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SYNTHESIS AND CHARACTERIZATION
OF SOME NEW PEROVSKITE TYPE
MIXED OXIDE MATERIALS

Ph.D. Thesis
Submitted to
Saurashtra University, Rajkot, India

By
Rujuta R. Doshi

Research Guide
Prof. D.G. Kuberkar

May 2010
SYNTHESIS AND CHARACTERIZATION
OF SOME NEW PEROVSKITE TYPE
MIXED OXIDE MATERIALS

Thesis
Submitted to
Saurashtra University, Rajkot, India

For the Degree of
Doctor of Philosophy
In Science
In the Subject of Physics

By
Rujuta R. Doshi

Under the Supervision of
Dr. D.G. Kuberkar
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Department of Physics
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Rajkot, India

May 2010
STATEMENT UNDER O. Ph.D. 7 OF THE SAURASHTRA UNIVESRITY

This is certified that, the work presented in the thesis is my own work, carried out under the supervision of Prof. D.G. Kuberkar and leads to some important contributions in Physics supported by necessary references

Rujuta R. Doshi
(Research Scholar)

This is to certify that, the work submitted for Ph.D. degree in Physics to Saurashtra University, Rajkot by Ms. Rujuta R. Doshi has been the result of more than four years of work under my supervision and is a good contribution in the field of Solid State Physics and Materials Science

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या कुन्देन्दुलीतारहारधवला या शुभवस्त्रावृत्ता
या वीणावरदण्डमणिदतकरा या श्वेतपञ्चासना।
या ब्रह्माच्युतश्रीरप्रभुतिभिर्देवः सदा चन्दिता
सा मां पातु सरस्वती भगवती निषेषजार्यापहा॥

जे ठेवी भोगशानं हृद्रा, यंद्र अने भरक ठेवा गोळा यह।
जे शरद वस्त्रवाणं यह, जे श्रेष्ठ दीर्घा नामं वाजिंत यात्रां धारया करे यह;
जे भोज रीढ़ा कमणां आसन ऊपर विराजतें यह, जे ठेवी निरंतर अलंक, विस्वं, शंकर वगऱे ठेवो वंदन करे यह अने जे
जडनुलिनो जडमूलती नाश करे यह ते भगवती सरस्वती ठेवी मां रक्षक करो।
This thesis is dedicated to

My Beloved Parents and Family
My Research Guide
My Nanaji and Pratap Mama
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Rujuta R. Doshi
Preface

Research in colossal magnetoresistance (CMR) manganites is of much interest owing to the phenomena of charge ordering (CO) exhibited by them. CO in manganites reveals extraordinary variety in the properties which include their fine sensitivity to the average size of the A-site cations, pressure, magnetic and electrical fields, as well as isotopic and chemical substitutions. Based on the properties of the CO state in manganites, a number of device approaches are being explored like Magnetic field sensors, Electric field effect devices, Bolometric uncooled infrared (IR) sensors using the metal - insulator transition at the Curie temperature and Low temperature hybrid HTS - CMR devices. Structural properties like size-mismatch and disorder of A-site cations play an important role on the magnetic and transport properties of the manganites, which has attracted researchers to study structure-property correlation. Selected complex Charge Order and near to charge order manganites are very important from fundamental research as well as applications point of view. Charge ordered systems are basically disordered systems which give rise to phase coexistence at low temperature due to which distinct phenomenon of arrestation of kinetics has been studied. Temperature dependent Neutron Diffraction studies have been carried out for charge ordered systems to understand structure-property correlation and impact on electronic and magnetic properties. During the course of present work, bulk polycrystalline manganites of the type (LaTb)(Ca/Sr)MnO$_3$ were synthesized by solid state reaction method and structural understanding was carried out using Neutron Diffraction studies while the nanostructured manganites of the type LaCaMnO$_3$ and NdSrMnO$_3$ were synthesized using novel Sol - Gel route and sintered at different temperatures to understand the effect of grain size and grain morphology on transport, magnetotransport. Materials synthesis work was carried out at Oxide materials laboratory in the Department of Physics, Saurashtra University, Rajkot. Transport, magnetotransport and magnetic measurements on all the samples studied were carried out at UGC-DAE CSR, Indore while Neutron Diffraction measurements were performed at DHRUVA facility, B.A.R.C., Mumbai.
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# Chapter 1

## Introduction to CMR Manganites

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1.1 Introduction

The rare-earth perovskites LnTMO\textsubscript{3}, with Ln a rare-earth element and TM a transition metal have been intensively studied because of large variety of physical phenomena such as superconductivity, ferroelectricity and colossal magnetoresistance, exhibited by them. Out of these interesting materials, colossal magnetoresistive manganites are currently being investigated by a sizable fraction of the condensed matter community and their popularity is reaching levels comparable to that of the high-temperature superconducting cuprates. Mixed valent manganites with the perovskite structure have been studied for almost 50 years. The system offers a degree of chemical flexibility which permits the relation between the structural, electronic and magnetic properties of these oxides to be examined in a systematic way. Research on the manganites has revealed new phenomena such as colossal magnetoresistance (MR) \cite{1} and dense granular magnetoresistance \cite{2} which led to the understanding of various physical concepts such as Zener double exchange (ZDE) \cite{3, 4} and the Jahn-Teller (JT) effect etc. \cite{5, 6}. Early research was motivated by a need to develop insulating ferromagnets with a large magnetization for high-frequency applications. More recent work has been driven by a desire to understand and exploit the large negative magnetoresistance effects which appear near and below the Curie temperature. The manganites also have potential as solid electrolytes, catalysts, sensors and novel electronic materials. Their rich electronic phase diagrams reflect the fine balance of interactions which determine the electronic ground state. These compounds represent the interplay of experiment, theory and application which an important aspect of condensed matter physics research.

1.1.1 CMR effect in Manganites

Materials are known by their intrinsic and extrinsic properties are classified accordingly for different applications. Manganese based oxide materials, known as manganites, possess unique intrinsic property of, change in the electrical resistance under
the application of magnetic field, known as magnetoresistance (MR) which can be expressed as -

\[ MR\% = \frac{\rho_0 - \rho_H}{\rho_0} \times 100 \]

where \( \rho_0 \) and \( \rho_H \) are the resistivities in the absence and presence of magnetic field respectively. The value of magnetoresistance (MR) may be negative and positive depending on the fall or rise in the resistivity with the applied magnetic field.

During last five decades, the following forms of magnetoresistance have been studied having their origin in different physical aspects.

1. Anisotropic magnetoresistance (AMR)
2. Granular and tunneling magnetoresistance (TMR)
3. Giant magnetoresistance (GMR)

Large negative MR ~ 20 to 50\% is reported in metallic multilayers [7, 8], hence termed as ‘Giant magnetoresistance’ (GMR). Owing to such a large negative MR, these materials were in application for a quite some time. Though, the search for better magnetoresistive materials never ended and in 1993, the ABO\(_3\) perovskite structured oxide materials of type \((\text{Ln}_{1-x}\text{A}_x)\text{MnO}_3\) (R = trivalent rare-earth cation, A = divalent cation) became the center of attention for research, after the work of Von Helmolt et al. [9] and Charara et al. [10] reporting a huge magnetoresistance. Simultaneously, Jin et al. [1] reported magnetoresistance ~ 99\% in similar compounds having large value of MR termed as a ‘Colossal Magnetoresistance’ (CMR). The big boost to the research on manganites led to the present explosion of interest in the subject produced by the discovery of the CMR effect. The origin of MR in manganites is quite different than that observed in other forms of MR. CMR effect is an intrinsic property of crystal structure and has its origin in the spin disorder of conduction electron, which can be suppressed by an application of the magnetic field resulting in large magnetoresistance [9, 10]. The discovery of CMR effect in manganites and its relation to various electronic and magnetic properties revived the research interest in similar compounds.
1.1.2 Structure of Manganites

The doped LnAMnO$_3$ type perovskite structure has cubic unit cell. At the corner, Mn ions are surrounded by octahedral oxygen units known as the MnO$_6$ octahedra and the R occupying the holes between the octahedra which form the stable skeleton of the structure. The undistorted cubic parent structure is schematically depicted in fig. 1.1.

![Figure 1.1 ABO$_3$ type perovskite structure (simple cubic system)](image)

The relative ion size requirements for stability of the cubic structure are quite stringent, so slight buckling and distortion of MnO$_6$ octahedra, can produce several lower-symmetry distorted structure, in which the coordination numbers of Ln (and A) cations, Mn cations or both are reduced. Tilting of the MnO$_6$ octahedra reduces the coordination of an undersized Ln cation from 12 to as low as 8. Conversely, off-centering of an undersized Mn cation within its octahedron allows it to attain a stable bonding pattern. Complex perovskite structures contain two different Mn-site cations. This results in the possibility of ordered and disordered structures. The orthorhombic and tetragonal phases are most commonly observed non-cubic structures for doped manganites. In LnAMnO$_3$ structure with Pnma space group, there are two nonequivalent oxygen positions, apical (O$_1$) and equatorial (O$_2$), which characterize the distortion of MnO$_6$ octahedra in terms of the Mn-O-Mn bond angles and Mn-O bond lengths.
The transport properties of manganites can be governed by the structure of MnO$_6$ octahedra [11] which can be decided by MnO$_6$ octahedra distortions, Q$_2$ mode in basal plane, lattice distortion, its band width of charge carriers to move freely, difference between the apical (O$_1$) and equatorial (O$_2$) Mn-O bond lengths and Mn-O-Mn bond angles.

1.2 Parameters and effects in manganites

1.2.1 Tolerance Factor (t)

In ABO$_3$ type perovskite structure, octahedral tilting type distortion was first examined by Goldschmidt in 1926 [12]. The mismatch or degree of distortion between the A-O and B-O bond lengths in ABO$_3$ perovskite can be determined using the following equation,

$$ t = \frac{<r_A> + r_O}{\sqrt{2}<r_B> + r_O} = \frac{d_{A-O}}{\sqrt{2}d_{B-O}} $$
where $<r_A>$, $<r_B>$ and $r_O$ are the average A-site, average B-site cation and anion ionic radii (purely ionic bonding is assumed) respectively. The structure is ideally cubic when $t$ is unity with B-O-B bond angle $180^\circ$. $t < 1$ or $t > 1$ makes the system strained and drives it towards the lower symmetry space group, away from its ideal cubic symmetry. Cubic perovskite structure is stabilized for the $t$ values between $0.89 < t < 1$, while the structure changes to rhombohedral for $0.96 < t < 1$ and orthorhombic for $t < 0.96$ which sets the critical limit on $<r_A>$ and $<r_B>$ cationic radii. The perovskite structure adjusts to $t < 1$ by a cooperative rotation of the BO$_6$ octahedra around a cubic [001] axis as in tetragonal, a cubic [111] axis as in rhombohedral (R-3c), a cubic [110] axis as in orthorhombic (Pbnm or Pnma) or a cubic [101] axis as in orthorhombic (Imma). These cooperative rotations bend the B-O-B bond angle from $180^\circ$ to $180^\circ$-$\varphi$. The application of hydrostatic pressure has the same influence on the physical properties as an increase in the tolerance factor [13], which indicates that, the B-O bond is more compressible than the A-O bond in the paramagnetic phase.

1.2.2 Average A-site Cationic Radius ($<r_A>$)

Average A-site cationic radius, $<r_A>$, can be determined using the following formula,

$$
<r_A> = \sum_i x_i r_i
$$

where, $r_i$ is the ionic radii of $i$:th cation. The variation of $<r_A>$ at A-site cation in ABO$_3$ perovskite has a similar effect as an external pressure which enhances the B-O-B transfer integral through a change in B-O-B bond angle and a measure of the degree of radial distortion of the BO$_6$ octahedra [14]. There is a linear relationship found between $T_C$ and $<r_A>$, and both of them exhibit inverse correlation with MR [15].

A smaller change in $<r_A>$, gives rise to the structural distortion at B-O-B bond angle up to a large extent and hence bending of B-O-B bond angle which in turn tilts the BO$_6$ octahedra for $t < 1$ and narrowing the $e_g$ electron bandwidth affecting the electronic transport [16].
1.2.3 Size variance ($\sigma_A^2$)

This factor, first introduced by L.M. Rodriguez-Martinez and J.P. Attfield [17] is related to the ionic mismatch due to the doping of divalent alkali and alkaline cations or trivalent rare earth cations at A-site and is quantified as,

$$\sigma_A^2 = \sum x_i r_i^2 - <r_A>^2$$

where, $x_i$ is the fractional occupancies of the different $i$ cations of $r_i$ radii. Size variance is attributed to the displacements of the oxygen atoms due to the A site disorder, as shown by the simple model in fig.1.3 [17]. This shows that, $\sigma$ provides a measure of the oxygen displacements $Q$ due to A-site cation size disorder and that ($r_A^0 - <r_A>$) is the complementary measure of displacements due to $<r_A>$ being less than the ideal value $r_A^0$.

![Diagram](image)

Figure 1.3 Model for local oxygen displacements in ABO$_3$ perovskites. A fragment of ideal cubic structure with A cations of radii $r_A^0$ is shown schematically in (a) and as spherical ions in (b) Cation size disorder in (c) gives rise to random oxygen displacements $Q = \sigma$ and a reduction in the A site radius in (d) leads to ordered oxygen displacements $Q = r_A^0 - r_A$
The structural disorder creates local oxygen displacement resulting into bond angle fluctuations and bond length variations leading to carrier localization due to the Jahn-Teller distortion of BO$_6$ octahedra thereby affecting the electrical transport, $T_P$ and $T_C$ in manganites. The analogous effect of increasing $\sigma^2$ have been extensively investigated for Ln$_{0.7}$A$_{0.3}$MnO$_3$ [Ln = La$^{3+}$, Pr$^{3+}$, Sm$^{3+}$, Pm$^{3+}$ and Nd$^{3+}$ and A = Ca, Sr and Ba] at fixed carrier concentration $x = 0.3$ and $<r_A>$ which shows the linear reduction in $T_P$ with $\sigma^2$ [18].

1.2.4 Zener Double Exchange (ZDE) Mechanism

Most of the early reported theoretical work on manganites was focused on the qualitative aspects of the experimentally discovered relation between transport and magnetic properties, namely the increase in conductivity upon the polarization of the spins. Not much work was devoted to the magnitude of the magnetoresistance effect itself. The formation of coexisting clusters of competing phases was not included in the early considerations.

The states of manganites were assumed to be uniform and double exchange (DE) was proposed by Zener in 1951, in terms of his theory of indirect magnetic exchange between 3d atoms wherein ferromagnetic interactions are favored when the magnetic atoms are fairly well separated and conduction electrons are present. The theory was applied to the manganese perovskites with the aim of explaining the strong correlation between conductivity and ferromagnetism [19]. Starting from the insulating antiferromagnetic LaMnO$_3$ end member where electrons are localized on the atomic orbitals, Zener showed how the system should gradually become more ferromagnetic upon hole doping (introduction of Mn$^{4+}$). He considered the problem of the exchange between Mn$^{3+}$ and Mn$^{4+}$ ions via an oxygen ion and introduced the concept of simultaneous transfer of an electron from the Mn$^{3+}$ to the oxygen and from the oxygen to the neighboring Mn$^{4+}$ [fig. 1.4].
1.2.5 Carrier Density

Doping determines the carrier concentration and sign of the charge carriers (i.e. positively charged holes or negatively charged electrons) in the Ln\(_{1-x}A_x\)MnO\(_3\) (Ln = Rare earth cation, A = divalent or trivalent smaller cation) mixed valent manganites. Carrier density decides the fluctuated valence of the transition metal cations i.e. Mn\(^{3+}\)/Mn\(^{4+}\) in manganites which is responsible for the ferromagnetic Zener Double Exchange (ZDE) [20]. At a fixed amount of doping, perovskite compounds exhibit very rich phase diagram as a function of temperature, magnetic field, external and internal chemical pressure, etc. which in turn governs their physical properties.

![Figure 1.4](image)

(a) Sketch of the Double Exchange mechanism which involves two Mn ions and one O ion. (b) The mobility of e\(_g\) - electrons improves if the localized spins are polarized. (c) Spin-canted state which appears as the interpolation between ferromagnetic (FM) and antiferromagnetic (AFM) states in some mean field approximations.
1.2.6 Jahn-Teller (JT) Distortion

The discovery of high-temperature superconductivity in the copper oxides and of colossal magnetoresistance (CMR) in the manganese oxides with perovskite structure has reawakened interest in dynamic, cooperative Jahn-Teller (J-T) deformations in solids, particularly where they occur at a cross-over from localized to itinerant electronic behavior. Whereas electrons in a partially filled cation shell are localized in a transition metal compound. High site symmetry at the cation may leave the localized electron manifold orbitally degenerate. In this case, the cation becomes a JT ion. With localized $d^n$ configuration, a cubic crystalline field quenches the orbital angular momentum of a twofold orbital degeneracy leaving behind orbital angular momentum at a threefold orbital degeneracy. An appropriate local JT site deformation to lower symmetry removes the orbital degeneracy at a JT cation, the deformation may be static or dynamic.

In mixed valent manganites, the electronic properties are intimately related to the lattice. Many of the interesting phenomena exhibited by them involve a complex interplay between the spin, charge and orbital degrees of freedom, accompanied with subtle displacements in the crystal lattice. In the perovskite manganites $Ln_{1-x}A_xMnO_3$, the $Mn^{3+}$ ion has a $d^4$ configuration. In octahedral symmetry, the d level splits into three $t_{2g}$ and two $e_g$ orbitals. The $Mn^{3+}$ ion has high-spin configuration, with three electrons occupying the three $t_{2g}$ orbitals and one electron occupying the doubly degenerate $e_g$ orbitals as $t_{2g}^3e_g^1$. According to the Jahn-Teller (JT) theorem, the structure will distort thereby removing the degeneracy of the $e_g$ orbitals. In solids, the orbital degree of freedom of the $Mn^{3+}$ ion often shows long range ordering associated with the cooperative JT effect. It is observed for the most extensively studied compounds throughout the $LnAMnO_3$ series, i.e. $LaMnO_3$, that below a transition temperature $T_{JT}$, the $3d_{3x^2−r^2}$ and $3d_{3y^2−r^2}$ orbitals are ordered in the ab plane in an alternating fashion [fig. 1.5]. Fig. 1.6 shows the energy band structure affected by the JT effect.
There are two types of distortions associated with the JT effect: Q₂ and Q₃. The Q₃ is a tetragonal distortion which results in an elongation or contraction of the MnO₆ octahedron corresponding to the filled 3z² - r² orbital or x² - y² orbital, respectively [Fig. 1.7 (a) and (b) respectively]. The Q₂ is an orthorhombic distortion [Fig. 1.7 (c)] obtained by a certain superposition of the 3z² - r² and x² - y² orbitals [21, 22].
The oxygen framework is described in Pbnm [space group No. 62] symmetry by two oxygen positions: the O₁ position situated on the mirror plane and attributed to the out-of-plane oxygens; the O₂ position attributed to the in-plane oxygens [see fig. 1.8 (a)]. The rotations of the octahedra are reflected in the deviation from 180° of the Mn-O-Mn tilting angle. The JT effect in LnMnO₃ is dominated by the Q₂ distortion with alternating long (l) and short (s) Mn-O₂ bond lengths in the ab plane and a medium out of plane Mn-O₁ (m) bond length as shown in fig. 1.8 (b). The medium bond length m deviates from the average bond length, such that m < (l + s)/2, indicating that the JT distortion is not of a pure Q₂ type. A contribution of the Q₃ distortion is also present.
1.3 Microstructure

Since the discovery of CMR effect in manganites, the interest in the microstructural studies on these materials in relation to their electrical and magnetic properties has grown exponentially. The physical behaviour of material is directly related to the crystal structure as well as its microstructure. An interrelated structural, transport, magnetotransport and magnetic properties of manganites are strongly governed by the grain morphology and grain boundary nature [23 - 25].

The structure and properties of grain boundaries depend on how the material was prepared and on the subsequent thermal history. It has also been observed that, as the sintering temperature decreases, the width of transition broadens which suggests that, at low sintering temperatures, grains are loosely connected, which in turn directly affect the $T_C$ and $T_P$ of the material. Lowering of sintering temperature reduces the metallic transition temperature and hence the concomitant increase in resistivity. Hence, it should be expected that, the physical properties of the systems can be governed by the nature and
number of grain boundaries and will directly affect the transport and magnetotransport of material. It is well known that, the lattice structure of the grain surface is often distorted. This may cause a structural relaxation from the surface to the core of the grain. Since the surface plays a dominant role as the particle size decreases, the internal structure of the grains may be more influenced by the surface for manganite system.

In the manganites, a deviation of $T_C$ and $T_P$ has been attributed to the effect of the surface strain-induced grain-boundary effects [26, 27]. The deviation from ideal oxygen stoichiometry does not generally show such a strong variation of $T_C$ and $T_P$ as explained by Rivas et al [26]. Huang et al [28] pointed out that, there occur antiferromagnetic insulating regions near the grain boundaries. Such regions do not modify the transition temperature, but can make the electrical transition shift to a low temperature [29]. Magnetoresistive properties of manganites can be tailored by the grain morphology specifically grain boundaries in polycrystalline bulk, thin films, nanomanganites and devices. For polycrystalline manganites with charge ordering, the grain-boundary contribution results in a small Coulomb barrier of electrostatic origin. This can cause low temperature insulating state.

1.4 Transport and Magnetotransport

Doping of divalent ions like $\text{Ca}^{+2}$, $\text{Sr}^{+2}$ or $\text{Ba}^{+2}$ etc at Ln site in $\text{LnMnO}_3$ insulator results in to interesting behavior in $\text{Ln}_{1-X}\text{A}_X\text{MnO}_3$ ($A = \text{divalent ion}$) which has been explained on the generation of $\text{Mn}^{+4}$ state in the compound with the interplay between $\text{Mn}^{+3}$ and $\text{Mn}^{+4}$ due to the electron hopping from one site to another leading to electronic transport in them. Doped manganites exhibit two types of transitions. One is electrical transition from insulator to metal transition ($T_P$) accompanied with magnetic transition from paramagnetic to ferromagnetic transition ($T_C$). At room temperature, most of the manganites are in paramagnetic - semiconducting or insulating (PMI) state and with decreasing temperature, they show signs of increase in electrical resistivity but when cooled below $T_C$, insulator-metal (I-M) transition occurs in the vicinity of paramagnetic to ferromagnetic transition. In the case of half doped manganites, at low temperature, below $T_P$ one can observe an increase in the resistivity along with decrease in
magnetization at temperature $T_N$ known as Neel’s temperature. In the $T < T_N$, there is a real space ordering of all Mn$^{3+}$ and Mn$^{4+}$ ions which causes the increment of resistivity and reduction in magnetization in this low temperature region. The doped manganites, with doping level $x = 1/3$ demonstrate very interesting behaviour, as we decrease the temperature, compound exhibits a transition from high temperature PMI state to a low temperature ferromagnetic metallic (FMM) state.

