilities for data storage, their applications encompass a wide variety of technical problems, such as magnetic field detection, or microwave, x-ray and neutron sources [68].

Resistive switching in ferromagnetic materials can be obtained by employing magnetic tunnel junctions [66] constructed from a thin insulating layer sandwiched between two ferromagnetic layers. The magnetization direction of one of these layers is pinned, while the other can be switched parallel or antiparallel to the first. In the parallel
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case only electrons of one spin state are strongly scattered, while in the antiparallel case, both electron spins are subject to scattering. Oxide-diluted magnetic semiconductors [69], such as Co:TiO$_2$ thin films are highly interesting materials for spintronics, where there distribution and dynamics of the magnetic ions is of crucial importance for a detailed understanding of the materials properties. Dilute magnetic semiconductors offer attractive lab systems for fundamental physics [77], even though, Curie temperatures well below room temperature so far preclude wide technical application. Current challenges include obtaining detailed theories how interfaces, surfaces and point defect influence the formation and propagation of ferroic domains.

Another highly important emerging technology based on oxides lies in advanced catalysis. The need to find sustainable methods of energy production leads to a demand for new methods of energy storage and distribution. While for ground transportation, storing electric energy from sustainable sources in batteries is demonstrated to be quite successful, this solution is out of the question for air travel. Here, chemical fuels for air-breathing engines may never be replaceable, due to their superior energy per weight ratio. At the current state of the art, the bulk of chemical fuels is produced by refining fossil hydrocarbons, i.e. Petrol. Most current technologies to produce chemical fuels from renewable biomass are extremely inefficient and therefore are neither economically viable nor do they offer ecological advantages [70]. Therefore, new methods to increase the energy density of biologically obtained hydrocarbons need to be developed.

Oxide catalysts have for long been used in oxidation catalysis and especially reducible oxides display high activity also at low temperatures. Therefore, oxide catalysts have been important in the development of efficient air cleaning systems operative at room temperature and been considered for the potential application in fuel cells, where low temperatures are required. Interestingly, while the catalytic activity of these compounds have been known for long, recent experiments for the reducible oxides of cobalt [78] and cerium [79] have shown a large dependency of the catalytic activity with the nature of the oxide catalyst in terms of size and morphology. Furthermore, the catalytic activity of oxides can be strongly influenced by surface and subsurface point defects [73], while the ongoing reaction can strongly influence the distribution of point defects on and within the oxide catalyst itself [74]. Oxide catalysts may allow better
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control over the reaction products than conventional noble metal catalysts through defect level engineering [71] and are therefore a promising route towards the development of more efficient catalysts. One exciting example of novel oxide catalysts is nanoscale gold oxide centers [72].

Besides being catalytically active, oxide materials are often used in conjunction with catalytically active metals as catalytic promoters. For example, in the case of automotive catalysis using the three-way catalyst, ceria (CeO$_2$) has for long been used as oxygen buffer to provide oxygen at reducing conditions [80]. Interestingly, as with the catalytic activity, a size dependent effect on the oxygen transfer from the oxide compound to the catalytically active metal particles has been observed [81]. While in this case, the role of the promoting oxide is clear; this is not always the case. In industrial catalysis, it is well known that synergetic effects between catalytically active metals and metal oxide compounds are important for the overall efficiency. Most often, the role of the catalytically active metal is well known, but the actual role of the promoting oxide compound is far less understood. Recently, a combined experimental and theoretical study have elucidated the role of ZnO in methanol synthesis over Cu based industrial catalysts [82]. In contrast to most studies where ZnO is considered as a as support for Cu nano-particles, it was shown that the role of ZnO is to provide active sites through Zn atoms decorating steps on the Cu metal particle [82]. This example illustrates the complexity when it comes to understanding the role of oxides in heterogeneous catalysis which depend crucially on the nature of the oxide compound in terms of size, morphology, stoichiometry and possible defects. A detailed understanding of possible synergetic effects is identified as a key challenge when it comes to develop new more efficient catalytic concepts.