When magnetic field is applied to the materials, the resistivity decreases sharply, particularly in the region of the insulator-metal transition $\sim T_P$. The decrease in resistivity can be almost 100% and, hence, the use of the term colossal while referring to the magnetoresistance in these materials. There are various parameters such as doped compound, average ionic radius, size variance, grain morphology, heat treatment, etc. which can directly affect the transport and magnetotransport properties.

To explain the resistivity in semiconducting or insulating region, there are several models proposed -

1. Nearest neighborhood hopping or the activation beyond the mobility edge [30], given by
   \[ \rho = \rho_0 \exp\left(\frac{E_a}{kT}\right) \]

2. Adiabatic nearest neighbor hopping model of small polaron conduction [31, 32],
   \[ \rho = A T \exp\left(\frac{E_a}{kT}\right) \]

3. Schklovskii - Efros (SE) type of Variable Range Hopping with a soft gap due to the modification of the density of states by the Coulomb interaction [33],
   \[ \rho = \rho_0 \exp\left(\frac{T_0}{T}\right)^{\frac{1}{2}} \]

4. Variable Range Hopping (VRH) of the Mott type for uncorrelated carriers [34 - 36], given by
   \[ \rho = \rho_0 \exp\left(\frac{T_0}{T}\right)^{\frac{1}{2+d}} \] where $d$ is the dimensionality and this becomes,
\[ \rho = \rho_0 \exp \left( \frac{T_0}{T} \right)^{\frac{1}{n}} \] for three dimensional systems

In doped manganites the size disorder increases with doping level x which generates random spin and Coulombic potential fluctuations. Hence, the carriers experience some potential difference beyond the \( \text{Mn - O} \) distances to hop at farther distances and hence conduct through the Mott’s type of Variable Range Hopping. The \( T_0 \) occurring in the VRH relation can be related to the carrier localization length by the expression,

\[ kT_0 = \frac{18}{L^3} N(E) \]

where \( k \) is the Boltzmann constant, \( L \) is the carrier localization length and \( N(E) \) is the density of states [37] the values of the localization length should be comparable to \( \text{Mn - O} \) distances for the VRH type of conduction [37].

The electron transport mechanism and the cause of resistivity in the conducting region have been understood by fitting the resistivity data to a general Zener-Double Exchange polynomial law,

\[ \rho = \rho_0 + \rho_2 T^2 + \rho_n T^n \]

where \( \rho_0 \) is the residual resistivity, \( \rho_2 \) is the resistivity contributed by an electron-electron and electron-phonon scattering mechanism, \( n \) is a higher order term (\( n = 2.5, 3, 4.5 \) and 7.5) and \( \rho_n \) is the corresponding resistivity coefficient [38 - 43]. In this law, \( n = 2.5 \) and 3 correspond to the one magnon scattering process whereas \( n = 54.5 \) and 7.5 correspond to two magnon scattering phenomena.

1.5 Types of MR

Two types of MR are observed depending upon the temperature range the field required to observe them. One is the, intrinsic MR governed by the intrinsic properties of the materials, \( e_g \) spins, requires relatively large magnetic field (\( > 1 \text{T} \)) and is exhibited around metal to insulator transition. The cause for intrinsic MR can be explained on the
basis of zener double exchange (ZDE) mechanism. Second is the extrinsic MR generally achieved below the metal to insulator transition temperature can be governed by the external parameters like, synthesis route used, sintering temperature, time and environment, grain morphology, grain boundary density and nature etc. This component of MR at low temperature requires relatively low field ($\leq 1T$). This can be explained on the basis of intergranular spin polarized tunneling or spin dependent scattering phenomena [2, 44].

1.6 Magnetic Behavior

The magnetic properties of the manganites are governed by exchange interactions between the Mn ion spins. These interactions are relatively large between two Mn spins separated by an oxygen atom and are controlled by the overlap between the Mn d-orbitals and O p-orbitals. The corresponding super exchange interaction depends on the orbital configuration following the rules of Goodenough [45]. Generally, for Mn$^{4+}$-O-Mn$^{3+}$, the interaction is antiferromagnetic (AFM), whereas in the divalent doped LaMnO$_3$ manganite, both ferromagnetic and antiferromagnetic interactions coexist for Mn$^{3+}$-O-Mn$^{4+}$ configuration [3]. The LaMnO$_3$ end member is AFM, with ferromagnetic planes having alternating magnetic spins while the other end member CaMnO$_3$ is AFM with each Mn$^{4+}$ surrounded by the six closest neighbors having opposite spins. Other doping levels result in to different types of AFM orderings but in the doping range of $x \approx 0.3$, the samples are FM. Goodenough has explained the magnetic structures for different doping levels in terms of different types of bonding, where some bonds are FM and others are AFM or paramagnetic (PM) [45]. This is determined by the relative orientation of occupied and unoccupied orbitals of the Mn-O-Mn pairs. Around the FM Curie temperature, $T_C$, the materials also undergo an insulator-metal transition. Metallicity below $T_C$ occurs because only those electrons possessing ferromagnetically aligned spins are involved in the conduction process. When magnetic field is applied to these materials, the resistivity decreases appreciably, particularly in the region of the $T_C$. 

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Introduction to CMR Manganites
1.7 Charge and Orbital Ordering (CO and OO)

Charge Ordering (CO) refers to the ordering of the metal ions in different oxidation states in specific lattice sites of a mixed valent material. Such ordering generally localizes the electrons in the material, making it insulating or semiconducting due to the charge localization which in turn restricts the electron hoping from one cation site to another. Charge-ordering is not a new phenomenon in metal oxides. One of the earliest examples of charge-ordering in inorganic solids is that of Fe$_3$O$_4$ (magnetite), which undergoes a disorder-order transition, popularly known as the Verwey transition, at 120 K [46]. The study of charge-ordering phenomena in doped rare earth manganites with the general formula, Ln$_{1-x}$A$_x$MnO$_3$ (Ln = rare earth, A = alkaline earth) has recently attracted much attention because of the discovery of colossal magnetoresistance and other interesting properties exhibited by these materials [47, 48]. Charge-ordering had been reported by Wollan and Koehler [49] and later by Jirak et al. [50] and is associated with novel properties which are useful in understanding the electronic behavior of compounds studied.

In doped manganites, the charge-ordered phases are novel manifestations arising from the interaction between the charge carriers and the phonons where in the Jahn Teller distortions play a significant role. Charge ordering arises because the carriers are localized into specific sites below a certain temperature known as charge ordering temperature, T$_{CO}$, giving rise to long-range order throughout the crystal structure. Although, charge ordering would be expected to be favoured when doping level $x = 0.5$, due to the presence of equal proportions of the Mn$^{3+}$ and Mn$^{4+}$ states, it is found in various compositions in the doping range $0.3 < x < 0.75$, depending on the Ln and A ions. In the charge-ordered (CO) state, the Mn$^{3+}$ and Mn$^{4+}$ ions are regularly arranged in the ab plane with the associated ordering of the $d_{2r^2}$ and $d_{2r^2}$ orbitals [51] as shown in fig. 1.9. Charge ordering also competes with double exchange, and promotes insulating behaviour and antiferromagnetism. Furthermore, the Mn$^{3+}$ ($e_g$) orbitals (3$d_{z^2}$) and the associated lattice distortions (long Mn - O bonds) also develop long-range order, giving rise to orbital ordering, which is responsible for the anisotropy of the electron-transfer interaction. This gives rise to complex spin-orbital coupled state. The orbital-ordering is
coupled with Jahn Teller distortion. Charge-ordering competes with double-exchange, giving rise to an unusual range of properties which are sensitive to factors such as the size of the A-site cations, internal and external pressure, chemical melting of CO state by doping and melting of CO state by application of magnetic field.

Figure 1.9  CE-type AFM charge ordering in $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$. The lobes show the $d_{x^2-r^2}$ or $d_{y^2-r^2}$ orbitals (from Okimoto et al [51])

At low temperatures, the rare earth manganites are antiferromagnetically ordered with CE - or A - type ordering, but only the former occurs in the charge-ordered materials where the $e_g$ electrons are localized. The CE - type spin ordering is characterized by the ordering of Mn$^{3+}$ and Mn$^{4+}$ ions alternately. The spin ordering in the ab plane is somewhat complex and it stacks antiferromagnetically along the c axis. In the A-type spin ordering, the spins order ferromagnetically in the ab plane (with the moments pointing towards the a-axis) and these planes stacked antiferromagnetically along the c axis. In fig 1.10, CE and A-type AFM ordering in half-doped manganites ($x = 0.5$) can be seen clearly. Orbital ordering can occur in both A - and CE - type AFM ordering, but they differ in detail. The CE - type AFM state is attained on cooling a ferromagnetic state or a charge-ordered paramagnetic state. Fig. 1.11 depicts the three dimensional views of A -, C - and F - type charge and orbital ordering.
Two distinct types of charge-orderings can be delineated. In one, a ferromagnetic metallic (FMM) state transforms to the charge-ordered (CO) state on cooling the material. In the other, the CO state is found in the paramagnetic ground state and there is no ferromagnetism down to the lowest temperatures. Magnetic field transforms the CO state to the FMM state, when the average radius of the A-site cations is sufficiently large.
(<r_A> > 1.17 Å). Fig. 1.12 shows the schematic diagram of different charge ordering behaviors of Ln_{0.5}A_{0.5}MnO_3 depending on <r_A>. Accompanying with these all factors, cooperative Jahn Teller effect induces additional effects such as lattice distortion and electron localization in the charge-ordered state. Fig. 1.13 reveals the effect of charge ordering on structural, transport and magnetic properties of Nd_{0.5}Sr_{0.5}MnO_3 compound, which is a ferromagnetic metal with a T_C ~ 250K and transforms to an insulating CO state around 150 K [51]. The FMM – CO transition is accompanied by spin and orbital ordering, and the CO insulator is antiferromagnetic (CE type). At the low temperature, around T_{CO}, compound shows a sign of structural transition which can be observed from the changes in structural parameters as well as resistivity increases due to charge ordering, which localize electrons and suppress the ZDE and the value of magnetization also decreases due to CE – type antiferromagnetic ordering. Application of a magnetic field destroys the CO state, and the material becomes metallic. The transition is first order showing hysteresis and is associated with changes in unit cell parameters.

![Figure 1.12 Schematic diagram of charge ordered state of Ln_{0.5}A_{0.5}MnO_3 depending on <r_A>, Key: FMM, ferromagnetic metal; PMI, paramagnetic insulator; AFMI, antiferromagnetic insulator; CO, charge-ordered state.](image)
1.8 Applications of CMR materials

Magnetoresistance (MR) is important in many technological applications, such as magnetic data storage, read-write heads, magnetic-bolometric sensors, Magnetic tunnel junction (MTJ) and magnetoresistive random access memory (MRAM). The discovery of colossal magnetoresistance has launched a new scientific event mainly aimed at understanding and improving their magnetoresistance properties. On the other hand, manganites are opening up vast and exciting possibilities for basic condensed matter physics. The delicate interplay between different sources of energy, such as the kinetic and electro-static energies of the mobile carriers and their coupling to the lattice, and strong coupling between spin, charge, and lattice degrees of freedom, leads to a wide range of striking physical phenomena. These interactions can be tuned by simply modifying the chemical composition. These materials provide a unique opportunity to study the physics of complex systems in which electrons, spins and phonons are strongly...
coupled, and in particular, to elucidate the interplay between local structural deformations and macroscopic transport, magnetic and optical properties.

Based on the properties of CMR materials discussed above, few applications of CMR materials are listed below-

1. Magnetic field sensors
   (a) Using the CMR effect in a film
   (b) Using a spin valve structure
   (c) as a microwave CMR sensor.

2. Electric field effect devices
   (a) Using a SrTiO₃ gate
   (b) Using a ferroelectric gate.

3. Bolometric uncooled infrared (IR) sensors using the metal-insulator transition at the Curie temperature.

4. Low temperature hybrid HTS-CMR devices
   (a) Flux focused magnetic transducers
   (b) Spin polarized quasi-particle injection devices.

The industrial requirements for a magnetic sensor can be summarized as follows.

1. Operation at room temperature and up to 100 K above room temperature.

2. At least a 20% response at a field of 100 Gauss.

3. Temperature independent CMR values over 350 - 50 K.

4. Acceptable noise values.

5. Retention of magneto-transport properties in patterned films at dimensions approaching sub-1000Å scales. (The current thinking is that oxide-based CMR sensors will have maximum impact only on memory systems approaching densities of 100 Gb/cm²)
1.9 Motivation of the present work

During the course of this thesis work, I have synthesized, nearly half doped and half doped manganites using conventional SSR method and detailed study of the temperature dependent ND measurements have been carried out. The present work is mainly aimed at understanding the charge ordering and its related phenomena which still remain unclear hence need detailed understanding in the context of manganites. For this purpose, the system selected is half doped manganites having large size disorder and ND and magnetization measurements are the tools employed. Magnetization measurements were carried out to throw light on the magnetic nature of the presently studied manganites and also to correlate them with the ND results taken at various temperatures. The manganite systems investigated during the present work are La_{0.7-x}Tb_xCa_{0.3}Sr_{2x}MnO_3 (LTCSMO) (x = 0.125), La_{0.375}Tb_{0.125}Ca_{0.5}MnO_3 (LTCMO) and La_{0.375}Tb_{0.125}Sr_{0.5}MnO_3 (LTSMO). The earlier studies on the La_{0.7-x}Tb_xCa_{0.3}Sr_{2x}MnO_3 (x = 0.05 \leq x \leq 0.1) system by our group member [D.S. Rana, Ph.D. Thesis, 2005, Saurashtra University] has revealed several interesting results on the transport, magnetotransport and magnetic properties of this system. It was necessary to understand the structure - property correlation in these samples and to study the dependence of transport, magnetotransport and magnetic properties on the variation in structural parameters such as bond length and bond angle variations, estimated using ND study. The detailed magnetization measurements were carried out on the Tb^{3+} and Ca^{2+} and / or Sr^{2+} doped LaMnO_3 polycrystalline bulk manganites reveal an interesting results and strong similarity with the magnetic properties derived from ND measurements. Effect of size variance on the transport and magnetoresistive properties in bulk and nanoscale single phasic polycrystalline La_{0.7}Ca_{0.3}MnO_3 (LCMO) and Nd_{0.7}Sr_{0.3}MnO_3 (NSMO) manganites having equal \langle r_A \rangle \sim 1.2 \, \text{Å}, sintered at various temperatures have been studied. The interplay between the intrinsic and extrinsic MR behavior and its dependence to the grain growth mechanism is very well studied in mixed valent manganites.

Keeping in mind the above mentioned aspects of various structural, microstructural, transport, magnetotransport and magnetic properties of manganites and their dependence on the synthesis parameters, structure, microstructure, size variance,
carrier concentration, during the course of present work, detailed studies on La_{0.7-x}Tb_xCa_{0.3}Sr_{2x}MnO_3 (x = 0.125), La_{0.375}Tb_{0.125}Ca_xMnO_3 (LTCMO) La_{0.375}Tb_{0.125}Sr_xMnO_3 (LTSMO) x = 0.5 manganites have been carried out. In addition, the effect of grain size and grain morphology on various properties of nanostructured La_{0.7}Ca_{0.3}MnO_3 (LCMO) and Nd_{0.7}Sr_{0.3}MnO_3 (NSMO) manganites synthesized by Sol-Gel route have been carried out.
References


[42] M.B. Salamon and M. Jaime, Rev. Mod. Phys. 73, 583 (2001)


Chapter 2

Experimental Techniques for Materials Characterization

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2.1 Introduction

The synthesis and characterization of material is the first and foremost important step during the experimental research in condensed matter physics and materials science. The quality of samples depends to a great extent on the synthesis method used. In addition, the proper selection of synthesis parameters helps to carry out desired properties in the samples to be characterized along with desired potentials. Structure, surface morphology, grain growth, transport of electrons within material and magnetic properties depend on material synthesis. There are various methods available for the synthesis of polycrystalline bulk materials like Solid State Reaction (SSR) route for synthesizing bulk manganite samples, Sol-Gel route, Co-precipitation method, Citrate Route, Nitrate Route, etc for preparing the nanostructured manganites. In order to characterize the polycrystalline bulk and thin films of manganites, such as X-ray diffraction (XRD), Neutron diffraction (ND) and electron diffraction (ED) for structure, scanning electron microscopy (SEM), atomic force microscopy (AFM), transmission electron microscopy (TEM) for microstructure, d.c. four probe resistivity with and without field for transport and magnetotransport and VSM for magnetic properties are employed. The following section gives a brief explanation about various characterization techniques with special emphasis on ND and Rietveld analysis of the data.

2.2 Synthesis

2.2.1 Solid State Reaction (SSR)

Most widely used method for synthesizing the polycrystalline solids (powders) is the direct reaction, in the solid state, of a mixture of solids as starting materials. Solids do not usually react together at room temperature over normal time scale so it is necessary to heat them at much higher temperature for long time duration for reaction to occur at an appreciable rate. All the bulk polycrystalline manganite samples studied during present work were synthesized using SSR method as per the steps shown in the flowchart [fig. 2.1]. There are two factors, namely thermodynamic and kinetic, which are important in solid state reaction, the former determines the possibilities of any chemical reaction to
occur by the free energy considerations which are involved while the later determines the rate at which the reaction occurs [1, 2]. The atoms diffuse through the material to form a stable compound of minimum free energy. Different compounds or phases might have the lowest free energy at various temperatures or pressures or the composition of the gas atmosphere might affect the reaction. In order to prepare a single-phase sample, the conditions during any reaction are very important. During synthesis, the parameters such as temperature, pressure, gas flow and time for the reaction are needed to be varied according to the phase requirements in the sample. Mapping of all variables has to be made to find the conditions, which are best for each material and phase.

Figure 2.1 Steps involved in the solid state reaction route for synthesizing the polycrystalline manganites
The general steps involved in solid state reaction method for synthesizing high temperature superconductors are described below

1. All starting materials were high purity powders of carbonates, oxides, nitrides, etc. They were preheated for appropriate time and temperature. After preheating powders were weighed for desired composition using high precision electronic weighing machine.

2. In the solid state reaction, for the reaction to take place homogeneously, it is very important to mix and grind the powders thoroughly for long duration to obtain homogeneous distribution of components (starting materials) in required proportions of the desired stoichiometric compound.

3. After mixing of stoichiometric amounts of all powder materials, proper grinding using pestle-mortar is very important. Thorough grinding decreases the particle size of mixed powder. This is necessary for obtaining close contact among the atoms so the right material is formed.

4. This powdered mixture was then heated (calcined) in air for the first time. During the first calcination, CO₂ is liberated from the mixture.

5. After the first heating, obtained powder was ground thoroughly for three to four hours. To maintain uniform particle size, the powder was sieved using 100 and 50 micron sieve, and then was palletized at 4-5T pressure using hydraulic press.

6. The pellets were subsequently sintered at 1000, 1100, 1200 and 1250 °C respectively for 48 hours with intermittent grindings to obtain single phase samples.

7. Final sintering was carried out at 1375 °C for 72 hours to obtain the desired structural phase.

The solid state reaction method has proved to be the most suitable for synthesizing reproducible samples of CMR manganites.
2.2.2 Sol - Gel

Out of several methods for synthesizing polycrystalline manganites, Sol-Gel is the cost-effective method, easy to handle and yields stoichiometrically predefined compounds. It offers a variety of starting materials as precursors to choose. Sol-Gel has become an alternate method to the conventional solid state reaction route, allowing more accurate control over the phase formation, desired stoichiometry and uniformity in particle size. In Sol-Gel technique, materials are obtained from chemical solution via gelation. It is more controllable technique for synthesizing glasses and polycrystalline materials. For nanomaterials synthesis, it is necessary to have control over grain size and also on the phase formation at much lower temperature which can be achieved by using such chemical methods.

Nanostructured manganites synthesized by Sol-Gel possess physical properties which are sensitive to sintering conditions. Sintering of particulate compacts without the intentional addition of low melting dopants; however, low melting phases may be present due to impurities. In the course of sintering, the microstructure evolves as follows -

At an intermediate stage, the pores are arranged at the grain boundaries. On further sintering, small pores remaining at the boundaries “dissolve” via the vacancy migration along grain boundaries toward the larger pores or the free surface. Simultaneously, normal grain growth develops as the drag force exerted by the pores vanishes gradually. Normal grain growth can be inhibited by solute drag, due to grain boundary segregation reducing the grain boundary energy and mobility. In some cases, abnormal grain growth commences during sintering. A decreased drag force resulting from an accelerated “dissolution” of pores at the boundaries with a liquid phase layer can trigger abnormal grain growth. Due to an increased grain size in the matrix, the abnormal grain growth is usually incomplete, which results a duplex grain size after firing. In the absence of abnormal grain growth, microstructure is relatively fine-grained and homogeneous. The microstructure of multiphase sintered products is always fine-grained due to inhibition of abnormal grain growth. Finally, as an effect of lower sintering (sufficient in Sol-Gel technique) on the nanostructured manganite properties, the grain size reduces with increasing grain boundary density results into the better (enhanced)
surface influence. This can engineer the transport, magnetotransport and magnetic properties in the manganites. Fig. 2.2 shows the typical flow chart of Sol-Gel synthesis method.

![Flow chart of Sol-Gel method](image)

**Figure 2.2** Typical flow chart of Sol-Gel method

### 2.3 Diffraction Techniques

For the structural characterization of 3-D polycrystalline bulk, 2-D thin films of manganites, usually XRD technique is used to identify the phase purity, types of phases and crystallographic structure of the sample. For detailed structural studies like bond length and bond angle variations, magnetic structure refinement etc, ND is a powerful tool. During the course of present work, both the experimental techniques of structural characterization have been used. Three sources of radiation are important: X-rays, synchrotron radiation and neutrons. The laws of diffraction, i.e. the interference of diffracted beams holds equally well for all radiations.
2.3.1 X-ray Diffraction (XRD)

Diffraction occurs when waves interact with a regular structure whose repeat distance is about the same as the wavelength of X-ray waves. X-rays have wavelengths of the order of a few angstroms, the same as typical interatomic distances in crystalline solids so they can interact with atoms and can gain the information at atomic level. Crystalline materials can be described by their unit cell which is the smallest unit describing the material. In the material, this unit cell is then repeated over and over in all directions. This will result in planes of atoms at certain intervals. Fig. 2.3 shows the schematic representation of x-ray diffractometer.

![Schematic representation of X-ray diffractometer](image)

Figure 2.3 Schematic representation of X-ray diffractometer
X-ray powder diffraction is a powerful non-destructive testing method for
determining a range of physical and chemical characteristics of materials. It is widely
used in all fields of science and technology. The applications include phase analysis, i.e.
the type and quantities of phases present in the sample, the crystallographic unit cell and
crystal structure, crystallographic texture, crystalline size, macro-stress and microstrain,
and also electron radial distribution functions. X-ray diffraction results from the
interaction between X-rays and electrons of atoms. Depending on the atomic
arrangement, interferences between the scattered rays are constructive when the path
difference between two diffracted rays differs by an integral number of wavelengths. This
selective condition is described by the Bragg equation, also called “Bragg’s law”:

\[ n \lambda = 2d_H \sin \theta_H \]

where \( d_H \) = inter planar distance (d-spacing), \( \theta_H \) = half angle between incident and
reflected beam (or the angle between the incident/reflected beam and particular crystal
planes under consideration), \( n \) = order of reflection (integer value), \( \lambda_H \) = wave length of
x-rays. H describes the Miller indices triplet \((h \ k \ l)\) of each lattice plane [fig. 2.4].

Figure 2.4  Schematic representation of diffraction of x-rays by crystallographic plane
(Bragg’s Law)
2.3.2 Neutron Diffraction (ND)

Neutron diffraction is based on nuclear interaction between neutrons and matter on the one hand, and on magnetic interaction with magnetic moments of the atoms due to its magnetic moments. It is the basis for the investigation of magnetic ordering and magnetic structures. The elucidation of magnetic structures is a major application in neutron diffraction. The (ordered) magnetic moments show sometimes very complicated arrangements of the spins or magnetic moments.

To obtain a diffraction pattern of a specimen two experimental methods can be used, independent of radiation:

[1] The “angular dispersive technique” where the X-rays or neutrons are monochromatic and the patterns are obtained by step-scanning the detector with small increments $\Delta(2\theta)$. The increments, i.e. the step size may be between 0.02° and 0.001° in $2\theta$. The decision for the chosen step size is governed besides instrumental, i.e. mechanical conditions of the diffractometer by the time available to collect the diffraction pattern. Recent developments in instrumentation have led to position sensitive detectors which are used more and more in powder diffraction. Commercially available detectors are in general one-dimensional, which record a large portion of the diffraction pattern simultaneously without moving the detector. For the analysis there is no difference to step-scanning procedures. Two-dimensional detectors are also becoming available, which record the complete Debye-Scherrer ring if used with Debye-Scherrer geometry. They are useful to overcome the problems of preferred orientation.

[2] The “energy dispersive technique” where polychromatic X-rays or neutrons are used and the energy of the diffracted X-rays or neutrons is measured at a fixed diffraction angle $2\theta = \text{constant}$. Energy dispersive technique is especially advantageous in experiments at extreme conditions or for kinetic studies, since the complete pattern is available at all times. In the case of neutrons the energy dispersive technique is gaining importance with the availability of spallation sources.
The diffraction patterns look the same in both the cases. The difference is seen in the abscissa, where the 2θ-step scan value is replaced by an energy value $E_H$. The transformation from 2θ to energy is simple:

$$\lambda_{H} = 2d_{H} \sin \theta_{0} = \frac{hc}{E_{H}} = \frac{12.4(keV \times \AA)}{E_{H}}$$

The analytical technique, i.e. the analysis of the diffraction patterns discussed here is independent of radiation and diffraction techniques.

Neutrons tell you “where the atoms are and what the atoms do” (Nobel Prize citation for Brockhouse and Shull 1994). ND is a complementary technique to x-ray diffraction (XRD) and electron diffraction (ED) and possesses a central importance especially for magnetic materials because information about magnetic materials can not be attainable with other two techniques. It can be equally well applied to study crystalline solids, gasses, liquids or amorphous materials. It is very difficult to access source of neutrons for ND technique and it is also very expensive. Then also, there are few good reasons for using neutrons as a materials probe:

- The neutron has no charge therefore not any concomitant coulomb effect and it can penetrate high into matter and so one can study bulk materials
- Neutrons possess a $\frac{1}{2}$ spin with magnetic moment $\mu_n = -1.913$ Nuclear Magneton so that they can interact with magnetic moment including those arising from the electron cloud around an atom. ND can therefore reveal the microscopic magnetic structure of a material
- Neutrons have thermal energies 10 - 100 meV and wavelength (Å) comparable to typical interatomic spacing and vibrational energies of atoms so; one can study both atomic structure and dynamics of material. Thermal neutrons are therefore, useful in studying Atomic Positional Correlations in condensed matter physics
- Neutrons interact directly with the nucleus of the atom, and neutron scattering cross section varies randomly through the periodic table and is isotope dependent so one can distinguish light and heavy atoms or atoms of similar atomic number (Z) enabling the technique of isotopic substitution/contrast variation. It is also often the case that
light (low Z) atoms contribute strongly to the diffracted intensity even in the presence of large Z atoms. The scattering length varies from isotope to isotope rather than linearly with the atomic number.

✔ Magnetic scattering does require an atomic form factor as it is caused by the much larger electron cloud around the tiny nucleus. The intensity of the magnetic contribution to the diffraction peaks will therefore dwindle towards higher angles.

**Instrumental requirements**: Research reactors are typical source of the neutrons. Neutrons in reactor possess too high energies which are thermalized with a moderator consisting of heavy water. The thermal neutrons have kinetic energies extending over a considerable range (continuous Maxwellian distribution), but a monochromatic beam of neutrons with a single energy can be obtained by diffraction from a single crystal and this diffracted beam can be used in diffraction experiments [3]. The neutron powder diffraction measurements on the presently studied \( \text{La}_{0.325}\text{Tb}_{0.125}\text{Ca}_{0.3}\text{Sr}_{0.25}\text{MnO}_{3} \) (LTCSMO) and \( \text{La}_{0.375}\text{Tb}_{0.125}\text{Ca}_{0.5}\text{MnO}_{3} \) (LTCMO) and \( \text{La}_{0.375}\text{Tb}_{0.125}\text{Sr}_{0.5}\text{MnO}_{3} \) (LTSMO) manganites has been carried out using wave length (\( \lambda = 1.249\text{Å} \)) at TT1013 Powder Neutron Diffractometer at Dhruva (100MW), BARC (India). Figure 2.5 shows the schematic illustration of typical neutron powder Diffractometer. The neutrons of wavelength 1.249Å, passing through a Germanium (331) monochromator with flux \( \sim 5 \times 10^{5}\text{n/cm}^2\text{/sec} \) at the sample are focused on the powder sample, kept in vanadium can and cooled to desired temperature using a closed cycle refrigerator (CCR). Diffracted beams is collected by the Position Sensitive Detector (PSD) which can scan \( 2\theta = 3^\circ - 140^\circ \). The typical parameters of neutron powder diffractometer at DHRUVA are summarized in Table 2.1.
Figure 2.5  Powder Neutron diffractometer (schematic)

Table 2.1  Instrument parameters of Neutron diffractometer of DHRUVA, BARC, Mumbai, India

<table>
<thead>
<tr>
<th>Powder Neutron Diffractometer (Instrument parameters) at DHRUVA</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Beam hole No.</strong></td>
</tr>
<tr>
<td><strong>Monochromator</strong></td>
</tr>
<tr>
<td><strong>Incident wavelength (λ)</strong></td>
</tr>
<tr>
<td><strong>Range of scattering angle (2θ)</strong></td>
</tr>
<tr>
<td><strong>Flux at sample</strong></td>
</tr>
<tr>
<td><strong>sinθ / λ</strong></td>
</tr>
<tr>
<td><strong>Sample size</strong></td>
</tr>
<tr>
<td><strong>Detector (1D-PSD)</strong></td>
</tr>
<tr>
<td><strong>Resolution (Δd/d)</strong></td>
</tr>
</tbody>
</table>

The planes in the polycrystalline sample act as grating to the neutron beams, and diffract them. In order to determine crystal structure, it is necessary to record the full diffraction pattern. The diffracted intensities from the sample are measured by neutron detector (D). Both the sample table and the detector arms are rotated in predetermined
step. The sample and the detector move in coupled $\theta$ - 2$\theta$ mode, in angular steps say $\sim 2\theta = 0.05^\circ$. The span of 2$\theta$ scan is over $3^\circ$ - $140^\circ$ for the sample studied. Neutron counts are recorded at each step for a fixed amount of monitor counts. Suitable collimation for in-pile before monochromator ($a_0$), monochromator to sample table ($a_1$) and sample table to detector d ($a$) is provided by a mild steel collimators with slits. The collimators used for the present study from the in-pile to the detector end (D) were 0.5°, 0.7°, 0.5° of arc.

Neutron being a neutral particle, its detection is based on a range of nuclear reactions, which produce energetic charged particles; the most important once are,

\[
^1n_0 + ^3He_2 \rightarrow ^3T_1 + ^1p_1 \quad (a)
\]

\[
^1n_0 + ^{10}B_5 \rightarrow ^7Li_3 + ^1p_1 \quad (b)
\]

Gas counters are filled with $^4_2$He gas or BF$_3$ gas enriched in $^{10}_5$B are employed for neutron detection. For the present experimental set-up, the diffracted neutrons are collected by the Position Sensitive Detector (PSD), which is filled with helium gas. For every neutron falling on the PSD, the reaction (a) takes place, and eventually, the intensity is observed. One incoming neutron interacts with the molecule of Helium gas, and breaks it into one tritium and one proton. Protons are charged particles, which ionizes the helium gas thus producing ions. These ions are recorded, as pulses by the “cathode – anode setup” kept under high potential. The whole cathode length is distributed or sliced into 1024 channels in the Dhruva reactor setup. The counts (pulses i.e., the number of ions falling on the cathode) at each channel are recorded. The multi-channel analyzer (MCA) records the data from each channel and using a discriminator separates out the neutron pulses from the background pulses (which occur due to gamma ray etc.). The data from MCA is fed into the computer from where the intensity vs. channel spectrum can be analyzed and recorded. Using appropriate calibration constants, the channels are converted into corresponding angles. The data collected was analyzed using FULLPROF and/or WINPLOTR based Rietveld refinement suites as described below [4].
2.3.3 Rietveld Analysis

There are six factors affecting the relative intensities of the diffraction lines on a powder pattern, namely, i) polarization factor, ii) structure factor, iii) multiplicity factor, iv) Lorentz factor, v) absorption factor and vi) temperature factor. A very important technique for analysis of powder diffraction data is the whole pattern fitting method proposed by Rietveld (1969) [5]. The Rietveld method is an extremely powerful tool for the structural analysis of virtually all types of crystalline materials not available as single crystals. The method makes use of the fact that the peak shapes of Bragg reflections can be described analytically and the variations of their width (FWHM) with the scattering angle $2\theta$. The analysis can be divided into number of separate steps. While some of these steps rely on the correct completion of the previous one(s), they generally constitute independent task to be completed by experimental and depending on the issue to be addressed by any particular experiment, one, several or all of these tasks will be encountered [6].

The parameters refined in the Rietveld method fall into mainly three classes: peak-shape function, profile parameters and atomic and structural parameters. The peak shapes observed are function of both the sample (e.g. domain size, stress/train, defects) and the instrument (e.g. radiation source, geometry, slit sizes) and they vary as a function of $2\theta$. The profile parameters include the lattice parameters and those describing the shape and width of Bragg peaks (changes in FWHM and peak asymmetry as a function of $2\theta$, $2\theta$ correction, unit cell parameters). In particular, the peak widths are smooth function of the scattering angle $2\theta$. It uses only five parameters (usually called U, V, W, X and Y) to describe the shape of all peaks in powder pattern. The structural parameters describe the underlying atomic model include the positions, types and occupancies of the atoms in the structural model and isotropic or anisotropic thermal parameters. The changes in the positional parameters cause changes in structure factor magnitudes and therefore in relative peak intensities, whereas atomic displacements (thermal) parameters have the effect of emphasizing the high angle region (smaller thermal parameters) or de-emphasizing it (larger thermal parameters). The scale, the occupancy parameters and the thermal parameters are highly correlated with one another and are more sensitive to
the background correction than are the positional parameters. Thermal parameter refinement with neutron data is more reliable and even anisotropic refinement is sometimes possible. Occupancy parameters are correspondingly difficult to refine and chemical constraints should be applied whenever possible [7].

Once the structure is known and a suitable starting model is found, the Rietveld method allows the least-squares refinement [chi-square ($\chi^2$) minimization] of an atomic model (crystal structure parameters) combined with an appropriate peak shape function, i.e., a simulated powder pattern, directly against the measured powder pattern without extracting structure factor or integrated intensities. With a complete structural model and good starting values of background contribution, the unit cell parameters and the profile parameters, the Rietveld refinement of structural parameters can begin. A refinement of structure of medium complexity can require hundred cycles, while structure of high complexity may easily require several hundreds. The progress of a refinement can be seen from the resultant profile fit and the values of the reliability factors or R-values. The structure should be refined to convergence. All parameters (profile and structural) should be refined simultaneously to obtain correct estimated standard deviations can be given numerically in terms of reliability factors or R-values [8].

The weighted –profile R value, $R_{wp}$, is defined as,

$$R_{wp} = 100 \left( \frac{\sum_{i=1,n} w_i \mid y_i - y_{c,i} \mid^2}{\sum_{i=1,n} w_i y_i^2} \right)^{1/2}$$

Ideally, the final $R_{wp}$, should approach the statistically expected R value, $R_{exp}$,

$$R_{exp} = 100 \left[ \frac{n - p}{\sum_i w_i y_i^2} \right]^{1/2}$$

where, N is the number of observations and P the number of parameters. $R_{exp}$ reflects the quality of data. Thus, the ratio between the two (goodness of fit),
\[ \chi^2 = \left( \frac{R_{wp}}{R_{exp}} \right)^2 = s^2 \]

An R value is observed and calculated structure factors, \( F_{hkl} \), can also be calculated by distributing the intensities of the overlapping reflections according to the structural model,

\[ R_F = 100 \frac{\sum_h |F_{obs,k} - F_{calc,k}|}{\sum_h |F_{obs,k}|} \]

Similarly, the Bragg-intensity R value can be given as,

\[ R_B = 100 \frac{\sum_h |I_{obs,k} - I_{calc,k}|}{\sum_h |I_{obs,k}|} \]

R values are useful indicators for the evaluation of refinement, especially in the case of small improvements to the model, but they should not be over interpreted. The most important criteria for judging the quality of a Rietveld refinement are i) the fit of the calculated pattern to the observed data and ii) the chemical sense of structural model.

The neutron diffraction measurement requires a neutron source (e.g. a nuclear reactor or spallation source), a sample (the material to be studied), and a detector. Sample sizes are large compared to those used in X-ray diffraction. The technique is therefore mostly performed as powder diffraction. At a research reactor, other components such as crystal monochromators or filters may be needed to select the desired neutron wavelength. Some parts of the set-up may also be movable. At a spallation source, the time of flight technique is used to sort the energies of the incident neutrons, so no monochromator are needed, just a bunch of electronics.
2.4 Microstructure

2.4.1 Scanning Electron Microscopy (SEM)

In this class of microscopes that use electrons are used rather than visible light, to produce magnified images, especially of objects having dimensions smaller than the wavelengths of visible light, with linear magnification approaching or exceeding a million \((10^6)\). An electron microscope forms a three dimensional image on a cathode ray tube by moving a beam of focused electrons across an object and reading both the electrons scattered by the object and the secondary electrons produced by it. High powered indirect microscope produces an image by bombarding a sample with a beam of high energy electrons. The electrons emitted from the sample are then scanned to form a magnified image which allows the examination of the structure, relief and morphology of materials. In addition to its great magnification, the SEM also has a great depth of field. Most SEM also have a facility to analyze the X-rays given off by the target as a result of its bombardment and, as each element in the periodic table produces its own X-ray spectrum, this can be used to determine the elemental content of the sample.

Scanning electron microscope (SEM) is used for studying the surface topography, microstructure, and chemistry of metallic and nonmetallic specimens at magnifications from 50 up to \(~ 100,000\) X, with a resolution limit \(< 10\)nm (down to \(~ 1\)nm) and a depth of focus up to several \(\mu m\) (at magnifications \(~ 10,000\) X). In SEM, a specimen is irradiated by an electron beam and data on the specimen are delivered by secondary electrons coming from the surface layer of thickness \(~ 5\)nm and by backscattered electrons emitted from the volume of linear size \(~ 0.5\)\(\mu m\). Due to its high depth of focus SEM is frequently used for studying fracture surfaces. High resolving power makes SEM quite useful in metallographic examinations. Sensibility of backscattered electrons to the atomic number is used for the detection of phases of different chemistry. Electron channeling in SEM makes it possible to find the orientation of single crystals by electron channeling pattern (ECP) or of grains by selected area channeling pattern (SACP).
Accelerated electrons in an SEM carry significant amount of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD) that are used to determine crystal structures and orientations of minerals, photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered
Electrons are most valuable for illustrating contrasts in composition in multiphase samples. Characteristic X-rays are produced for each element in a mineral that is "excited" by the electron beam. SEM analysis is considered to be "non-destructive"; that is, X-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly. The schematic block diagram of SEM is shown in Fig. 2.6 indicating the interaction of the electron beam with a sample producing secondary, reflected electrons, X-rays, etc. Depending on the type of the detector, the radiation emitted by the sample is transformed into electrical signals which, after amplification, are used to modulate a cathode-ray tube display where an image of the sample surface is formed.

2.4.2 Atomic Force Microscopy (AFM)

Atomic force microscope (AFM) device is used for studying the surface atomic structure of solids. AFM is similar, in design, to Scanning tunneling microscope (STM), but measures the force between the sharp microscope tip and surface atoms. AFM is device for studying the surface topography of solid electronic conductors with a lateral resolution better than the atomic size. In STM, a sharp microscope tip is scanned over the specimen surface without touching it, and at the same time, the tunneling current between the tip and the surface atoms, proportional to the distance between them, is recorded. The results obtained are transformed into the images displaying the atomic structure of a clean surface or an atomic arrangement.

Fig. 2.7 shows the schematic representation of AFM indicating that, the AFM consists of a microscale cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface. The cantilever is typically silicon or silicon nitride with a tip radius of curvature of the order of nanometers. When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooke's law. Depending on the situation, forces that are measured in AFM include mechanical contact force, Van der Waals forces, capillary forces, chemical bonding, electrostatic forces, magnetic forces etc. Typically, the deflection is measured using a laser spot reflected from the top of the cantilever into an array of
photodiodes. Other methods that are used include optical interferometry, capacitive sensing or piezoresistive AFM probes. These probes are fabricated with piezoresistive elements that act as a strain gage. Using a Wheatstone bridge, strain in the AFM probe due to deflection can be measured, but this method is not as sensitive as laser deflection or interferometry.

If the tip were scanned at a constant height, there would be a risk that the tip would collide with the surface, causing damage. Hence, in most cases a feedback mechanism is employed to adjust the tip-to-sample distance to maintain a constant force between the tip and the sample. Traditionally, the sample is mounted on a piezoelectric tube that can move the sample in the z direction for maintaining a constant force, and the x and y directions for scanning the sample. Alternately a 'tripod' configuration of three piezo crystals may be employed, with each responsible for scanning in the x, y and z directions. This eliminates some of the distortion effects seen with a tube scanner.

![Figure 2.7 Schematic representation of AFM](image)

2.5 Resistance and Magnetoresistance (MR) measurements

Resistivity is an important measurement for mixed oxide materials. For manganite material, MR is most important which decide the application of material. The samples
under present studies were characterized for their electrical and magneto transport studies by the experimental techniques described below-

2.5.1 Four Probe Resistivity Measurements

Resistivity measurement is quite easy and straightforward to provide much useful information about the electrical properties of the sample. The measurement of electrical resistance as a function of temperature gives information about the various temperature dependent electronic phase transitions. It also gives information about value of critical temperature as well as the quality of the sample. A low contact resistance is desirable due to the small resistance of the samples. To accomplish this requirement, standard four-probe method was used for measuring resistance of the samples [9]. To measure the resistivity using this technique, the samples were cut in a rectangular bar shape using a diamond saw. For the electrical contacts of the probes with the sample, silver paint has been used. Fine slurry of the silver paint is made by dissolving it with an appropriate solvent (n-butyl acetate or thinner). This silver paste is applied at the ends for current and voltage contacts. Due to very less resistance, thin copper wires were connected with silver paint as shown in fig. 2.8 and the whole assembly was put onto a sample holder, where the wires were connected with leads to the measurement instruments. This type of sample holder is known as resistivity puck for measuring resistivity using a Physical Property Measurement System (PPMS).

![Figure 2.8](image)

Figure 2.8 Four probe contacts of current and voltage supplies to the sample during the resistivity measurements.
Samples have low resistance at room temperatures, so a precise accurate current source is used which can pass current of a few microampere and voltmeter used, has a measuring range from nanovolts to a few volts. As shown in the figure, current is passed through the outer probes (+I & -I) and resultant potential difference developed between two points is measured using the inner probes (+V & -V). The resistance can be calculated using the ohm’s law $V = IR$, where $I$ is the current passed and $V$ is the voltage developed. It is crucial to keep the voltage probes between the current probes in a linear way. Using dimensions, shown in figure, the exact resistivity ($\rho$) of the sample can be calculated using the relation 

$$\rho = \frac{RA}{T}$$

where $R$ is the resistance, $A$ ($A = b \times t$) is the cross-sectional area of the sample. Here, it is mentioned that thermo emf is automatically compensated during the measurements. The samples were cooled down using liquefied He. The samples were then heated in a controlled way by using a heater and resistance was measured with slowly increasing temperature.

To study magneto resistive characteristics of the samples, resistance was measured by using the standard four probe method as explained in the previous section, in the presence of an external magnetic field in a Quantum Design Physical Property Measurement System (PPMS). At a constant applied field, resistance was measured as a function of temperature (magneto R-T) in the range of room temperature to ~ 5 K. All the manganites samples studied in the present work were characterized by using this technique.

The PPMS, manufactured by Quantum design [fig. 2.9] basically is a platform with for getting desired magnetic field and temperature with an excellent control. It is versatile and indispensable instrument with a provision to measure many physical properties such as d.c. and a.c. resistivity, specific heat, a.c and d.c. magnetizations, thermopower measurements, hall effect, etc. as a function of temperature, magnetic field and time. During, the course of this thesis work, we have used PPMS for measuring resistivity.
Magnetoresistance is very important property of manganite based materials. Manganite materials show enormous changes in resistance under application of magnetic field around transition temperature ($T_P$) such MR behaviour decides the application of the material. To study the magnetoresistive properties of manganite bulk samples, magnetoresistance (MR) versus temperature and applied magnetic field ($H$) isotherms of the samples were recorded using the standard four probe method as explained above in the presence of an external magnetic field using PPMS (Quantum Design). At constant temperature resistivity was measured with different applied magnetic field, from that MR was calculated for different magnetic fields from 1 to 9T. At a constant temperature, resistance was measured as a function of applied field (MR vs $H$ isotherms) in the range of 50 to 300K.
2.6 Magnetic property measurements

2.6.1 Magnetization studies using Vibrating Sample Magnetometer (VSM)

A Vibrating Sample Magnetometer (VSM) is used to measure the magnetic behavior of magnetic materials. VSM operates on Faraday's law of induction; a changing magnetic field will produce an electric field. This electric field can be measured and can give us information about the changing magnetic field.

When a sample is placed within a uniform magnetic field and made to undergo sinusoidal motion (i.e. mechanically vibrated), there is some magnetic flux change. This induces a voltage in the pick-up coils, which is proportional to the magnetic moment of the sample. Fig. 2.10 shows the block diagram of a typical VSM setup.