1.4 Motivation of the Present Work:

The objective envisaged to be achieved during the course of present work were, to fabricate high quality nanostructured thin films of mixed valent manganites using CSD
method and to study their structural, microstructural and transport properties. In order to understand the basic mechanisms responsible for charge transport. It is also planned to synthesis the nanostructure GdMnO$_3$ manganites synthesized by low cost and vacuum free Sol-Gel method to understand the effect of sintering temperature on their electrical properties.

$Y_{0.95}Ca_{0.05}MnO_3$ (YCMO) manganite shows p-type semiconducting nature from room temperature to liquid nitrogen temperature. Synthesis parameters are the key factor to tune the device characteristics of YCMO thin films grown on single crystalline (100) Si substrate using CSD method. Effect of the annealing temperature and thickness of the film was studied for the modification in structural and microstructural properties, especially strain at film-substrate interface, granular morphology and their correlation with Current - Voltage (I-V), Capacitance – Voltage (C - V) characteristics where discussed in detail. Also field dependent electro resistance and responsible charge transport mechanism were discussed in the context of thermal processes and few other charge transport model.

Now-a-days RMnO$_3$ manganites are most important compound due to their antiferromagnetic insulating (AFM) insulating ground state and possibility of phase separation scenario possessed by them. Due to which large number of practical applications are possible for better spintronics based devices. A series of GdMnO$_3$ samples were synthesized using low cost Sol-Gel method having nano-structured granular morphology were found to exhibit interesting electrical property with structural aspect. The effect of sintering temperature on the electrical properties and their dependence on the structural property of GdMnO$_3$ has been studied.

**Chapter wise Contents**

**Chapter I**

Chapter I deals with the introduction of the functional oxide materials and the details about the various functional materials like High Temperature Superconductor (HTSC), Multiferroics, Perovskite Manganites, Diluted Magnetic Semiconductor (DMS), etc. At the end of the chapter various applications of the functional oxide materials in the
SPINTRONIC devices has been given which motivate the present studies on the thin film manganites.

Chapter II

Chapter II describes various techniques for synthesis of the bulk as well as thin film of the functional oxide materials. This chapter includes the detailed understanding of the Sol-Gel, Co-precipitation and CSD, which has been used during the synthesis of the present work in this Thesis. This chapter also includes various characterization techniques of structural, microstructural and transport properties such as XRD, AFM, MFM, I-V, C-V used during present studies.

Chapter III

80nm thin $Y_{0.95}Ca_{0.05}MnO_3$ (YCMO) films were grown on single crystalline (100) Si substrate using Sol-Gel method followed by annealing at two different temperature 700°C and 900°C. As an effect of annealing temperature the modifications in the strain at interface has been observed and its impact on the I-V characteristic has been studied in chapter. Temperature dependent I-V characteristic were studied in the context of various responsible transport mechanism and models. The dependence of the modification in the state of inter face on the annealing temperature and its effect on the C-V behavior of nanostructured junction have been discussed.

Chapter IV

Chapter IV deals with the studies on the chemical solution deposition (CSD) grown 140 nm thin YCMO films for their structural, microstructural, transport and electro resistance. XRD, AFM, MFM measurements were carried out to understand and study structure and microstructure of film annealed at two different temperature 700°C and 900°C. Temperature dependent I-V and C-V were studied in the context of charge transport mechanism to verify the electric field response of the films under study. Electrical field dependent variation in resistance has been investigated for both the films.

Chapter V

It is well known fact that all the physical properties of the materials changes at nanoscale as compare to bulk counterparts. In this chapter VI have prepared
nanostructure orthorhombic manganite GdMnO₃ by using wet chemical technique via acetate route and studied its frequency dependent electrical properties such as AC conductivity and impedance spectroscopy have been studied at different sintering temperatures.
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