A VSM operates by first placing the sample to be studied in a constant magnetic field. If the sample is magnetic, this constant magnetic field will magnetize the sample by aligning the magnetic domains, or the individual magnetic spins, with the field. If the value of the applied constant magnetic field is higher, then, magnetization will be higher. The magnetic dipole moment of the sample will create a magnetic field around the sample, sometimes called the magnetic stray field. As the sample is moved up and down, this magnetic stray field changes as a function of time and can be sensed by a set of pick-up coils. The alternating magnetic field will cause an electric field in the pick-up coils according to Faraday's law of induction. This current will be proportional to the magnetization of the sample. If the sample possesses higher magnetization, induced current will be higher.
The induction current is amplified by a lock-in amplifier. The various components are hooked up to a computer interface. Using controlling and monitoring software, the system can give information about the magnetization value of sample and how its magnetization depends on the strength of the constant magnetic field. A typical measurement on a sample is taken in the following manner:
The strength of the constant magnetic field is set

The sample begins to vibrate

The signal received from the probe is translated into a value for the magnetic moment of the sample

The strength of the constant magnetic field changes to a new value. No data is taken during this transition

The strength of the constant magnetic field reaches its new value

The signal from the probe again gets translated into a value for the magnetization of the sample

The constant magnetic field varies over a given range, and a plot of magnetization (M) versus magnetic field strength (H) is generated
References


Chapter 3

Neutron Diffraction Studies on
La_{0.325}Ti_{0.125}Ca_{0.30}Sr_{0.25}MnO_3 (LTCSMO) Manganite

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3.1 Introduction

A formidable amount of work has been devoted aiming towards the understanding of the structure and properties of colossal magnetoresistance (CMR) manganites [1]. Manganites are sensitive to changes in external conditions as well as composition and exhibit rather complex phase diagrams. Mixed valent manganites with the general formula $R_{1-x}A_xMnO_3$ (R = trivalent rare earth ion and A = divalent ion like Sr$^{+2}$, Ba$^{+2}$, Pb$^{+2}$, Ca$^{+2}$ etc.) are found to exhibit variety of phenomena such as charge, spin and orbit ordering, electronic magnetic and structural transitions depending on the type and/or amount of doping (x). It has been accepted that, the double exchange (DE) mechanism can not by itself account for all the observed effects, in the CMR materials [2, 3]. Other mechanisms involving, electron - phonon coupling [4], electron - magnon interactions [5], phase and charge segregation [6, 7] and other electronic effects [8, 9] have been proposed to explain the variety of observed phenomena. In the mixed valent manganites, Mn ion in Mn$^{+3}$ and Mn$^{+4}$ oxidation states, occupying the specific lattice sites, known as charge ordering is responsible for electron localization thereby restricting the hoping of electrons from one site to another. The doped manganites with doping level $x = 0.5$ such as La$_{0.5}$Ca$_{0.5}$MnO$_3$, La$_{0.5}$Sr$_{0.5}$MnO$_3$ etc have attracted the attention due to the interesting charge and orbital ordering correlation exhibited by them [10, 11]. These half doped manganites show transformation from a ferromagnetic metallic (FMM) to charge ordered (CO) antiferromagnetic (AFM) state at a certain temperature below Curie point ($T_C$) [10, 11]. The co-existence of AFM and CO states has its origin in long-range co-operative Jahn-Teller effect and regular alternate arrangement of Mn$^{3+}$ and Mn$^{4+}$ ions i.e. real space ordering of Mn$^{3+}$ and Mn$^{4+}$ ions [10]. It is reported that, charge ordered (CO) state in manganites is sensitive to chemical substitution at Mn site, A - site ionic radii mismatch, average size of A - site cations etc [12]. The A - site ionic radii mismatch leads to size variance $\sigma^2$ which is quantified as $\sigma^2 = \Sigma x_i r_i^2 - <r_i>^2$, where $x_i$ is a fractional occupancy and $r_i$ is the corresponding ionic radius. It is established that, size mismatch and disorder at A - site affect the MnO$_6$ octahedra and also Mn-O-Mn bond angles, play an important role in the modification of magnetic and transport properties of the manganites [13].
Consider the cases of half doped La\(_{0.5}\)Ca\(_{0.5}\)MnO\(_3\) (LCMO), having \(<r_A>\sim 1.198\text{Å} \) and insulator – metal transition temperature, \(T_{IM}\sim 220\text{K} \) and antiferromagnetic transition temperature \((T_N)\sim 170\text{K} \) with \(\sigma^2 \sim 3.24 \times 10^{-4} \text{Å}^2 \) \[14\] and La\(_{0.5}\)Sr\(_{0.5}\)MnO\(_3\) (LSMO), having \(<r_A>\sim 1.263\text{Å}, \ (T_{IM})\sim 300\text{K} \) and \(\sigma^2 \sim 22.09 \times 10^{-4} \text{Å}^2 \) much higher than that of LCMO. The simultaneous substitution of smaller magnetic Tb\(^{+3}\) ion and larger Sr\(^{+2}\) ion at La\(^{+3}\) site with the stoichiometric composition \((\text{La}_{0.325}\text{Tb}_{0.125})(\text{Ca}_{0.3}\text{Sr}_{0.25})\text{MnO}_3\) (LTCSMO) results into \(\sigma^2 \sim 45.2 \times 10^{-4} \text{Å}^2\) and \(<r_A>\sim 1.213\text{Å} \) which is greater than that of LCMO and smaller than that of LSMO half doped manganites. This may result into the modifications in the structural, transport and magnetic properties of LTCSMO. It is reported that, with \(x = 0.0 - 0.3\) in \((\text{La}_{1-x}\text{Tb}_x)_{2/3}\text{Ca}_{1/3}\text{MnO}_3\), \(T_{IM}\) shifts toward lower temperature with resistivity suppression under applied field \[15\].

During the course of present work, the detailed temperature dependent neutron diffraction (ND) studies on \((\text{La}_{0.325}\text{Tb}_{0.125}\text{Ca}_{0.3}\text{Sr}_{0.25})\text{MnO}_3\) (LTCSMO) compound were carried out to understand the effect of simultaneous Tb and Sr doping \([\text{Tb}(x) = 0.125 \& \text{Sr}(2x) = 0.25]\) in LCMO on the modifications in the structural behavior in the light of variations in Mn-O distances and Mn-O-Mn bond angles. The modifications in cell parameters, thermal parameters and various inter atomic distances as a function of temperature has been studied using neutron diffraction. In addition, the presence of coexisting magnetic phases, at lower temperatures, in the LTCSMO has been investigated using temperature dependent neutron diffraction studies.
3.2 Synthesis and Experimental Details

The bulk polycrystalline sample of \((\text{La}_{0.73-3x}\text{Tb}_x)(\text{Ca}_{0.3}\text{Sr}_{2x})\text{MnO}_3\) (LTCSMO) with \(x = 0.125\) was synthesized using conventional solid state reaction (SSR) method. Various steps involved in the synthesis of bulk LTCSMO samples are shown in fig. 3.1. The high purity starting materials, \(\text{La}_2\text{O}_3\), \(\text{Tb}_2\text{O}_3\), \(\text{CaCO}_3\), \(\text{SrCO}_3\) and \(\text{MnO}_2\) were mixed in stoichiometric ratio and calcined at \(950^\circ\text{C}\) for 24 hours. The calcined powder was then ground, palletized and sintered at various temperatures between 1100 - 1375\(^\circ\text{C}\) with intermittent grindings.

Figure 3.1 Schematic diagram of Solid State Reaction route used
The structural studies were carried out using Rigaku X-Ray diffractometer, to confirm the single phasic nature of the sample. The Neutron Diffraction measurements were performed at various temperatures (RT - 20K) using multiposition sensitive detector based powder neutron diffractometer on the beam line T-1013 at Dhruva reactor, BARC, Mumbai. The transport and magnetotransport properties were investigated using the D.C. four probe resistivity technique in the temperature range 45-300K with and without applied fields. The field cooled (FC) and zero field cooled (ZFC) magnetization measurements were carried out using VSM facility in the temperature range 5-325K to understand the magnetic behavior of the sample.

3.3 Structural Studies

3.3.1 X-ray Diffraction

Fig. 3.2 shows the XRD pattern (raw data) of LTCSMO with the reflections indexed using Powder-X software. The detailed structural information was obtained by fitting the XRD data using the Rietveld refinement technique employing Fullprof code [16]. Fig. 3.3 shows the Rietveld refined XRD pattern of LTCSMO compound. Refinement was done in different steps to achieve proper fitting parameters. Lorentzian 1 function was used to fit the XRD pattern. Very less difference between observed and calculated pattern reveals the reliability of fitted pattern. Within the instrumental resolution, no extra peaks were observed confirming the goodness of fit. LTCSMO crystallizes in orthorhombic structure having \( Pnma \) space group.
Neutron Diffraction Studies on La$_{0.325}$Tb$_{0.125}$Ca$_{0.3}$Sr$_{0.25}$MnO$_3$ (LTCSMO) Manganite

Figure 3.2  XRD pattern of La$_{0.325}$Tb$_{0.125}$Ca$_{0.3}$Sr$_{0.25}$MnO$_3$

Figure 3.3  Rietveld refined XRD pattern of La$_{0.325}$Tb$_{0.125}$Ca$_{0.3}$Sr$_{0.25}$MnO$_3$
3.3.2 Neutron Diffraction

Neutron Diffraction (ND) is a powerful and popular technique, which is primarily used to determine the structure of crystalline materials. The temperature dependent Neutron Diffraction patterns were recorded on the multi-position sensitive detector based powder diffractometer on the beam line T - 1013, using wavelength $\lambda = 1.249\text{Å}$, at the Dhruva reactor, BARC, Mumbai in the $2\theta$ range of $6^\circ$ to $140^\circ$ at selected temperatures between 20 - 300K. For Neutron Diffraction experiment, powder sample weighing ~ 7 gms was filled in Vanadium container of 6mm diameter and attached to close cycle refrigeration (CCR) in order to investigate the temperature dependent modifications in the structural and magnetic behavior of the sample.

Fig. 3.4 shows the Neutron Diffraction patterns (raw data) taken at different temperatures. At 100K one can observe the emergence of peak at lower angle, $2\theta \sim 9^\circ$ which becomes more intense at 50 and 20K (as shown by arrow in the figure). At 20K two more peaks arise at $2\theta \sim 11.4^\circ$ and $13.3^\circ$, indicated by downward arrows in ND plot taken at 20K fig. 3.5 shows the magnified view of the low angle peaks observed in the ND patterns at 100, 50 and 20K in LTCSMO.
Figure 3.4 Neutron Diffraction patterns (raw data) recorded at different temperatures of LTCSMO
Pseudo - Voigt profile shape was used to fit the ND patterns collected at different temperatures because the Voigt function has one of the best symmetrical components for the peak shape which is used for constant wavelength X-Ray and Neutron Diffraction data analysis [17]. The Rietveld refinement using FULLPROF code was carried out in various steps. First, zero point of the detector with background parameters and scale factor were varied, followed by the variation in the full width half maximum parameters. Subsequently, general positions and thermal parameters were varied with the occupancies of the various atoms of the unit cell. In the last, magnetic phases were taken into account for ND patterns taken at 100, 50 and 20K and the moments of Mn$^{+3}$ and Mn$^{+4}$ ions were varied in both A - type and CE - type AFM phases. Figs. 3.6 (a - f) show typical Rietveld refined and fitted ND patterns of LTCSMO sample, data taken at different temperatures ranging between 20 - 300K. Detailed analyses of ND patterns yield interesting information about the nuclear and magnetic phases present in the sample. The values of various structural parameters, positions and refinement parameters at different
temperatures obtained from the Rietveld analysis are given in Table 3.1. These values indicate the goodness of fit for the patterns taken at different temperatures.

An attempt was made to fit the low temperature ND data of LTCSMO using the nuclear phase which resulted in the inability to fit some low angle magnetic peaks present in the data. Using A-type AFM phase, it was possible to fit the magnetic peak at $2\theta \sim 9^\circ$ in the low temperatures ND patterns taken at 100, 50 and 20K [shown by arrow in the figs 3.6 (d), (e) & (f)]. The other two low intensity peaks at $2\theta \sim 11.4^\circ$ and $13.3^\circ$ observed in 20K ND data [shown by asterisk* in the inset of fig 3.6 (f)] could not be fitted satisfactorily. In order to fit all the peaks present in the ND pattern at 20K, CE-type AFM phase was added, resulting in a complete profile fitting. This suggested the coexistence of two magnetic phases, namely, A-type and CE-type AFM phase present in the sample at 20K.

![Graph](image-url)
Neutron Diffraction Studies on La$_{0.325}$Tb$_{0.125}$Ca$_{0.3}$Sr$_{0.25}$MnO$_3$ (LTCSMO) Manganite

(b) 200K

(c) 150K
Neutron Diffraction Studies on La$_{0.325}$Tb$_{0.125}$Ca$_{0.3}$Sr$_{0.25}$MnO$_3$ (LTCSMO) Manganite
Figure 3.6  Rietveld refined pattern shows observed (o symbol) and calculated (line) Neutron Diffraction data for La$_{0.325}$Tb$_{0.125}$Ca$_{0.3}$Sr$_{0.25}$MnO$_3$, recorded at (a) 300K, (b) 200K, (c) 150K, (d) 100K, (e) 50K and (f) 20K. Tick mark below the diffraction profile mark the position of allowed Bragg reflections. The difference between the observed and calculated values is given at the bottom. [Inset of figure 3.9 (f) shows the A - type AFM phase indexed as (020) and CE - type AFM phase indexed as (01½) and (½1½)]

The inset of fig. 3.6 (f) shows the low intensity magnetic peaks, indicating the characteristic of A - type and CE - type AFM phases respectively present in the sample at 20K. It is reported that, in charge ordered La$_{0.5}$Ca$_{0.5-x}$Sr$_x$MnO$_3$ (LCSMO); x = 0.0 - 0.3, CE-type AFM phase exist below Sr$_{(x)}$ = 0.4, above which, A - type AFM phase occurs in La$_{0.5}$Ca$_{0.1}$Sr$_{0.4}$MnO$_3$ sample [18]. This indicates that, Sr - doping helps in the development of A - type AFM phase in the sample.
Table 3.1 Structural parameters of (La\textsubscript{0.325}Tb\textsubscript{0.125})(Ca\textsubscript{0.3}Sr\textsubscript{0.25})MnO\textsubscript{3} obtained from the Rietveld refinement of the neutron diffraction patterns collected at different temperatures.

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<th>150K</th>
<th>200K</th>
<th>300K</th>
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</tr>
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<td>1.9072(6)</td>
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<td>1.9238(9)</td>
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<tr>
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<tr>
<td>Mn-O\textsubscript{22} (Å)</td>
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<tr>
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<td>0.25</td>
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<tr>
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<td>-0.0033</td>
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<td>-0.0064</td>
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<td>0.4950</td>
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<td>9.97</td>
<td>9.72</td>
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<tr>
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</tbody>
</table>
3.4 Transport Properties

During the course of present studies, the transport properties of simultaneously Tb$^{3+}$ and Sr$^{2+}$ doped (La$_{0.7-3x}$Tb$_x$)(Ca$_{0.3}$Sr$_{2x}$)MnO$_3$; $x = 0.125$ sample have been investigated and an effort is made to establish a structure-property correlation in this sample using the temperature dependent ND studies and transport and magneto transport measurements.

Earlier studies, by our group, on the resistivity behaviour of (La$_{0.7-3x}$Tb$_x$)(Ca$_{0.3}$Sr$_{2x}$)MnO$_3$; $x = 0.025$ - $0.1$ samples by Rana et al [19] show that, the insulator-metal transition temperature ($T_{IM}$) decreases with increase in doping level ($x$) which has been attributed to the increase in the size variance. The presently studied (La$_{0.325}$Tb$_{0.125}$)(Ca$_{0.3}$Sr$_{0.25}$)MnO$_3$ (LTCSMO) sample, having $x = 0.125$ is different from the reported (La$_{1-x}$Tb$_x$)$_{0.7}$Ca$_{0.3}$MnO$_3$ system [15] in a way that, substitution of Sr$^{2+}$ along with Tb$^{3+}$ results in an increase in carrier density while in the reported system [15], it remains constant.

![Figure 3.7](rho_vs_T_plots.png)

Figure 3.7 $\rho$ vs $T$ plots of La$_{0.325}$Tb$_{0.125}$Ca$_{0.3}$Sr$_{0.25}$MnO$_3$ under various applied fields
It can be seen from fig. 3.7 that, under 0 and 1T fields, the sample exhibits insulating behavior with large resistivity value (~ 10.54Ωcm) due to the size variance effect. The robust orbital ordering at and below 100K leading to insulating behavior can not be broken under 1T field. However, under application of 5T field, the sample exhibits a broad insulator - metal transition at \( T_{\text{IM}} \sim 73\text{K} \) which increases to \( \sim 83\text{K} \) under 8T field. It can be observed that resistivity decreases with increasing applied field and \( T_{\text{IM}} \) shift towards higher temperature.

To study and understand the electronic transport in semiconducting region doped manganites, mainly four models are reported in the literature.

1. Nearest neighbor hopping or the activation beyond the mobility edge given by
\[
\rho = \rho_o \exp \left( \frac{E_a}{kT} \right) \quad [20]
\]

2. Adiabatic nearest neighbor small polaron hopping (SPH) model
\[
\rho = AT \exp \left( \frac{E_a}{kT} \right) \quad [21, 22]
\]

3. Schklovskii-Efros (SE) type of Variable Range Hopping with a soft gap due to modification of density of states by Coulomb interaction given by
\[
\rho = \rho_o \exp \left( \frac{T_o}{T} \right)^{1/2} \quad [23]
\]

4. Variable Range Hopping (VRH) of Mott type for uncorrelated carriers
\[
\rho = \rho_o \exp \left( \frac{T_o}{T} \right)^{1/4} \quad [24, 25]
\]

To understand the nature of electronic conduction in the semiconducting region of the presently studied LTCSMO sample, an effort was made to fit resistivity data under different fields, using the above mentioned models. It was observed that the data fits best in the VRH model of Mott type for uncorrelated carriers, where \( \rho_o \) is the residual resistivity and \( T_o \) is related to carrier localization length. In order to understand the nature of electron conduction in LTCSMO, the \( \rho - T \) data has been fitted in Variable Range Hoping (VRH) model, as shown in the fig. 3.8.
The values of activation energy, $E$, calculated using the equitation $T_0 = \frac{E}{K}$ [K is Boltzmann constant (8.617×10^{-5} eV/K)] are 48.26, 47.72, 35.23 and 10.22 K at 0, 1, 5 and 8T fields respectively. It can be seen that, the activation energy decreases with increasing applied magnetic field suggesting that, the localization length is suppressed favoring the hopping of charge carriers from one site to another with increasing field.
3.5 Magnetotransport Properties

Due to the magnetoresistive properties of the manganites, they are very useful compounds from fundamental understanding as well as application point of view. Magnetoresistance (MR) is calculated using the formula -

$$MR \% = \frac{\rho_0 - \rho_H}{\rho_0} \times 100$$

where $\rho_0$ and $\rho_H$ are the resistivities measured under the applied field of zero and H, respectively. The resistivity measurement on the LTCSMO shows that it remains insulating up to 45K (under 0 and 1T fields) within the limit of resistivity instrument. The variation in MR calculated at 5 and 8T fields (under which metal-insulator transition was observed) is shown in fig. 3.9. It is clear that, MR increases with decreasing temperature and increasing field which can be attributed to the insulating nature of the sample under zero applied fields.

![Variation in MR with temperature under 5 and 8T fields for LTCSMO](image_url)

**Figure 3.9** Variation in MR with temperature under 5 and 8T fields for LTCSMO
Considering this constrain during the course of the magneto transport studies on LTCSMO sample, the MR vs H isotherms in the field range 0 - 8T, were collected at 50, 100, 200 and 300K in order to understand variation in MR with applied field below $T_P$, around $T_P$ and well above $T_P$. Fig. 3.10 shows the MR vs H isotherms obtained at various temperatures for LTCSMO sample.

![MR vs H isotherms](image)

**Figure 3.10** MR vs H isotherms collected at various temperatures for $\text{La}_{0.325}\text{Tb}_{0.125}\text{Ca}_{0.3}\text{Sr}_{0.25}\text{MnO}_3$

It can be clearly seen that, MR increases with applied field which can be attributed to the magnetic field induced suppression in magnetic disorder and reduction in scattering of the charge carriers. It is also clear that, high field magnetoresistance (HFMR), under 9T field, is suppressed with increase in temperature. The HFMR is ~ 50, 35, 19 and 5% observed at 50, 100, 200 and 300K. This can be understood in terms of increase in electron phonon coupling and lattice vibrations with temperature resulting in the reduction of HFMR. There is no any significant MR under low applied field indicating the absence of the role of microstructure.
3.6 Magnetic Measurements

In order to investigate the role of non magnetic Sr$^{2+}$ substitution along with magnetic Tb$^{3+}$ ion on the modification in magnetic behaviour of $(\text{La}_{0.7-3x}\text{Tb}_x)(\text{Ca}_{0.3}\text{Sr}_{2x})\text{MnO}_3$ (x = 0.125) nearly half doped manganite, we have carried out magnetization measurements in the temperature range of 20 - 325K and under 150Oe field, both in Zero-field-cooled (ZFC) and field-cooled (FC) states using Vibrating Sample Magnetometer (VSM) at SSPD, BARC, Mumbai. Fig. 3.11 shows the $M_{\text{FC}}$ and $M_{\text{ZFC}}$ plots for LTCSMO sample.

![Graph showing ZFC and FC magnetization plots of La$_{0.325}$Tb$_{0.125}$Ca$_{0.3}$Sr$_{0.25}$MnO$_3$.](image)

It is clear from the fig. 3.11 that, sample exhibits the Curie temperature $T_C \sim$ 47K ($T_C$ taken as the bifurcation temperature of $M_{\text{ZFC}}(T)$ and $M_{\text{FC}}(T)$ curves). Our earlier, group study, showed that, in the $(\text{La}_{0.7-3x}\text{Tb}_x)(\text{Ca}_{0.3}\text{Sr}_{2x})\text{MnO}_3$ (x = 0.25, 0.50, 0.75, 0.1 & 0.125) series, $T_C$ continuously decreases with increase in doping level x which has been explained as due to the size disorder, resulting in a random displacement of oxygen ions.
from their normal crystallographic positions [19]. As shown in inset of fig. 3.11, magnetization curve shows, two low temperature transitions obtained from the ND measurements (discussed below) first at ~ 47K which indicates the CE-type antiferromagnetic ordering while second at ~ 147K indicating the presence of A-type AFM ordering.

3.7 Discussion and Conclusions

In manganites, variations in structural parameters like lattice constants, Mn-O-Mn bond angles and Mn-O bond lengths play a crucial role in governing the physical properties and their correlations. In order to understand the structural changes with temperature in LTCSMO derived from the Rietveld refinement of ND data, the variation in lattice parameters, cell volume, Mn-O bond distances and Mn-O-Mn bond angles with temperature is shown in fig. 3.12 (a)-(d). It is clearly seen that, with decrease in temperature below 100K, lattice parameters a and c increase while b decreases appreciably with the corresponding decrease in cell volume. Such a behavior is normally observed in sample exhibiting CE - type AFM phase associated with orbital ordering [14]. At and below 100K, the marginal variations in cell parameters indicate the signature of orbital ordering results into the CE - type AFM phase [26]. The variation in Mn-O bond length with temperature plotted in fig. 3.12 (c) depicts that, there is no large change in Mn-O₁ bond length except a slight decrease to lower value at 200K. The average Mn-O bond length remains almost constant over the complete temperature range studied. The two oxygen positions in MnO₆ octahedron are nomenclatured as apical - O₁ and basal - O₂ respectively. The nature of variation in Mn-O₂₁ and Mn-O₂₂ bond lengths as a function of decrease in temperature is opposite indicating the MnO₆ octahedral distortion. At and below 100K, the difference between Mn-O₂₁ and Mn-O₂₂ bond lengths decreases, suggesting the suppression in octahedral distortion. This observation is supported by the reduction in difference between Mn-O₁-Mn and Mn-O₂-Mn bond angles at 100K and below, due to the suppression in MnO₆ octahedral distortion, as depicted in fig. 3.12 (d).
Using the observed Orbital Ordering (OO) present at low temperatures in LTCSMO compound, sample exhibits insulating behavior. This OO can not be broken under the application of 1T field. However, under the application of 5T field, the sample exhibits a broad insulator - metal transition at $T_{IM} \sim 73K$ which increases to $\sim 83K$ under 8T field.
In our LTCSMO sample, A-type AFM reflection, indexed in a $\times$ 2b $\times$ c unit cell having Pnma space group is (020) while CE-type AFM reflections are indexed as (01½) and (½1½). For CE-type structure, there are two different occupancy sites for Mn$^{3+}$ and Mn$^{4+}$. At 20K, magnetic moments obtained from the Rietveld refinement for CE-type AFM phase are 2.258 and 3.794 $\mu_B$/Mn for Mn$^{3+}$ and Mn$^{4+}$ ions respectively while the magnetic moment of Mn$^{3+}$ ion obtained in a-b plane is 3.271 $\mu_B$/Mn in A-type AFM phase. Fig. 3.13 shows the variation in integrated intensity of the A-type AFM reflection (020) with temperature below 200K for LTCSMO sample. Linear fit to the data points intercept X-axis at $\sim$ 143K suggests an absence of A-type AFM ordering above this temperature. There is no evidence of enhancement in the intensity of the low angle fundamental Bragg reflections particularly below the ferromagnetic transition.
temperature, 47K. From the reported M vs T behavior [19], it is observed that, for a given field and temperature, M decreases with increase in x. Absence of signature of long range order in ND pattern indicates that, the moment is too small to be detected in ND measurements. However, coexistence of nano clusters of FM and AFM cannot be ruled out. The inset of fig. 3.13 shows the variation in integrated intensity of the CE - type AFM reflection with the temperature for LTCSMO compound indicating that the ordering temperatures of the two antiferromagnetic phases are significantly different. It is of interest to note that, the nature of magnetic structure, orbital ordering, and charge ordering behavior in LTCSMO is similar to that observed in half doped compounds where the ratio of Mn$^{3+}$ and Mn$^{4+}$ is 1:1. Similar observation of ‘Pseudo-CE’ - type magnetic structure has been reported in the case of Pr$_{0.7}$Ca$_{0.3}$MnO$_3$ [27].

The $\rho$-T plots highlighting an absence of semiconductor to metal transition under zero and one tesla fields and field induced transitions occurring at ~ 73 and 83K under 5 and 8T fields, suggest the removal of robust orbital ordering at and below 100K under higher applied magnetic fields (5 and 8T). Mott type VRH model nicely fitted to the semiconducting region in the $\rho$-T plots shows the field induced suppression in localization length which results into the enhancement in hoping of charge carriers. The insulating nature of the sample under zero applied field provides an enhancement in MR with decreasing temperature which exhibit two slope behaviors, one upto 120K in which MR increases gradually while second, below 120K, in which MR increases sharply with decreasing temperature under 5 and 8T fields. The sharp increase in MR below 120K can be attributed to the zero field insulating behavior and field induced metallic nature under 5 and 8T fields.
References


Chapter 4

Studies on $\text{La}_{0.375}\text{Tb}_{0.125}\text{A}_{0.5}\text{MnO}_3$ ($\text{A} = \text{Ca and Sr}$)

Half Doped Manganites

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4.1 Introduction

Doped rare earth manganites are of research interest from last two decades owing to the structural, transport, magnetic and magnetotransport and magnetic properties exhibited by them [1]. Various interesting phenomena such as charge ordering (CO), orbital ordering (OO) and spin ordering (SO) observed in half doped manganites have been explored and studied to understand transport and magnetic state of the system [2]. The CO state has been a cynosure of scientific interest because of (i) the spin, charge and orbital correlations resulting in sudden and sharp electronic and magnetic transformations, (ii) melting of antiferromagnetic insulating state to a ferromagnetic metallic state on the application of magnetic field resulting in huge magnetoresistance, (iii) sensitivity of CO state to the internal pressure resulting from variations in average cation size of A-site and mismatch in the size of the various cations at A-site [3]. There are few attempts to study the substitutional effects in such half-doped systems but true understanding of the structural distortions and magnetoelectronic properties is still lacking [4]. The multiple cation substitution has been an interesting issue since it helps us to understand the structural, orbital, spin and charge correlations resulting into the variations in structural, electronic and magnetic behavior [5].

In this context, a complex system with multi component doping at La-site and near to half doping such as La$_{0.325}$Tb$_{0.125}$Ca$_{0.30}$Sr$_{0.25}$MnO$_3$ (LTCSMO) has been studied and results are discussed in Chapter - 3. The temperature dependent Neutron Diffraction study on LTCSMO showed the co-existence of A-type and CE-type AFM magnetic ordering at low temperature ~ 50K [6]. In order to investigate the role of independent substitution of Ca$^{2+}$ having comparative smaller ionic radius (~ 1.18 Å) and Sr$^{2+}$ doping (ionic radius ~ 1.31 Å) at La-site (ionic radius ~ 1.216 Å) in LaMnO$_3$ manganite, the structural, transport and magnetic properties of (La$_{0.375}$Tb$_{0.125}$)Ca$_{0.5}$MnO$_3$ (LTC) and (La$_{0.375}$Tb$_{0.125}$)Sr$_{0.5}$MnO$_3$ (LTS) have been investigated in the light of ionic radii and size disorder effects. La$_{0.5}$Ca$_{0.5}$MnO$_3$ (LCMO) and La$_{0.5}$Sr$_{0.5}$MnO$_3$ (LSMO) half doped charge order systems are well studied [7, 8] and the effect of Tb$^{3+}$ (x = 0.125) substitution at La-site in modifying various properties of LTC and LTS systems needs to be investigated.
The values of average ionic radii $<r_A>$ for La$_{0.5}$Ca$_{0.5}$MnO$_3$ (LCMO) and La$_{0.5}$Sr$_{0.5}$MnO$_3$ (LSMO) are 1.198 Å and 1.263 Å respectively while size variance values are $\sigma_A^2 \sim 3.24 \times 10^{-4}$ Å$^2$ and $\sim 22.09 \times 10^{-4}$ Å$^2$, respectively. As compared to these, the values of average ionic radii for LTC and LTS are 1.182 Å and 1.247 Å and size variance $\sigma^2$ are $\sim 15.58 \times 10^{-4}$ Å$^2$ & $54.20 \times 10^{-4}$ Å$^2$, respectively. The smaller value of $<r_A>$ and $\sigma_A^2$ of LTC and LTS as compared to parent LCMO and LSMO systems affect the structure, transport and magnetic properties of the systems [9, 10].

CO manganites are investigated in detail to understand the interrelated structure - property correlations, mainly magnetic structure properties exhibited by them. Quenched disorder in the system plays an important role in governing the structure and magnetic properties of CO manganites by modifying the magnetic lattice of the magnetic structure having lattice points corresponding to eg electron spins. The sources of this quenched disorder are: (i) strongly correlated nature, (ii) large size variance, (iii) highly disordered nature of multi-component system (iv) inherent disordered in bulk.

Generally, CO manganites exhibit paramagnetic (PM) insulator (I) to ferromagnetic (FM) metal (M) to antiferromagnetic (AFM) insulator (I) transitions on lowering the temperature. Sufficiently large applied magnetic field and / or temperature variation can suppress the AFM ground state in CO manganites and convert it into FMM state. Hence, competition between the FM and AFM states and transition from FM to AFM and vice versa can be tuned by the field and / or temperature. The broadened transition with a spatial distribution of the magnetic field and temperature range across the samples can be achieved due to the quenched disorder in the samples. This temperature and / or field induced broadened transition is known as First Order Phase Transition (FOPT).

FOPT is the cause of intrinsic disorder in materials and doped manganites are intrinsically disordered systems [11]. Out of them, half doped manganites are always interesting, because FOPT may be caused by varying control variables like temperature or field which results into giant response of some physical properties of manganites. Moreover, in manganites, transformation from AFM to FM phase can be triggered by
variation of temperature and magnetic field which results into interesting (H, T) phase diagrams and low temperature phase coexistence with kinetic arrest like phenomenon.

During the course of this work, two charge ordered samples with $A^{2+}$ ($Ca^{2+}$ and $Sr^{2+}$, separately) doping into $(La_{0.375-x}Tb_x)0.5A_{0.5}MnO_3$, $x = 0.125$, have been studied in detail using temperature dependent neutron diffraction and magnetization measurements. Magnetic properties have been studied in detail, using $M$ vs $T$ and $M$ vs $H$ measurements at different temperatures and fields using three different protocols.

4.2 Synthesis

Polycrystalline bulk samples of $(La_{0.375-x}Tb_x)0.5Ca_{0.5}MnO_3$ (LTC) and $(La_{0.375-x}Tb_x)0.5Sr_{0.5}MnO_3$ (LTS) ($x = 0.125$) were synthesized using conventional solid state reaction route. Different steps involved in the synthesis of bulk LTC and LTS samples are already given in chapter 3 (fig. 3.1). Structural studies using X-Ray Diffraction (XRD) at (room temperature) RT were carried out to confirm the phase formation and phases present in the samples. Neutron Diffraction (ND) measurements were performed at various temperatures in the range 5 - 300K using multiposition sensitive detector based powder neutron diffractometer on the beam line T-1013 at Dhruva reactor, BARC, Mumbai. The transport and magnetotransport properties were investigated using d.c. four probe method in the temperature range 5 - 300K with and without applied fields of 1, 5 and 8T. The magnetization measurements were carried out using three different protocols: Zero Field Cooled (ZFC), Field Cooled Cooling (FCC) and Field Cooled Warming (FCW) using VSM facility at UGC-DAE CSR Indore in the temperature range 5 - 300K to understand the nature of FOPT and magnetic behavior of the samples.
4.3 Structural Studies

4.3.1 X-ray Diffraction

Fig. 4.1 shows the indexed XRD patterns (raw data) of LTC and LTS samples. The detailed structural analysis has been carried out by fitting the XRD data using the Rietveld refinement technique employing FULLPROF suite [12].

![XRD patterns of La_{0.375}Tb_{0.125}Ca_{0.5}MnO_3 and La_{0.375}Tb_{0.125}Sr_{0.5}MnO_3](image)

Fig. 4.2 shows the Rietveld refined XRD patterns of LTC and LTS samples. Refinement was done in different steps to achieve proper fitting parameters. Modified Lorentzian 1 function was used to fit the XRD patterns. Small difference between observed and calculated patterns reveals the reliability of fitted patterns and the goodness of fit.
of fit. Within the instrumental resolution, no extra peaks were observed which reveals single phasic nature of the samples. LTC crystallizes in orthorhombic structure having \textit{Pnma} space group (No. 62) whereas LTS crystallizes in \textit{Fmmm} space group (No. 69).

![Rietveld refined XRD patterns of La$_{0.375}$Tb$_{0.125}$Ca$_{0.5}$MnO$_3$ and La$_{0.375}$Tb$_{0.125}$Sr$_{0.5}$MnO$_3$.](image)

Figure 4.2: Rietveld refined XRD patterns of La$_{0.375}$Tb$_{0.125}$Ca$_{0.5}$MnO$_3$ and La$_{0.375}$Tb$_{0.125}$Sr$_{0.5}$MnO$_3$. 

Studies on La$_{0.375}$Tb$_{0.125}$A$_{0.5}$MnO$_3$ (A = Ca and Sr) Half Doped Manganites
4.3.2 Neutron Diffraction

Neutron powder diffraction is a complimentary technique to X-Ray Diffraction and Electron Diffraction. Neutrons are charge less particles with magnetic moment which is very useful to probe the magnetic structures of the materials. The temperature dependent Neutron Diffraction (ND) patterns of LTC and LTS samples were recorded on the multi-position sensitive detector based powder diffractometer on the beam line T-1013, using wavelength $\lambda = 1.249\,\text{Å}$, at the Dhruva reactor, BARC, Mumbai in the $2\theta$ range of 6° to 140° at selected temperatures ranging between 22 - 300K. For Neutron Diffraction experiment, powder sample weighing ~ 10 gms was filled in ~ 6mm dia Vanadium container placed in closed cycle refrigeration (CCR) for temperature dependent ND measurements.

La$_{0.375}$Tb$_{0.125}$Ca$_{0.5}$MnO$_3$ (LTC)

Fig. 4.3 depicts the raw data of ND patterns collected at various temperatures for LTC manganite. Inset of fig. 4.3 shows the enlarged view of the low temperature ND patterns in the $2\theta$ range of 5 - 25°. In order to observe the low temperature magnetic ordering in LTC sample, the ND patterns were collected at large number of temperatures in the range 300K - 22K, it can be seen that, LTC sample do not exhibit any low angle reflection up to 22K. All the patterns were further fitted using Rietveld refinement. A small hump like peak structure is seen in the low temperature ND patterns at 9.3° which points towards the existence of short range AFM ordering in LTC sample.
Rietveld refinement of ND patterns was carried out using FULPROF suite [12]. In first refinement step, scale factor, background and zero point of detector were varied, followed by the variation in fullwidth half maximum parameters. Subsequently, atomic positions and thermal parameters were varied. Using these steps, whole pattern was fitted for LTC sample. Figs. 4.4 (a - n) show Rietveld refined ND patterns of LTC sample collected at various temperatures ranging between 22 and 300K. Tables 4.1 and 4.2 lists various structural parameters derived from the Rietveld refinement of the ND patterns of various temperatures.
Studies on La$_{0.375}$Tb$_{0.125}$A$_{0.5}$MnO$_3$ (A = Ca and Sr) Half Doped Manganites
Studies on La\(_{0.375}\)Tb\(_{0.125}\)A\(_{0.5}\)MnO\(_3\) (A = Ca and Sr) Half Doped Manganites
Studies on La$_{0.375}$Tb$_{0.125}$A$_{0.5}$MnO$_3$ (A = Ca and Sr) Half Doped Manganites

(e) $200K$

(f) $175K$

Intensity (a.u.)

$\theta$ (deg.)

Observed
Calculated
Difference
Bragg reflections
Studies on La$_{0.375}$Tb$_{0.125}$A$_{0.5}$MnO$_3$ (A = Ca and Sr) Half Doped Manganites
Studies on La$_{0.375}$Tb$_{0.125}$A$_{0.5}$MnO$_3$ (A = Ca and Sr) Half Doped Manganites
Studies on La$_{0.375}$Tb$_{0.125}$A$_{0.5}$MnO$_3$ (A = Ca and Sr) Half Doped Manganites

Graphs showing intensity vs. 2θ for La$_{0.375}$Tb$_{0.125}$Ca$_{0.5}$MnO$_3$ at 65K and La$_{0.375}$Tb$_{0.125}$Ca$_{0.5}$MnO$_3$ at 50K. The graphs compare observed, calculated, and difference intensities for Bragg reflections.
Figure 4.4 Rietveld refined patterns show observed (o symbol) and calculated (line) Neutron Diffraction data for La$_{0.375}$Tb$_{0.125}$Ca$_{0.5}$MnO$_3$, recorded at 300 - 22K (a - n). Tick mark below the diffraction profile mark the position of allowed Bragg reflections. The difference between the observed and calculated values is given at the bottom.
Table 4.1 Structural parameters of La$_{0.375}$Tb$_{0.125}$Ca$_{0.5}$MnO$_3$ obtained from the Rietveld refinement of the neutron diffraction patterns collected at 22, 35, 50, 65, 75, 100, and 125K.

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Table 4.2 Structural parameters of La$_{0.375}$Tb$_{0.125}$Ca$_{0.5}$MnO$_3$ obtained from the Rietveld refinement of the neutron diffraction patterns collected at 150, 175, 200, 225, 250, 275 and 300K.

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<td>5.42</td>
<td>5.50</td>
<td>5.44</td>
<td>5.69</td>
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It is clear from fig. 4.4 (a - n) that, no structural transition takes place in LTC up to 22K. It is reported that, presence of Tb\(^{3+}\) at A-site modify the magnetic properties of manganites by modifying the magnetic lattice [13, 14]. In our earlier study on LTCSMO sample, temperature dependent ND measurements show A-type AFM ordering emerging at \(\sim 9^\circ\) [6]. In the present case of ND measurements on LTC at various temperatures, the similar small intensity peak it is found emerge at low angle \(\sim 9.3^\circ\) (same as LTCSMO) at low temperatures \(\leq 50K\), indicating the presence of short range A-type AFM ordering at low temperature [inset of fig. 4.4]. Presence of a weak AFM ordering at low temperatures in presently studied LTC sample may be due to the large size variance in the sample and higher doping of Tb\(^{3+}\) in LaCaMnO\(_3\) which modify the magnetic structure [15]. It is reported that, the presence of Sr\(^{2+}\) ion at A-site in LSMO is responsibly for the A-type AFM ordering at low temperatures [7, 8] while this is not the case for LCMO sample where any A-type ordering is absent [7]. Table 4.1 and 4.2 depicts the variation in structural parameters like, cell parameters, cell volume, Mn-O bond distances and Mn-O-Mn bond angles derived from Rietveld refinement of ND patterns at various temperatures, which play a crucial role in structural, transport and magnetotransport properties of the sample. \(\chi^2\), \(R_{WP}\), \(R_{exp}\) are agreement factors, values of these factors decide goodness of fitting. \(R_{WP}\) is the weighted profile and \(R_{exp}\) is expected weighted profile, if the ratio of both the factor is low then fitting can said to be good. In our case both factors have nearest value for higher temperature fittings.

\(\La_{0.375}\Tb_{0.125}\Sr_{0.5}\MnO_3\) (LTS)

Fig. 4.5 shows the neutron diffraction raw data of LTS sample clearly depicting the emergence of a peak at lower angle \(2\theta \sim 9.3^\circ\) (shown by the hollow circle) below 100K. The peak intensity becomes prominent at low temperature. In addition, few ND peaks show the doublet behavior at low temperature (indicated by asterisk), as shown in fig. 4.5.
Figure 4.5 Neutron Diffraction raw data at various temperatures of LTS sample [hollow circles indicate emergence of low temperature peak and asterisks indicate doublets in patterns]

Fig. 4.6 (a - e) depicts the Rietveld refined ND patterns of LTS sample collected at 300, 200, 100, 50 and 22K. Similar steps were followed during refinement of ND data of LTS sample but the low angle peak at $2\theta \sim 9.3^\circ$ observed in this sample at temperature below 100K could not be fitted. It is reported that, in LSMO, at low temperature, A-type AFM phase is preset [8] while LTCSMO sample also exhibit A - type AFM behavior, as reported in chapter 3. Thus, initially A - type AFM phase was added to the LTS profile for refining the ND data at low temperature. Subsequently moments of the Mn$^{3+}$ and Mn$^{4+}$ ions were varied. This resulted in fitting all the peaks properly.
During Rietveld refinement of magnetic phase, it was found that, nuclear phase is not compatible with magnetic phase and hence, both the phases were fitted separately for ND data at 100K. Fig. 4.6 (c - 1), (d - 1) and (e - 1) shows the nuclear phase fitting where fig. 4.6 (c - 2), (d - 2) and (e - 2) depicts the magnetic phases in LTS sample with hollow circles indicating the presence of A - type AFM phase. This clearly shows that, Tb - doping does not affect largely the magnetic phase of LSMO.

![Diagram of La$_{0.375}$Tb$_{0.125}$Sr$_{0.5}$MnO$_3$ at 300K](image)
Studies on La$_{0.375}$Tb$_{0.125}$A$_{0.5}$MnO$_3$ (A = Ca and Sr) Half Doped Manganites

(b) 200K

La$_{0.375}$Tb$_{0.125}$Sr$_{0.5}$MnO$_3$

- Observed
- Calculated
- Difference
- Bragg reflections

(c - 1) 100K

La$_{0.375}$Tb$_{0.125}$Sr$_{0.5}$MnO$_3$

Nuclear Phase

- Observed
- Calculated
- Difference
- Bragg reflections
Studies on La$_{0.375}$Tb$_{0.125}$A$_{0.5}$MnO$_3$ (A = Ca and Sr) Half-Doped Manganites

100K

Magnetic Phase

$\text{Intensity (a.u.)}$

$\text{2\theta (deg.)}$

La$_{0.375}$ Tb$_{0.125}$ Sr$_{0.5}$ MnO$_3$

100K

Observed

Calculated

Difference

Bragg reflections

50K

Nuclear Phase

$\text{Intensity (a.u.)}$

$\text{2\theta (deg.)}$

La$_{0.375}$ Tb$_{0.125}$ Ca$_{0.5}$ MnO$_3$

Observed

Calculated

Difference

Bragg reflections
Studies on La_{0.375}Tb_{0.125}A_{0.5}MnO_{3} (A = Ca and Sr) Half Doped Manganites

Magnetic Phase

Nuclear Phase
Figure 4.6 Rietveld refined ND patterns of LTS recorded at 300 - 22K (a - e) showing observed (o symbol) and calculated (line). Tick mark below the diffraction profile mark the position of allowed Bragg reflections. The difference between the observed and calculated values is given at the bottom. Fig. (e - 2) showing A - type AFM with hollow circles indexed as (001) and (0-12).

Table 4.3 indicates the variation in Rietveld refined structural parameters like a, b, c, cell volume (V) and variations in Mn-O bond lengths and Mn-O-Mn bond angles. Decrement of cell parameters results in to lowering of cell volume indicating shrinking of unit cell at low temperature. Bond angle Mn-O1-Mn is increase with decrease in temperature and Mn-O2-Mn is decrease with decrease in temperature whereas Mn-O3-Mn is constant. The ratio of $R_{WP}$ and $R_{exp}$ known as $\chi^2$, is near to one which shows goodness of pattern fitting.
Table 4.3  Structural parameters of La$_{0.375}$Tb$_{0.125}$Sr$_{0.5}$MnO$_3$ obtained from the Rietveld refinement of the neutron diffraction patterns collected at 20, 50, 100, 200 and 300K

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<tr>
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Studies on La$_{0.375}$Tb$_{0.125}$A$_{0.5}$MnO$_3$ (A = Ca and Sr) Half Doped Manganites
4.4 Transport and Magnetotransport Properties

During the course of present work, the transport measurements on LTC and LTS samples were carried out to understand the structure - transport correlations in Tb$^{+3}$ doped LCMO and LSMO samples using four probe resistivity measurements in the temperature range 5 - 300K in the absence and presence of applied fields. It can be seen from $\rho$ - T plots of LTC sample, in fig. 4.7, that, under 0 and 1T field, the sample exhibits insulating behavior with large resistivity values due to the large size variance as compared to LCMO. In ND pattern at low temperature ~ 50K small peak with very low intensity around ~ 9.3° has been observed which is due to very weak short range A - type antiferromagnetic ordering [inset of fig 4.3]. Under large applied fields, 5 and 8T, LTC exhibits insulator to metal transition at $T_P$ ~ 108 and 132K, respectively, can be attributed to the melting of CO and field induced A - type CO - AFM to FM transformation. Earlier studies on (La$_{1-x}$Tb)$_{2/3}$Ca$_{1/3}$MnO$_3$ (x = 0.0 to 0.4) and La$_{0.5-x}$Y$_x$Ca$_{0.5}$MnO$_3$ (x = 0, 0.1 and 0.18) [7, 14] have shown that, the most important parameter in governing magnetic and transport properties is average ionic radii $<r_A>$ which plays a very important role in the transport properties of manganites. It can be observed that, resistivity decreases with increasing field and $T_P$ shifts toward higher temperature. This can be understood as: LCMO has an average ionic radius $<r_A>$ ~ 1.198Å, which becomes ~ 1.182Å in LTC sample. As average ionic radius decreases, Mn-O-Mn bond angle leading to a narrower one electron bandwidth reduces the transport by decreasing the transfer of $e_g$ itinerant electrons [16].

Fig. 4.8 illustrates the variation in resistivity with temperature in the absence and presence of applied field for LTS sample. Under 0T field LTS exhibits insulating like behavior. Under the application of magnetic field, metallic behavior can be observed with a hump like metal to insulator/charge ordered transition ($T_{CO}$) exhibited by the sample which decreases with applied field. Applied magnetic field of 1T induces the transition at $T_{CO}$ ~ 197K. Under 5 and 8T fields, the $T_{CO}$ ~ 180 and 161K, respectively, is exhibited as shown in inset of fig. 4.8. Below $T_{CO}$, the resistivity increases appreciably indicating the setting of AFM state. Moreover the resistivity gets suppressed with magnetic field. For LSMO, such a behavior is reported earlier [8, 17, 18] Although, Tb$^{+3}$ is very small as
compared to Sr\textsuperscript{2+} in LTS sample, and average ionic radius $<r_A>$ of LTS is smaller than that of LSMO and size variance is larger, it does not largely affect the resistivity behavior. The variation in $T_{CO}$ and resistivity with field can be attributed to the field induced suppression in CO state and increase in FM state above $T_{CO}$ and hence suppression in resistivity.

![Figure 4.7](image1.png)

Figure 4.7 $\rho$ vs $T$ plots of La\textsubscript{0.375}Tb\textsubscript{0.125}Ca\textsubscript{0.5}MnO\textsubscript{3} under various applied fields

![Figure 4.8](image2.png)

Figure 4.8 $\ln \rho$ vs $T$ plots of La\textsubscript{0.375}Tb\textsubscript{0.125}Sr\textsubscript{0.5}MnO\textsubscript{3} under various applied fields [inset figure shows magnified view of $T_{CO}$ under 1, 5 and 8T fields]
Fig. 4.9 depicts the variation in normalized resistivity \( \rho_H / \rho_0 \) with applied field up to 9T plotted at various temperatures in the range 5 - 300K for LTS sample. Negative magnetoresistance (MR) \( [MR = (\rho_0 - \rho_{9T})/ \rho_0 \times 100] \sim 12 \% \) at 300K under 9T field increases monotonously with decrease in temperature and becomes \( \sim 92 \% \) at 5K under 9T field. Moreover, linearity of the curves is semi-logarithmic indicating the field independent differential \( \ln R \) behavior over the temperature region.

### 4.5 Magnetization Measurements

Intrinsically quenched disorder is inherent property of manganites due to (i) its multi-component nature, (ii) bulk property and (iii) large size disorder at ionic level [2]. Half doped charge ordered (CO) state in manganites with the general stoichiometry \( \text{La}_{0.5}\text{A}_{0.5}\text{MnO}_3 \) is an intrinsically disordered system having distinguishable real space ordering of \( \text{Mn}^{3+} \) and \( \text{Mn}^{4+} \) ions. A broad First Order Phase Transition (FOPT) can be observed in disordered systems under the variation in temperature and field. In such a system, coexisting ferromagnetic metallic (FMM) and antiferromagnetic insulating (AFI) phases have been observed at low temperature, controlled by traversing magnetic field.
(H) and temperature (T) [11]. It has been shown in many half doped manganites that, once a FMM state is achieved under magnetic field at low temperature, even under the removal of field, the original starting magnetic phase can not be reached back [19, 20] which results into two phase coexistence at low temperature and negligible possibility of reverse transformation and zero field cooled state of the sample. Such a type of phase co-existence phenomenon has been observed in the presently studied LTC and LTS systems. The condition of coexisting phases is similar to glass. When the dynamics of any material are arrested below a certain temperature, a glass state is formed. Normal definition of glass is ‘non crystalline solid material that yields broad, nearly featureless diffraction pattern’. The appropriate meaning of glass in the present context is ‘liquid in which kinetics of atoms or molecules (means kinetics related to atoms like atomic motion) are arrested’ [11]. Kinetic arrest in CO manganites can be understood as the transformation of high temperature magnetic phase into low temperature magnetic phase, with a fraction of high temperature phase coexisting at low temperature with low temperature stable phase.

To understand the magnetic properties of LTC and LTS samples studied, magnetization measurements (M vs H) at various temperatures and (M vs T) under various applied fields, were carried out using different protocols in the temperature range 5 - 300K under the field range 0 - ±14T using the high field VSM facility at UGC-DAE CSR, Indore. The protocols used to measure the magnetic properties are given below -

Protocols for M vs H measurements:

- Cool the sample from 300 to 5K (or 100K or 200K) with H = 0
- Increase H isothermally at 5K (or 100K or 200K) from H = 0 to 14 Tesla (or 8 Tesla) and measure ZFC, magnetization M vs field H
- Decrease H isothermally at 5K (or 100K or 200K) from H = 14 Tesla (or 8 Tesla) to 0 and measure M vs H
- Increase H isothermally at 5K from H = 0 to -14 Tesla & measure M vs H
- Decrease H isothermally at 5K from H = -14 Tesla to 0 & measure M vs H
- Increase H isothermally at 5K from H = 0 to 14 Tesla & measure M vs H
Protocols for M vs T measurements:

Temperature dependence of magnetization studies on LTC and LTS samples were carried out using three different protocols: Zero Field Cooled (ZFC), Field Cooled Cooling (FCC) and Field Cooled Warming (FCW), in the temperature range 5 - 300K under the fields up to ±14T. The steps involved in the three protocols are:

- Cool the sample from 300K to 5K with H = 0
- Increase field isothermally from H = 0 to H = H
- Heat the sample from 5K to 300K under H = H and measure M vs T (ZFC)
- Cool the sample from 300K to 5K under H = H and measure M vs T (FCC)
- Heat the sample from 5K to 300K under H = H and measure M vs T (FCW)

Magnetic property measurements on LTC sample

Half doped manganites are known to exhibit CO at low temperature which melts under the application of large applied fields [21]. AFM and FM phases in CO manganites are separated by a FOPT in the space of field (H) and temperature (T) control variables, the low temperature equilibrium phase is often masked by the glass-like arrest of the kinetics of the phase transformation [22].

From ND measurements, it has been seen that, the ground state for CO LTC sample is PM (under zero field, which becomes FM under the application of field) rather than AFM due to the large size disorder effect [7, 23]. Hence, in the presently studied LTC sample, the low temperature paramagnetic (PM) ground state can be masked by the high temperature stable AFM state. To explore and understand this phenomenon in the LTC manganite, the M vs T and M vs H measurements were performed using various protocols (as discussed above) in the temperature range 5 - 300K and under the field range 0 to ±14T.
Fig. 4.10 and fig. 4.11 show the M vs H behaviors of LTC sample under varying 0 - ±14T fields collected at 5 and 10K, respectively, while fig. 4.12 shows the M vs H plots for LTC sample collected at 100K under the field cycle of 0 - +14T - 0. At 5K, sample shows a sharp field induced AFM to FM transition in moderate field of ~ 4.95T in the initial field increasing cycle. As the field reaches up to 14T, the magnetization increases up to 3.5 $\mu_B$/f.u. as expected for the half doped manganites. The saturation can be observed ~ 10T field at 5K indicating the fully FM state. At 10K, similar behavior of field induced AFM to FM transition can be observed at ~ 3.8T with saturation of moments ~ 7.5T indicating the fully FM state (fig. 4.11). At 5 and 10K, once the fully FM state is achieved under higher applied fields, the reverse field cycles do not follow the initial path indicating stabilization of FM phase. Hence, it has been observed that, after achieving fully saturated FM state in the sample at low temperatures, the field increasing and decreasing cycles do not lead to the initially observed AFM - FM step like transition but a sharp transition without hysteresis like behavior is observed which shows the phase coexistence at low temperature. Further field cycles (decreasing and increasing) represent the soft FM phase in the sample. As shown in fig. 4.12, at 100K, the picture is different, because, field ~ 4.9T is required to achieve AFM to FM transition and hysteresis can be seen from M vs H behavior at 100K. This indicates the phase coexistence at 100K under an applied field of > 4.9T. Under high field (> 8T) the sample becomes FM. At 100K LTC do not exhibit any saturation in magnetization up to 14T field.
Figure 4.10  M vs H isotherms collected at 5K under the field of 0 - ± 14T
Inset: (a) M vs H isotherm collected at 5K in the field range 0 - +14T
Inset: (b) M-H isotherm collected at 5K in the field range +14T - 0 - +2T

Figure 4.11  M vs H isotherms collected at 10K under the field of 0 - ± 14T
Inset: (a) M vs H isotherm collected at 10K in the field range 0 - +14T
Inset: (b) M-H isotherm collected at 10K in the field range +14T - 0 - +9T
Figure 4.12  M vs H isotherms collected at 100K under the field of 0 - +14T - 0

Inset: M vs H isotherm collected at 100K in the field range 0 - +14T

Fig. 4.13 show the enlarged view of M - H isotherms collected at 5K under 0 - +14T having the insets (a), (b) and (c) depicting the three regions of M - H curve under 0 - 14T. Fig. 4.13 (a) shows the initial sharp step like transition with increasing field at ~ 4.95T while fig. 4.13 (b) clearly show a second broad rise in magnetization at ~ 7.6T, above which the moments saturate and the sample becomes fully ferromagnetic [fig. 4.13 (c)]. Fig. 4.14 and 4.15 show the enlarged view of initial M - H curves taken under 0 - 14T on LTC sample at 10 and 100K, respectively. The enlarged views of the observed M - H behavior having two regions in M - H, inset (a) up to 5T and inset (b) above 5T are also shown as inset of the respective figures.
Figure 4.13  M vs H isotherms collected at 5K in the field range 0 - +14T
Inset: Enlarged views of M-H curve under various field ranges

Figure 4.14  M vs H isotherms collected at 10K in the field range 0 - +14T
Inset: Enlarged views of M-H curve under various field ranges
Figure 4.15  M vs H isotherms collected at 100K in the field range 0 - +14T
Inset: Enlarged views of M-H curve under various field ranges

[B]  M vs T measurements

Fig. 4.16 shows the temperature dependent ZFC magnetization behavior (M vs T plots) under 2, 3, 4, 5 and 8T fields in the temperature range 5 - 300K. It can be seen that, magnetization increases with applied field. Paramagnetic (PM) to ferromagnetic (FM) transition is exhibited by LTC sample at $T_C \sim 80, 88, 102, 113$ and $146K$ under 2, 3, 4, 5 and 8T fields, respectively. The enhancement in $T_C$ with increasing field can be attributed to the field induced FM phase in the sample. FM to AFM transition has been observed under 2, 3 and 4T fields at 22, 13 and 7K respectively while LTC remains in FM state at low temperature ($\sim 5K$) without exhibiting any transition under high fields of $\sim 5$ and 8T. It can be seen that, the FM - AFM transition temperature ($T_N$) decreases with increasing field (up to 4T) which may be attributed to the field induced suppression in AFM phase fraction and increase in FM phase.
Fig. 4.17 shows the M vs T plots obtained using ZFC protocols under various applied fields (2, 3, 4, 5 and 8T) in the temperature range 5 - 300K. It can be seen that, at 5K, AFM phase fraction is 84.16% present under 2T which decreases up to 4.43% under 8T using ZFC protocol, while the AFM fraction of ~ 75.64% (2T) becomes 4.70% (5T) under FCC protocol and under 8T, LTC becomes fully FM exhibiting moment ~ 3.5μB/f.u. as expected for half doped manganites. This indicates, the field induced suppression in AFM phase fraction and conversion of AFM to FM phase in LTC sample studied.
Fig. 4.18 shows the M vs T plots obtained under FCC and Field Cooled Warming (FCW) condition in the temperature range 5 - 300K under various fields. Under all the fields, the sample exhibits hysteresis like behavior in FCC and FCW paths indicating a disorder - broadened first order phase transition from AFM to antiferromagnetic FM phase with decreasing temperature. This indicates the coexistence of AFM - FM phases in the sample. This coexistence can be justified due to the non saturation of magnetic moment observed under lower fields at 5K. As discussed in temperature dependent ND measurements on LTC sample [sec. 4.3.2], the ground state for LTC sample is PM (under zero applied field) and hence, the high temperature AFM phase is arrested in field induced FM matrix. The FCC and FCW curves become bifurcated at temperature, $T_B \sim 83, 91, 103, 113$ and $145K$ (on lowering of temperature) under 2, 3, 4, 5, and 8T.
respectively, indicating the field induced suppression in bifurcation temperatures. In addition, the width of the hysteresis curve reduces with increasing field and becomes ~ 32, 26, 18, 13 and 2K for curves under 2, 3, 4, 5, and 8T respectively. The increase in $T_B$ and decrease in hysteresis area with increasing field can be attributed to the field induced transformation of arrested AFM to FM phase, i.e. de-arrestation of arrested AFM phase in FM matrix [22]. Also, with increasing field, the arrested AFM phase fraction reduces and sample becomes fully FM at 5K under 8T field.

Figure 4.18  M vs T (FCC and FCW) plots of LTC sample collected under various applied fields

Inset: Enlarge view of FCC - FCW curves under 8T field
It can be observed from fig. 4.18 that, the magnetization is higher in FCW condition as compared to FCC under all the applied fields indicating, the increase in FM phase fraction on warming the sample while the AFM phase increases during FCC condition. Thus, under FCC, the strong arrestation of AFM phase in FM matrix leads to the lower magnetization, which becomes de-arrested, during heating of the sample, evident from the AFM to FM transition resulting in the increase in magnetization under warming the sample under various fields (FCW). Further, with increase in field, as described above, $T_C$ is enhanced with field signifying the de-arrestation of AFM phase at high applied fields.

Magnetic property measurements on LTS sample

[C] M vs H measurements

The results obtained from M-H measurements on LTS using various magnetic measurement protocols are given below -

CO LTS sample exhibits the low temperature AFM phase confirmed by temperature dependent ND measurements which indicates that, A-type AFM phase below $\sim 175K$ exists [sec. 4.3.2]. In this sample, FOPT signature in magnetization measurements can be used to understand the kinetics of the spins and the coexistence of FM and AFM phases at low temperature.

Fig. 4.19 shows the magnetization isotherms obtained at 5K in the field range 0 - $\pm 14T$ - 0 and fig. 4.20 and fig. 4.21 show M vs H isotherms collected at 100 and 200K, respectively, in the field range 0 - +8T - 0. It can be seen that, LTS sample exhibits hysteresis behavior in M vs H isotherms at 5 and 100K while at 200K sample does not exhibit hysteresis behavior. Magnetization does not saturate under the field of 14T. At low temperature (5K), with increasing field up to maximum possible value (+ 14T), the magnetization approaches to fully spin aligned values $\sim 3.5\mu_B/f.u.$ as expected for half doped manganites. Subsequent increase and decrease in $H$ (envelope) show the signature of the AFM - FM transition at 5 and 100K. The isothermal M - H at each temperature shows that, ZFC-AFM state transforms to FM state with increase in field above 0.4T at
5K and above 0.15T at 100K. The difference between the fields required to achieve FM state at 5 and 100K, is due to the fact that, normally CO compounds have AFM stable phase at low temperature while FM stable phase can be achieved at higher temperature. Hence, to transform AFM to FM at 5K, the required field is large as compared to at 100K. At 5K, sample shows the slow field induced transition from AFM to FM while at higher temperatures, 100 and 200K, sample shows a sharp increase in magnetization with increasing field which can be attributed to the strong AFM coupling at lower temperature and FM stable phase existing at higher temperatures.

Inset of figure 4.19 to 4.21 show the H/M vs $M^2$ plots for the virgin (0 to +H) M-H curves of LTS sample at 5, 100 and 200K, respectively, indicating the negative slope (in some parts) at 5 and 100K signifying the field induced FOPT from AFM to FM state while positive slope at 200K slope is positive signifying the field induced second order phase transition from AFM to FM state.

Figure 4.19  M vs H measurements at 5K for LTS sample
Inset: H/M vs $M^2$ plot for LTS sample
Figure 4.20  M vs H measurements at 100K for LTS sample
Inset: H/M vs M^2 plot for LTS sample

Figure 4.21  M vs H measurements at 200K for LTS sample
Inset: H/M vs M^2 plot for LTS sample
The hysteretic behavior of field induced AFM to FM transition in LTS is taken as a characteristic of a FOPT, where both the phases co-exist as (meta) stable phase between the upper critical field, \( H^{**} \) (field required for AFM to FM phase transition, during increasing field cycle) and lower critical field, \( H^* \) (field required for FM to AFM phase transition, during decreasing field cycle). In presently studied LTS system, the upper critical field, \( H^{**} \) is higher than \( H^* \), indicating the metastable nature of FM. The hysteresis behavior at 5 and 100K indicates that, the sample does not recover to its initial state after reversing the field or during the field decreasing cycles resulting in the co-existence of AFM and FM states at particular \((H, T)\) value. As the AFM and FM phases are separated by the FOPT, the low temperature equilibrium phase is often masked by the kinetically arrested high temperature metastable phase [22, 24 - 27]. In LTS sample, the equilibrium stable phase at low temperature is A-type AFM, as studied by the temperature dependent ND measurements while high temperature meta-stable state is FM (because at 200K, no hysteresis can be seen indicating a fully FM state and field induced AFM to FM transformation can be observed). The reason is that, on increasing field, the AFM is converted into FM state and on decreasing the field, the fully AFM cannot be achieved but some FM state exists at low field region and hence large \( M \) value can be seen on decreasing field cycle, as compared to increasing field cycles at 5 and 100K which is known as the arrested FM state preset at low temperatures. Such a behavior is not observed in 200K isotherm.

At high temperature (~ 100K), the area of hysteresis is small, indicating a small amount of arrested meta-stable FM state present. Such a hysteresis behaviors and abrupt change in \( M \) with \( T \), indicates the soft FM nature of sample at 5 and 100K. It can be seen from the M-H isotherms collected at 5K that, second field increasing cycle does not follow the same path as followed by virgin (first cycle of 0 to +14T) curve indicating the fact that, once FM state is arrested in the sample due to FOPT, it can not be regained on reducing field or under reverse field cycle.
Fig. 4.22 displays M-H curves obtained at 5 and 100K showing AFM to FM transition with increasing field while the inset of fig. 4.22 (a) and (b) shows the enlarged views of the M-H curves under low field region (a) and high field region (b) taken at 5 and 100K under increasing and decreasing field cycles. The forward curves (0 to $H_{\text{max}} = 14$T) show an increase in M with H, indicating a field induced AFM to FM transition. In low field region, (i.e. 0 - 3.7T) in forward cycle (0 to $H_{\text{max}}$), the field required for AFM to FM transition becomes smaller with increasing temperature from 5 to 100K while in reverse cycle ($H_{\text{max}}$ to 0), the field required for FM to AFM transition increases with
increasing temperature [inset (a) of fig. 4.22]. This opposite behavior of field requirement in forward and reverse cycles indicates that, at 100K, FM state is stable but at 5K, AFM is most favorable in half doped LTS manganite. While, in reverse cycle, the field required to induce FM to AFM transition, is lower at lower temperature and higher at higher temperature indicating, at 100K the FM is robust enough so that large field is required to transform FM to AFM phase.

Above 3.7T field [inset fig. 4.22 (b)], during forward cycle with increase in H, the field required for AFM to FM transition is less for 100K as compared to 5K, due to the fact that, at 5K, AFM state favored which requires higher field to achieve AFM to FM transition while at 100K, FM is stable state which do not need large field for FM - AFM transition. In reverse field cycle, the picture is totally opposite. The required field for FM - AFM transition decreases with increasing temperature, the reason for which is due to the sufficiently large applied field ($\geq 3.7T$) after the forward cycle which is responsible for the arrestation of FM phase at 5K. Hence, at 100K the FM to AFM transition requires lower field as compared to 5K where the strong FM arrested (meta) stable phase exists. The field value $\sim 3.7T$ may be considered as the field required for the kinetic arrest of FM phase at low temperature in the presently studied LTS manganite and is denoted as $H_K$ (kinetic arrest field).

[D] M vs T Measurements

The results obtained from M-T measurements on LTS sample using various measurement protocols are given below -

Fig. 4.23 shows the M vs T plots for LTS sample obtained at 1, 5 and 8T fields in the temperature range 5 - 300K using ZFC, FCC and FCW protocols. It can be seen from ZFC curves under various fields, that, LTS exhibits high temperature transition from PM to FM phase at $T_C \sim 296K$ (at which magnetization rise sharply). $M$ increases with increasing field and becomes higher at 300K under 5 and 8T fields. It can be also seen that, the onset of AFM is at different temperatures ($T_N$) under different field conditions. $T_N$ shifts toward lower temperature due to the field induced suppression in CO state and
hence AFM ordering. It is interesting to note that, under 1, 5 and 8T fields, divergence between the ZFC and FC (FCC ad FCW) curves increase with decreasing temperature (fig. 4.23). $T_N$, usually decreases with increasing field and has value of $\sim 179$, $158$ and $143$K under 1, 5 and 8T fields, respectively.

As shown in fig. 4.23, the ZFC curves under all the fields lie outside the envelop formed due to FCC - FCW condition, which is an anomalous behavior exhibited by LTS manganites. At 5K, the sample possesses substantial magnetization suggesting the persistence of FM phase which increases with the field indicating the enhancement in FM phase fraction at low temperature along with AFM phase (matrix). The FM phase arrestation can be understood as below -

Figure 4.23  M vs T measurements under 1T field with ZFC, FCC and FCW protocols for LTS sample

As shown in fig. 4.23, the ZFC curves under all the fields lie outside the envelop formed due to FCC - FCW condition, which is an anomalous behavior exhibited by LTS manganites. At 5K, the sample possesses substantial magnetization suggesting the persistence of FM phase which increases with the field indicating the enhancement in FM phase fraction at low temperature along with AFM phase (matrix). The FM phase arrestation can be understood as below -
After virgin curve (cooling curve, not shown here) up to low temperature under H = 0, the isothermal increase in field results into the enhancement in FM phase at low temperature. After ZFC, during FCC more FM phase fraction starts to build up and hence M is larger in FCC than in ZFC. This can be attributed to the larger arrested FM phase fraction present at low temperature during FCC. On warming the sample (FCW) M - T curve do not follow the FCC path resulting in hysteresis behavior indicating that a release of arrested FM phase and hence M is smaller in FCW than FCC. Although complete arrested FM phase can not be transformed to AFM at low temperature hence magnetization under FCW is larger than ZFC, indicating the de-arrestation of high temperature high field FM phase.

The above observations clearly show that, temperature dependence of ZFC, FCC and FCW curves under various applied fields lead to the presence of various magnetic states existing at various temperatures and fields. The suppression in the bifurcation of FCC and FCW curves with increasing temperature indicates that the FM phase is arrested at low temperature and the heating (FCW) leads to de-arrestation of FM phase.

The values of magnetization at low temperature (~ 5K) under 1, 5 and 8T fields are 0.58, 1.47 and 2.18\(\mu_B\)/f.u., respectively. Half doped manganites should exhibit the spin aligned value of M ~ 3.5\(\mu_B\)/f.u. or 3.5\(\mu_B\)/Mn accompanied by metallic conductivity. The observed value ~ 0.58\(\mu_B\)/f.u. at 5K, can be attributed to a frozen FM phase fraction of about 17% while under 5 and 8T fields, it becomes 42 and 62%, respectively. The low temperature AFM - FM transition temperature shifts toward lower temperature with increasing field indicating the field induced FM phase and reduction in AFM fraction.

The hysteresis between FCC and FCW paths indicate a disorder - broadened first order transition from AFM to FM with reducing temperature. The broadening becomes higher at higher fields, i.e. ~ 14K under 5T field and ~ 18K under 8T field, which indicates the first order phase transition from AFM to FM phase is due to the disorder in such a multi-component bulk manganite.
4.6 Discussion and Conclusion

Doping at A-site in mixed valent manganites of the type ABMnO$_3$ results in the modifications in the structural parameters such as average ionic radius, size variance and tolerance factor which in turn modify their lattice parameters, Mn-O-Mn bond angles and Mn-O bond lengths. It is reported that, a strong correlation exists between structure and magnetotransport properties of manganites. During the course of present studies, an effort is made to understand the changes in structural parameters of LTC and LTS manganites on the transport and magnetotransport in the light of variations in cell parameters, Mn-O-Mn bond angles and bond lengths etc. using the Rietveld refinement of the temperature dependent ND measurements. The discussion on the results obtained on LTC and LTS systems have been given in the following pages followed by the conclusions derived from the present study.

La$_{0.375}$Tb$_{0.125}$Ca$_{0.5}$MnO$_3$ (LTC)

The variations in unit cell parameters, cell volume, Mn-O bond lengths and Mn-O-Mn bond angles as a function of temperature, determined from the analysis of the ND data on LTC, have been shown in figs. 4.14 (a - d). It can be seen that, there is not much change in lattice parameters and hence cell volume with the temperature and the Mn-O bond lengths remain almost constant with temperature. Mn-O$_1$-Mn bond angle initially decreases with decreasing temperature below 300K while it marginally increases below 150K. Mn-O$_2$-Mn bond angle decreases monotonically with decrease in temperature. LTC is low bandwidth system and Mn-O$_2$-Mn is the basal plane angle which decreases with decreasing temperature and hence does not support the hopping of e$_g$ electrons from one site to another resulting in the insulating nature under 0 and 1T field while field induced A-type AFM to FM transition has been observed under 5 and 8T fields.

In addition, the analyses of ND data at different temperatures show that, LTC sample do not exhibit any structural transition up to 22K. an observation of a weak broad peak at $2\theta \sim 9.3^\circ$ in the ND patterns at 50, 35 and 22K indicates the short range A-type AFM ordering and sample.
The magnetization measurements perform on the LTC under various fields \([M - H (T)]\) and at different temperatures \([M - T (H)]\) revealed interesting magnetic behavior. An initial sharp step like AFM - FM transition with increasing field at \(\sim 4.9T\) has been observed in \(M - H\) measurements at 5K followed by a second broad step like transition. A
broad hysteresis behavior has been observed at 100K indicating the phase coexistence under the applied field of > 4.9T. M - T measurements at different applied fields using ZFC, FCC and FCW protocols reveal interesting disorder driven broad FOPT from AFM - FM and the kinetic arrestation of AFM phase in FM matrix at low temperatures and fields. Under high applied field (8T) the collapse of the hysteresis loop indicates the robust FM phase of the sample.

La$_{0.375}$Tb$_{0.125}$Sr$_{0.5}$MnO$_3$ (LTS)

The variations in unit cell parameters, cell volume, Mn-O bond lengths and Mn-O-Mn bond angles as a function of temperature, determined from the analysis of the ND data on LTC, have been shown in figs. 4.15 (a - d). It can be seen that, cell parameter a decreases appreciably whereas b and c increase marginally resulting in the suppression in cell volume. Such a behavior is observed in half doped manganites when charge ordering occurs [7] at certain temperature. Also, below 200K, Mn-O bond length decreases while Mn-O$_3$ bond length increase with no variation in Mn-O$_1$ with decreasing temperature indicating that the average Mn-O bond lengths is not affected by temperature. The Mn-O$_1$-Mn and Mn-O$_2$-Mn bond angle decrease below 200K thereby stabilizing the structure while Mn-O$_3$-Mn bond angle remains constant ~ 180° at all the temperatures studied. The emergence of low angle magnetic (001) and (0-12) peaks at $2\theta$ ~ 9.3° and 20.6° respectively below 175K clearly depict the presence of A - type AFM phase up to 22K with the increase in integrated intensity of (001) peak below 175K as shown in fig. 4.16. At 20K, magnetic moment obtained from the Rietveld refinement for A - type AFM phase is 4.105$\mu_B$/Mn for Mn$^{3+}$ ions in a-b plane.

It is of interest to note that, the nature of magnetic structure, orbital ordering and charge ordering behavior in this sample is similar to that observed in half doped compounds where the ratio of Mn$^{3+}$ and Mn$^{4+}$ is 1:1. Similar observation of A - type AFM magnetic structure has been reported in the case of La$_{0.5}$Sr$_{0.5}$MnO$_3$ [8].
Figure 4.15 Variation in (a) cell parameters, (b) cell volume, (c) Mn-O bond lengths and (d) Mn-O-Mn bond angles with temperature for La$_{0.375}$Tb$_{0.125}$Sr$_{0.5}$MnO$_3$.
LTS sample shows the field induced transition from FM to CO (A - type AFM) state under the application of low field ~ 1T. With increasing field, the metallic region increases along with reduction in resistivity at higher temperatures and the value of $T_{CO}$ decreases with increasing field.

Magnetization measurements carried out under different fields and temperatures using ZFC, FCC and FCW protocols on LTS sample show a prominent feature of FM phase arrestation under high field at low temperature which can be de-arrested under FCW. At 5K, LTS exhibit hysteresis like behavior in M - H with no saturation of moments up to 14T. At 200K, it exhibits sharp AFM - FM transition. LTS possesses AFM phase as a ground state (as observed from ND and M - T measurements) having in which high temperature FM phase arrested resulting in the coexistence of both phases at low temperatures.
In conclusion, the structural and magnetic properties of half doped LTC and LTS manganites show an interesting structure-property correlation which has been reflected in the ND and magnetization measurements. LTC sample shows the presence of short range AFM ordering at temperature below 50K evident from the presence of a weak reflection at low angle in ND data. In LTC, the disorder driven broad FOPT of AFM - FM phase is observed with the high temperature AFM phase getting kinetically arrested in FM matrix at low temperature and fields. Temperature dependent ND measurements on half doped LTS manganite show the presence of robust A - type AFM phase at low temperature evident from the observation of magnetic $(001)$ reflection in the ND patterns below 175K. An anomalous behavior of high temperature FM phase getting arrested at low temperature in the AFM matrix is exhibited by LTS which can be de-arrested under FCW condition.
References


Chapter 5

Studies on Nanostructured $R_{0.7}A_{0.3}MnO_3$
($R = La and Nd, A = Ca and Sr$) Manganites

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5.1 Introduction

The discovery of large magnetoresistance (MR) in hole doped manganites has created an enormous interest in ABO$_3$ type mixed valence perovskites during the last decade [1]. Magnetoresistive properties of manganites have been widely investigated because of their importance in fundamental research as well as technological applications [2, 3]. In the mixed valent manganites, having stoichiometric composition R$_{1-X}$A$_X$MnO$_3$, R - trivalent rare earth ion and A - divalent alkaline ion or lead, the chemical doping at A - site with different valence ions, leads to the charge imbalance which in turn modifies the Mn$^{3+}$/Mn$^{4+}$ ratio at B - site. The exchange of electrons between Mn$^{3+}$ and Mn$^{4+}$ ions take place via oxygen ions, phenomenon known as a Zener Double Exchange (ZDE) mechanism [4 - 6]. In ZDE, the hopping of charge carriers (itinerant eg electrons) is only possible when the spins of localized t$_{2g}$ electrons are parallel to each other. However, this model can not properly explain all the details of observed CMR effect hence other theories were developed which could explain the role of Jahn-Teller (JT) character of Mn$^{3+}$ ions in CMR materials by a variable phonon coupling [7]. A great variety of interrelated structural, microstructural, transport, magnetotransport and magnetic properties have been observed by changing various dopants (through different cations and also through different doping levels) in these materials.

It is observed that, two types of MR namely: intrinsic and extrinsic MR exists in manganites. The intrinsic MR is exhibited around ferromagnetic to paramagnetic transition (T$_C$) or metal to insulator transition (T$_P$) under relatively high applied magnetic field > 1T. It can be understood in terms of ZDE mechanism [4, 8]. Extrinsic MR is exhibited at temperature, T < T$_C$ or T$_P$ and is controlled by the external factors like grain morphology, grain size and nature of grain boundaries, under low applied field (≤ 1T). It is also termed as grain boundary MR (GBMR) or low field MR (LFMR) because grain boundaries are responsible for it. LFMR can be attributed to the spin polarized tunnelling (SPT) [8] or spin dependent scattering (SDS) [9]. Various methods of synthesizing bulk polycrystalline manganites are reported, out of which Sol-Gel is a simple alternative to the conventional solid state reaction (SSR) method because it allows the proper control over the phase formation, stoichiometry and particle size [9, 10].

Studies on Nanostructured R$_{0.7}$A$_{0.3}$MnO$_3$ (R = La and Nd, A = Ca and Sr) Manganites
In this chapter, the results of the studies on Sol - Gel grown polycrystalline nanostructured $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (LCMO) and $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (NSMO) manganites sintered at various temperatures (TS) have been reported to understand the effect of particle size, grain morphology on their transport and magnetotransport properties. Sintering temperature is the prime tool to modify the grain growth, grain size, grain boundaries and hence to modify the structural, microstructural, transport and magnetotransport properties of manganites. Moreover, as the size of the particles decrease, the surface to volume ratio increases and enhanced surface energy can modify the physical properties of the polycrystalline samples [11, 12]. The grain size, number of grain boundaries (GBs), grain morphology, nature of GBs, sintering time, number of sintering processes, sintering temperature, type of precursors used etc. decide the physical properties of the system.

In this chapter, an effort is made to study the effect of size variance ($\sigma^2$) on the transport and magnetotransport properties of the nanostructured LCMO and NSMO manganites. The reason behind selecting these nanostructured LCMO/NSMO systems is that, the ionic radius of $\text{Ca}^{2+}$ [1.18 Å] / $\text{Nd}^{3+}$ [1.163 Å] is smaller as compared to $\text{La}^{3+}$ [1.216 Å] / $\text{Sr}^{2+}$ [1.31 Å] which results in the distorted MnO$_6$ octahedra and hence lattice distortion plays an important role. As an effect of substitution of smaller $\text{Ca}^{2+}$ / $\text{Nd}^{3+}$ at larger $\text{La}^{3+}$ / $\text{Sr}^{2+}$ cations at A-site, Mn-O-Mn bond angles and Mn-O bond lengths get modified due to which, transport and magnetotransport properties of the systems get modified [13]. In the presently studied LCMO and NSMO systems, $<r_A> \sim 1.2$ Å is constant while the size variance $\sigma^2_A$ is twenty times larger in NSMO as compared to LCMO.
5.2 Synthesis and Experimental Details

The Sol-Gel method, used for the synthesis of nanostructured polycrystalline La$_{0.7}$Ca$_{0.3}$MnO$_3$ (LCMO) and Nd$_{0.7}$Sr$_{0.3}$MnO$_3$ (NSMO) manganites, consists of various steps as shown below in Fig. 5.1:

- **Solution of Precursors**
- **Condensation**
- **Gelation**
- **SOL colloid**
- **Dry**
- **Calcination**
- **Grind**
- **Powder**
- **Xerogel**
- **Press**
- **Sintering**
- **Final Product**
- **XRD**
- **SEM**
- **R-T & Magneto R-T**
- **Pellet Form**
- **Calcined Powder**
- **Grind**
- **Xerogel**

**Figure 5.1** Various steps involved in Sol-Gel synthesis of LCMO and NSMO manganites
La / Nd, Ca / Sr and Mn - acetates mixed in stoichiometric ratio, were dissolved in acetic acid and double distilled water (1:1 volume ratio), with continuous stirring at 90°C till clear solution was obtained with 0.4 molarity. Solution was dehydrated at 130°C to form a Sol through condensation process and further heating of 150°C converting the material into a Gel form through gelation. The brown Gel (of LCMO and NSMO) was calcined at 750°C for 12 hrs. The black powder thus obtained was sintered at different temperatures in the form of pellets. LCMO and NSMO samples were coded as LC7 / NS7, LC8 / NS8, LC9 / NS9 and LC11 / NS11 according to respective sintering temperatures of 700, 800, 900 and 1000°C. XRD measurements were carried out at RT for structure while Scanning Electron Microscopy (SEM) images were taken to understand the grain growth and grain morphology. To study the effect of the grain size on the transport and magnetotransport properties of LCMO compounds, the resistivity measurements in absence and presence of applied magnetic fields ~ 1, 5 and 8T in the temperature range of 300 - 5K were carried out. Resistivity vs applied field isotherms in the 0 - 8T range were obtained at different temperatures.

5.3 Structural Studies

Fig. 5.2 shows the raw XRD patterns of (a) LCMO and (b) NSMO samples sintered at different temperatures. The samples possess single phasic crystalline nature without any detectable impurities. Fig 5.3 shows an enlarged view of most intense (200) XRD reflections of all the samples studied, clearly revealing the reduction in intensity and shifting of the peaks toward higher 2θ values [Table 5.1] with decrease in TS. This is indicative of improved crystallinity in higher temperature sintered samples. It is also clear from the fig. 5.3 that, the broadening of the (200) peak increases with decrease in TS resulting into the enhancement in Full Width at Half Maximum (FWHM) [Table 5.1].
Figure 5.2  XRD patterns of all the (a) LCMO and (b) NSMO samples sintered at various temperatures
Table 5.1 lists the values of crystallite size (CS) determined using the Scherrer’s formula, \( t = \frac{0.9 \lambda}{B \cos \theta} \), where \( t \) is the crystallite size, \( B \) is the FWHM (value after subtracting the FWHM of an instrument used for the measurement), \( \theta \) is Bragg angle and \( \lambda \) is the wavelength used (in present case, for Cu K\( \alpha \), \( \lambda = 1.54178 \) Å). It is clear that, with increasing TS and decreasing FWHM, the CS increases due to the conglomeration of grains indicating better crystalline nature of the samples sintered at higher temperatures for both (LCMO and NSMO) nanostructured manganite systems.

![Graphs showing intensity vs 2θ for LCMO and NSMO samples](image)

Figure 5.3  An enlarged view of most intense (200) peak in (a) LCMO and (b) NSMO samples sintered at various temperatures
Table 5.1 Values of most intense \((200)\) peak position, FWHM and crystallite size (CS) for LCMO and NSMO samples sintered at various temperatures

<table>
<thead>
<tr>
<th>Sample</th>
<th>(L_{a_{0.7}Ca_{0.3}}MnO_3) (LCMO)</th>
<th>(Nd_{0.7}Sr_{0.3}MnO_3) (NSMO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS (^\circ\text{C})</td>
<td>((200)) peak position (deg.)</td>
<td>((200)) peak Intensity (counts)</td>
</tr>
<tr>
<td>700</td>
<td>32.92</td>
<td>764</td>
</tr>
<tr>
<td>800</td>
<td>32.76</td>
<td>1385</td>
</tr>
<tr>
<td>900</td>
<td>32.74</td>
<td>3292</td>
</tr>
<tr>
<td>1100</td>
<td>32.72</td>
<td>3917</td>
</tr>
</tbody>
</table>

Profile fitting refinement of powder diffraction patterns of all the LCMO and NSMO samples sintered at various temperatures were performed using FULLPROF [14], based on Rietveld method. The XRD profiles were modelled using a Modified 1 Lorentizian profile shape function. The atomic positions, occupancies, lattice parameters and FWHM parameters were refined. Figs. 5.4 and 5.5 shows the Rietveld fitted XRD patterns of all the four LCMO and four NSMO samples respectively. Insets in fig. 5.4 (LC7) and fig. 5.5 (NS7) show the most intense Rietveld refined \((200)\) peak depicting the fine and clear matching between the observed and calculated data. From Rietveld refinement, it is observed that, the unit cell structure is orthorhombic in nature having a space group \textit{Pnma} (No. 62) for all the LCMO and NSMO samples. Other Rietveld refined parameters like thermal parameters and R - factors are tabulated in Table 5.2 (LCMO) and Table 5.3 (NSMO). Parameters like Mn-O-Mn bond angles and Mn-O distances and their respective differences are also tabulated in Tables 5.4 and 5.5 for LSMO and NSMO samples, respectively.
Figure 5.4  Rietveld refined profile fittings for LCMO samples Inset: Most intense Rietveld refined peak for LC7

Figure 5.5  Rietveld refined profile fittings for all NSMO samples Inset: Most intense Rietveld refined peak for NS7
Tables 5.2 and 5.3 also include the values of the cell volume contraction for LC8 (NS8), LC9 (NS9) and LC11 (NS11) with respect to LC7 unit cell volume, determined, using the formula: contraction of $V_{8/9/11} = (V_7 - V_{8/9/11} / V_7) \times 100 \%$, where $V_7$, $V_8$, $V_9$ and $V_{11}$ are the unit cell volumes for the LCMO/NSMO samples sintered at 700, 800, 900 and 1100°C respectively. In addition to this, the orthorhombic unit cell anisotropy parameter calculated using $\delta = [b / (a^2+c^2)^{0.5}] - 1$ (for cubic unit cell $\delta = 0$). Low values of $\chi^2$ (close to one) indicate the goodness of the fit for all the LCMO and NSMO samples showing very good agreement between observed and fitted data.

Table 5.2 Values of Rietveld refined lattice parameters (a, b & c), unit cell volume (V), thermal parameters, R-factors, $\chi^2$, volume contraction and anisotropy for nanostructured LCMO samples sintered at various temperatures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>LC7</th>
<th>LC8</th>
<th>LC9</th>
<th>LC11</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>5.4633 (2)</td>
<td>5.4649 (3)</td>
<td>5.4807 (2)</td>
<td>5.4818 (7)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>7.7171 (6)</td>
<td>7.7193 (1)</td>
<td>7.7201 (3)</td>
<td>7.7353 (3)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>5.4822 (6)</td>
<td>5.4789 (5)</td>
<td>5.4617 (3)</td>
<td>5.4410 (4)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>231.1341</td>
<td>231.1285</td>
<td>231.0930</td>
<td>230.7167</td>
</tr>
<tr>
<td>$La // Ca$</td>
<td>$B_{iso}$ (Å²)</td>
<td>0.5055</td>
<td>0.5055</td>
<td>0.5055</td>
</tr>
<tr>
<td>$Mn$</td>
<td>$B_{iso}$ (Å²)</td>
<td>0.8214</td>
<td>0.8214</td>
<td>0.8214</td>
</tr>
<tr>
<td>$O_1$</td>
<td>$B_{iso}$ (Å²)</td>
<td>0.8155</td>
<td>0.8155</td>
<td>0.8155</td>
</tr>
<tr>
<td>$O_2$</td>
<td>$B_{iso}$ (Å²)</td>
<td>0.6069</td>
<td>0.6069</td>
<td>0.6069</td>
</tr>
<tr>
<td>$R_p$ (%)</td>
<td>11.3</td>
<td>11.8</td>
<td>8.82</td>
<td>10.2</td>
</tr>
<tr>
<td>$R_W$ (%)</td>
<td>19.9</td>
<td>20.4</td>
<td>14.6</td>
<td>18.0</td>
</tr>
<tr>
<td>Bragg R - Factor</td>
<td>5.70</td>
<td>7.56</td>
<td>6.57</td>
<td>5.11</td>
</tr>
<tr>
<td>$R_t$ - Factor</td>
<td>6.66</td>
<td>7.96</td>
<td>6.72</td>
<td>7.08</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>1.036</td>
<td>1.15</td>
<td>1.094</td>
<td>1.226</td>
</tr>
<tr>
<td>Unit cell volume contraction</td>
<td>0.0</td>
<td>0.0024</td>
<td>0.0178</td>
<td>0.1806</td>
</tr>
<tr>
<td>$\delta$ (10⁻³)</td>
<td>2.91</td>
<td>2.47</td>
<td>2.24</td>
<td>1.51</td>
</tr>
</tbody>
</table>
The unit cell volume contraction is smaller in LCMO samples as compared to NSMO indicating appreciable effect of TS on the structure of NSMO. The structural anisotropy in the samples sintered at higher temperatures is lower in LCMO while in NSMO samples, with increase in TS, the structural anisotropy increases.

Table 5.3 Values of Rietveld refined lattice parameters (a, b & c), unit cell volume (V), thermal parameters, R-factors, $\chi^2$, volume contraction and anisotropy for nanostructured NSMO samples sintered at various temperatures

<table>
<thead>
<tr>
<th>Sample</th>
<th>NS7</th>
<th>NS8</th>
<th>NS9</th>
<th>NS11</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>5.4449 (2)</td>
<td>5.4458 (8)</td>
<td>5.4462 (8)</td>
<td>5.4481 (4)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>7.7140 (3)</td>
<td>7.7251 (6)</td>
<td>7.7260 (9)</td>
<td>7.7277 (3)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>5.4678 (2)</td>
<td>5.4541 (3)</td>
<td>5.4495 (4)</td>
<td>5.4362 (2)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>229.6583</td>
<td>229.4504</td>
<td>229.3005</td>
<td>228.8710</td>
</tr>
<tr>
<td>Nd // Sr</td>
<td>Biso (Å²)</td>
<td>0.0457</td>
<td>0.1751</td>
<td>0.4788</td>
</tr>
<tr>
<td>Mn</td>
<td>Biso (Å²)</td>
<td>0.6892</td>
<td>-0.2097</td>
<td>-0.0244</td>
</tr>
<tr>
<td>O₁</td>
<td>Biso (Å²)</td>
<td>-0.2575</td>
<td>-0.1504</td>
<td>3.7547</td>
</tr>
<tr>
<td>O₂</td>
<td>Biso (Å²)</td>
<td>0.5098</td>
<td>0.4060</td>
<td>0.7649</td>
</tr>
<tr>
<td>Rp (%)</td>
<td>14.7</td>
<td>11.1</td>
<td>10.6</td>
<td>8.77</td>
</tr>
<tr>
<td>Rw (%)</td>
<td>23.3</td>
<td>19.9</td>
<td>19.1</td>
<td>15.8</td>
</tr>
<tr>
<td>Bragg R - Factor</td>
<td></td>
<td>6.57</td>
<td>4.32</td>
<td>4.03</td>
</tr>
<tr>
<td>Rf - Factor</td>
<td></td>
<td>7.59</td>
<td>5.38</td>
<td>6.20</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>1.5438</td>
<td>1.186</td>
<td>1.260</td>
<td>1.050</td>
</tr>
<tr>
<td>Unit cell volume Contraction</td>
<td></td>
<td>0.0</td>
<td>0.0905</td>
<td>0.1558</td>
</tr>
<tr>
<td>$\delta$ (10⁻³)</td>
<td></td>
<td>0.32</td>
<td>2.30</td>
<td>2.80</td>
</tr>
</tbody>
</table>

Table 5.4 and Table 5.5 lists Rietveld refined values of Mn-O-Mn bond angles and Mn-O bond lengths for LCMO and NSMO samples, respectively sintered at various temperatures. The transport in manganites depend on the structural features of MnO₆ octahedra such as MnO₆ distortions, $Q_2$ mode basal plane, band width of charge carriers, Mn - O bond lengths and Mn-O-Mn bond angles.
Table 5.4  Values of Rietveld refined Mn-O-Mn bond angles and Mn-O bond distances for nanostructured LCMO samples sintered at various temperatures

<table>
<thead>
<tr>
<th>Sample</th>
<th>LC7</th>
<th>LC8</th>
<th>LC9</th>
<th>LC11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn - O₁ - Mn</td>
<td>163.17 (2)</td>
<td>163.30 (2)</td>
<td>164.90 (3)</td>
<td>168.77 (2)</td>
</tr>
<tr>
<td>Mn - O₂ - Mn</td>
<td>173.67 (3)</td>
<td>173.67 (4)</td>
<td>171.80 (4)</td>
<td>170.54 (2)</td>
</tr>
<tr>
<td>Δ (°)</td>
<td>10.50</td>
<td>10.37</td>
<td>06.90</td>
<td>01.77</td>
</tr>
<tr>
<td>Mn - O₁ (Å)</td>
<td>1.9674 (2)</td>
<td>1.9642 (3)</td>
<td>1.9469 (4)</td>
<td>1.9386 (3)</td>
</tr>
<tr>
<td>Average Mn - O₂ (Å)</td>
<td>1.9373 (4)</td>
<td>1.9382 (2)</td>
<td>1.9393 (2)</td>
<td>1.9410 (4)</td>
</tr>
<tr>
<td>D (Å)</td>
<td>0.0301</td>
<td>0.0260</td>
<td>0.0076</td>
<td>0.0024</td>
</tr>
</tbody>
</table>

Table 5.5  Values of Rietveld refined Mn-O-Mn bond angles and Mn-O bond distances for nanostructured NSMO samples sintered at various temperatures

<table>
<thead>
<tr>
<th>Sample</th>
<th>NS7</th>
<th>NS8</th>
<th>NS9</th>
<th>NS11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn - O₁ - Mn</td>
<td>153.71 (4)</td>
<td>157.30 (3)</td>
<td>158.32 (5)</td>
<td>165.20 (20)</td>
</tr>
<tr>
<td>Mn - O₂ - Mn</td>
<td>168.24 (6)</td>
<td>167.38 (7)</td>
<td>166.29 (4)</td>
<td>166.20 (14)</td>
</tr>
<tr>
<td>Δ (°)</td>
<td>14.53</td>
<td>10.08</td>
<td>07.97</td>
<td>01.00</td>
</tr>
<tr>
<td>Mn - O₁ (Å)</td>
<td>1.9832 (3)</td>
<td>1.9732 (9)</td>
<td>1.9616 (4)</td>
<td>1.9500 (5)</td>
</tr>
<tr>
<td>Average Mn - O₂ (Å)</td>
<td>1.9360 (4)</td>
<td>1.9390 (2)</td>
<td>1.9415 (4)</td>
<td>1.9650 (3)</td>
</tr>
<tr>
<td>D (Å)</td>
<td>0.0472</td>
<td>0.0349</td>
<td>0.0201</td>
<td>0.0150</td>
</tr>
</tbody>
</table>

Fig. 5.6 shows the variation in lattice parameters and unit cell contraction for (a, c) LCMO and (b, d) NSMO samples. Insets of fig. 5.6 show the variation in anisotropy with TS for both the nanostructured manganite samples. From fig. 5.6 and Tables 5.2 and 5.3 it is clear that, the lattice parameters, a and b, increases while c decreases with increase in TS resulting in the unit cell contraction with increase in TS [Table 5.2 and 5.3].
As shown in fig. 5.7, six $O^{2-}$ anions and one $Mn^{3+}/Mn^{4+}$ cation forms the $MnO_6$ octahedron in which two $O_1$ ions are placed on C – axes and four $O_2$ ions make the basal plane. From Table 5.4 and Table 5.5, in both the manganite systems, it is clearly seen that, $Mn-O_1-Mn$ bond angle continuously increases and the value of $Mn-O_2-Mn$ bond angle in basal plane is suppressed marginally as an effect of $TS$. As listed in Table 5.4 and 5.5, the difference ($\Delta$) between $Mn - O_1 - Mn$ angle (c axis) and $Mn - O_2 - Mn$ (basal plane) angle has been calculated is found to decrease with increase in $TS$. Similarly, $Mn-O_1$ distance decreases marginally with $TS$. For basal plane $Mn-O$ distances, an average of two $Mn-O_2$ distance increases. This suggests, with increase in $TS$, overall $Mn-O_1-Mn$ angle value increases with suppression in $Mn-O_1$ distance and decrease in $Mn-O_2-Mn$ bond angle along with increased $Mn-O_2$ distance. The difference (D) between
the apical (c-axis) and basal plane bond distances is reduced with increase in TS [Table 5.4 and 5.5].

Figure 5.7 Representation of MnO₆ with O₁ and O₂ anions placed in an octahedral

5.4 Microstructural Properties

The microstructural measurements for understanding the grain growth and grain morphology of the LCMO and NSMO samples were carried out using SEM in secondary electron imaging mode at RT. Fig. 5.8 shows the representative images elucidating grain morphology of the LCMO and NSMO samples sintered at various temperatures. Average grain sizes ~ 850, 125, 80 and 40nm were observed in LC11, LC9, LC8 and LC7 respectively while NSMO exhibit grain size ~ 850, 500, 250 and 170nm for NS11, NS9, NS8 and NS7 samples respectively. It can be seen that, average grain size increases with increase in TS due to the conglomeration of smaller grains into the larger one. A large difference between the CS and grain size of the samples has been observed which increases with TS. This can be attributed to the fact that, the grains are composed of several crystallites probably due to the internal stress or defects in the structure [15]. In the samples sintered at 1100°C, the grains are well connected whereas with the reduction in TS, for LC7 and NS7, the connectivity becomes poor.
Figure 5.8  SEM micrographs of nanostructured manganite samples of LCMO and NSMO systems sintered at various temperatures
The grains and grain boundaries are not clear and long necks between two neighbouring grains are observed in the samples sintered at lower temperatures. With the increase in TS from 700 to 1100°C in LCMO and NSMO, the grain size becomes larger, grain boundaries become obvious and necks between the grains disappear. The reduced grain boundary effects result into the surface effects which decreases the surface to volume ratio ($D^{-1}$) due to the improved grain size with TS.

5.5 Transport Properties

The transport behaviour of LCMO and NSMO samples sintered at various temperatures was studied using resistivity measurements in the absence and presence of (1, 5 and 8T) applied magnetic fields in the temperature range 5 - 300K using four probe method as shown in fig. 5.9. All the samples exhibit I - M transition. With increase in sintering temperature, the resistivity decreases throughout the temperature range studied while the $T_P$ increases in both the systems. The values of transport parameters for LCMO and NSMO samples sintered at various temperatures are listed in Table 5.6. LC11 sample exhibits peak resistivity ($\rho_P$) $\sim$ 0.0822 $\Omega$cm which becomes $\sim$ 100 times higher in LC7 (8.6266 $\Omega$cm), whereas, $\rho_{RT}$ $\sim$ 0.0484 $\Omega$cm in LC11 becomes approximately 45 times higher in LC7 (2.1420 $\Omega$cm), under zero applied magnetic field. Similarly, NS11 sample exhibits $\rho_P$ $\sim$ 0.782 $\Omega$cm and $\rho_{RT}$ $\sim$ 0.192 $\Omega$cm which becomes $\sim$ 118.703 $\Omega$cm ($\sim$ 150 times higher) and $\sim$ 6.499 $\Omega$cm ($\sim$ 35 times higher) respectively in NS7. Similarly, residual resistivity ($\rho_0$) decreases with increase in TS (Table 5.6).

As shown in fig. 5.9, LC7 and NS7 samples show broader M - I transition which becomes sharper with increase in TS in both the manganite systems. In $\rho$ - T plots, all the samples show the resistivity up-turn at low temperature. $T_m$ is the minimum temperature below which the resistivity increases with lowering the temperature. The resistivity up-turn behaviour weakens and $T_m$ shift towards lower temperature values with increase in TS as well as applied magnetic field, as shown in fig. 5.9 and Table 5.6.
Figure 5.9  $\rho$ vs. T plots collected at various fields of 0, 1, 5 and 8T in the temperature range 5 - 300K for all the LCMO and NSMO samples
The observed reduction in resistivity and enhancement in $T_P$ values can be attributed to the peak intensity and crystallite size which increase in both the systems with TS resulting into the better crystallinity. Better crystalline samples exhibit improved transport in nanostructured LCMO and NSMO manganites which are sintered at higher temperature. Furthermore, the suppression of the resistivity throughout the studied temperature range, on the application of magnetic field can be explained using the exchange between Mn$^{3+}$ and Mn$^{4+}$ ions via an Oxygen (ZDE).

Table 5.6 Values of transport parameters including residual resistivity ($\rho_0$), resistivity at peak ($\rho_p$) and at RT ($\rho_{RT}$), transition temperature ($T_P$), minimum temperature ($T_m$) and resistivity at $T_m$ ($\rho_m$) for nanostructured LCMO and NSMO samples sintered at various temperatures

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\rho_0$ ($\Omega$cm)</th>
<th>$\rho_p$ ($\Omega$cm)</th>
<th>$\rho_{RT}$ ($\Omega$cm)</th>
<th>$T_P$ (K)</th>
<th>$\rho_m$ ($\Omega$cm)</th>
<th>$T_m$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LC7</td>
<td>4.3277</td>
<td>8.6266</td>
<td>2.1420</td>
<td>189</td>
<td>3.2932</td>
<td>33</td>
</tr>
<tr>
<td>LC8</td>
<td>1.0601</td>
<td>3.2724</td>
<td>1.3726</td>
<td>234</td>
<td>0.8921</td>
<td>32</td>
</tr>
<tr>
<td>LC9</td>
<td>0.1396</td>
<td>0.6815</td>
<td>0.3860</td>
<td>266</td>
<td>0.1316</td>
<td>28</td>
</tr>
<tr>
<td>LC11</td>
<td>0.0078</td>
<td>0.0822</td>
<td>0.0484</td>
<td>270</td>
<td>0.0076</td>
<td>19</td>
</tr>
<tr>
<td>NS7</td>
<td>114.167</td>
<td>118.703</td>
<td>6.499</td>
<td>132</td>
<td>74.525</td>
<td>41</td>
</tr>
<tr>
<td>NS8</td>
<td>4.039</td>
<td>7.270</td>
<td>1.656</td>
<td>174</td>
<td>3.486</td>
<td>34</td>
</tr>
<tr>
<td>NS9</td>
<td>1.650</td>
<td>3.748</td>
<td>0.996</td>
<td>188</td>
<td>1.488</td>
<td>31</td>
</tr>
<tr>
<td>NS11</td>
<td>0.109</td>
<td>0.782</td>
<td>0.192</td>
<td>222</td>
<td>0.104</td>
<td>27</td>
</tr>
</tbody>
</table>

Magnetic field can make electron spins parallel which results into lowering of resistivity along with shifting of $T_P$ towards higher temperatures. This is the reason why the structure of MnO$_6$ octahedra plays an important role in governing the transport properties of manganites.

Fig. 5.10 shows the dependence of residual resistivity ($\rho_0$), resistivity at peak ($\rho_p$) and at RT ($\rho_{RT}$) and $T_P$ on surface to volume ratio ($D^{-1}$) for presently studied LCMO [fig. 5.10] and NSMO [fig. 5.11] nanostructured systems. It is clear that, the resistivities increase whereas $T_P$ decreases with increase in $D^{-1}$. This can be attributed to the enhanced...
surface contribution at lower TS or lower grain size as well as to the potential barriers (as grain boundaries) between the neighbouring grains. Furthermore, the increasing $T_P$ with reduced $D^{-1}$ can be understood on the basis of enhanced total ZDE mechanism as a consequence of reduced surface area and hence reduced Mn-O dangling bonds on the surface with TS.

Figure 5.10  Dependence of (a) $\rho_0$ and $\rho_{RT}$ (b) $\rho_P$ and $T_P$ on $D^{-1}$ for nanostructured LCMO samples sintered at various temperatures

Figure 5.11  Dependence of (a) $\rho_0$ and $\rho_{RT}$ (b) $\rho_P$ and $T_P$ on $D^{-1}$ for nanostructured NSMO samples sintered at various temperatures
Fig. 5.12 shows the dependence of peak resistivity and transition temperature on TS for LCMO and NSMO nanostructured manganites sintered at various temperatures. It is clear that, the maximum resistivity in $\rho$ vs T plots for all the LCMO samples is lower than that in NSMO samples which can be attributed to the large (~ 20 times larger) size variance in NSMO in comparison with LCMO (both the systems possess equivalent average A-site cationic radius ~ 1.2 Å). The difference between the resistivities of LCMO and corresponding NSMO samples reduces with increase in temperature indicating the prominent effect of size variance in the samples sintered at lower temperatures. This indicates the strong dependence of size variance effect on the grain morphology in the samples. In similar way, due to the large size variance in NSMO samples, the $T_P$ values are observed to be small in NSMO samples in comparison with corresponding LCMO samples sintered at same temperatures.

![Graph](image)

Figure 5.12  Dependence of (a) $\rho_p$ and (b) $T_P$ on TS for nanostructured LCMO and NSMO samples sintered at various temperatures
5.6 Low Temperature Transport

In manganites at low temperatures electrons are localized and due to this resistivity upturn can be observed. This low temperature transition \((T_m)\) is known as resistivity minima. The \(T_m\) is the temperature above which the samples show the metallic behaviour and below which they exhibit the insulating properties. Various possible reasons for the occurrence of resistivity minima have been suggested which includes grain boundary effect, phase separation, Kondo effect and electron-electron \((e-e)\) scattering \([12, 16]\). It can be seen that, all the LCMO and NSMO samples show an unexpected resistivity up-turn at low temperature below 40K. Table 5.6 highlights the values of \(T_m\) that decreases with increase in TS.

This up-turn can be related to an electrostatic blockade of carriers \((e_g\) electrons) at grain boundaries. The decrease in \(T_m\) indicating the prominence of metallic behaviour over the up-turn as the TS increases. Similarly, magnetic field can flatten the resistivity up-turn and hence can reduce the \(T_m\). Electrostatic blockade model predicts a temperature dependence for the resistivity in the form \(\rho(T) \propto \exp(E_C/T)^{1/2}\) \([17, 18]\). This functional form can be observed from the fits in fig. 5.13 for LC7 sample and fig. 5.14 for NS7 sample under various applied fields while fig. 5.15 for LCMO samples and fig. 5.16 for NSMO samples (under zero applied field) sintered at various temperatures. \(E_C\) is the electrostatic blocking energy, also called as charging energy that is the required energy to pass the \(e_g\) electrons through the grain boundaries. The values of \(E_C\) are given into their corresponding plots with fitting. As shown in fig. 5.13 and fig. 5.14, with increase in magnetic field, the charging energy decreases indicating the magnetic field induced reduction in the scattering of the charge carriers and disorder at the grain boundaries through the alignment of the Mn-O-Mn bonds and Mn spins. Fig. 5.15 and fig. 5.16 show that, with increase in TS, the charging energy is largely reduced suggesting the suppression in grain boundary effect. This can be understood as an effect of TS on grain boundaries such that the number of grain boundaries decreases, the compactness of the grains increases, thickness of the grain boundaries reduces and the contact between the neighboring grains is enhanced with increase in TS.
Figure 5.13 Dependence of log $\rho$ (5-60K) on $T^{-0.5}$ under various fields for LC7 sample

Figure 5.14 Dependence of log $\rho$ (5-60K) on $T^{-0.5}$ under various fields for NS7 sample
Figure 5.15  Dependence of log $\rho$ (5-60K) on $T^{-0.5}$ under zero applied field for LCMO samples sintered at various temperatures

Figure 5.16  Dependence of log $\rho$ (5-60K) on $T^{-0.5}$ under zero applied field for NSMO samples sintered at various temperatures
Figure 5.17 Dependence of charging energy, $E_C$, on $D^{-1}$ (under zero applied field) and on applied field $H$ (for LC7 sample) for LCMO nanostructured manganites.

Figure 5.18 Dependence of charging energy, $E_C$, on $D^{-1}$ (under zero applied field) and on applied field $H$ (for LC7 sample) for LCMO nanostructured manganites.
It is reported that, the charging energy, $E_C$, increases with surface to volume ratio ($D^{-1}$) [11]. Figs. 5.17 and fig. 5.18 show the variation $E_C$ with $D^{-1}$ and $H$ for LCMO and NSMO nanostructured manganite samples respectively sintered at various temperatures. The $E_C$ increases with increase in $D^{-1}$ indicating that, the electrostatic blocking of $e_g$ electrons at grain boundaries increases rapidly with increase in surface effect through the grain morphology modifications, change in grain boundary nature and increased grain boundary density. The decrease in $E_C$ with increase in applied field, $H$, suggests the magnetic field induced spin polarization and spin arrangement improvement at low temperature (below $T_m$). This can be also attributed to the magnetic field induced suppression in the disorder at Mn-O-Mn bonds at grain boundaries.

![Graph](image)

**Figure 5.19** Variation in charging energy ($E_C$) with (a) TS (under zero applied field) and (b) field, $H$ (for 700$^\circ$C) LCMO and NSMO nanostructured manganite samples sintered at various temperatures

Fig. 5.19 shows the variation in charging energy with TS and H obtained from zero field minima fittings and under various fields for 700$^\circ$C sintered LCMO and NSMO nanostructured manganite samples sintered at various temperatures. It can be clearly seen that, with increase in TS and H, the $E_C$ decreases continuously as described in fig. 5.17 and fig. 5.18. The clear observation is that, the values of $E_C$ under zero applied field for

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all the LCMO and NSMO samples as well as under various applied fields for LCMO are smaller than that of NSMO samples. This can be attributed to the large size variance and hence largely disordered structure and grain growth in NSMO in comparison with LCMO. Furthermore, from fig. 5.19 (a), it can be seen that, the difference between the values of $E_C$ at various TS reduces with increasing TS. This is the observation as discussed earlier for $\rho_P$ indicating the prominent effect of size variance at lower TS. The values of $E_C$ reduces largely due to the increasing TS than H indicating that, the resistivity minima and hence the modifications in grain morphology in both the LCMO and NSMO manganite systems are highly affected by the TS than applied field H.

5.7 Magnetotransport Properties

Fig. 5.20 shows the MR vs T plots for LCMO samples sintered at various temperatures while the inset of fig. 5.20 shows the temperature dependence of MR% determined using the formula $MR\% = (\rho_H - \rho_0 / \rho_0) \times 100$ for LC7 sample under 1T. Fig. 5.21 shows the MR vs T plots for NSMO samples sintered at various temperatures under 1T field. Inset of fig. 5.21 shows MR-T plot for NS11 under 1T.

As shown in figs. 5.20 and 5.21, MR vs T plots of nanostructured LCMO and NSMO exhibit both the extrinsic and intrinsic components of MR. Intrinsic MR response is observed around M-I transition ($T_P$) which requires relatively large magnetic fields ($> 1T$) and can be tuned by the ZDE mechanism and the grain boundary density in the samples. Extrinsic MR component observed mostly in nanostructured manganites, can be modified by the grain morphology and grain boundary density at $T < T_P$ under fields $\leq 1T$. The values of MR at 5K under 1T field are 34, 32, 31, and 25% respectively for LC7, LC8, LC9 and LC11 samples which becomes $\sim 32\%$ in NS7, NS8 and NS9 samples while for NS11 it is 25% at 5K under 1T field. The relatively large MR values at 5K exhibited by all the nanostructured manganites indicate the presence of strong extrinsic MR behaviour in samples studied.
Figure 5.20  MR vs. T plots under 1T for nanostructured LCMO samples sintered at 800, 900 and 1100°C [Inset: MR vs. T plot for LC7 sample under 1T]

Figure 5.21  MR vs. T plots (range: 5 - 300K) under 1T for nanostructured NSMO samples sintered at 700, 800 and 900°C [Inset: MR vs. T plot for NS11 sample under 1T]
LC7, NS7, NS8 and NS9 samples exhibit linear variation in MR vs. T plots indicating the presence of intrinsic MR which is superimposed by LFMR appearing at low temperature < $T_P$, as a consequence of the granular morphology of the samples. CMR around $T_P$, the basic characteristic of the manganites, can be tuned by means of particle size variations [17]. The MR vs T plots for the above mentioned samples except LC11 and NS11 samples show constant decrease in MR with increase in temperature (fig. 5.20 and fig. 5.21), without any peak around $T_P$ suggesting the intrinsic MR response of the samples. LC11 and NS11 samples exhibit the peak in MR around $T_P$ (fig. 5.20 and inset of fig. 5.21). It can be see that, the variation in MR (under 1T) having peak MR ~ 11% in LC8 and 39% in LC11 and ~ 21% in NS11 can be attributed to intrinsic cause (intrinsic MR). The intrinsic MR can be governed by ZDE mechanism while extrinsic MR can be tuned by grain morphology which may be due to the spin polarized tunnelling (SPT) between the neighbouring grains [8].

To explore the systematic variation of MR with field for all the nanostructured LCMO and NSMO samples sintered at various temperatures, the MR vs H isotherms were recorded in the field up to 8T at various temperatures, as shown in fig. 5.22. All the samples exhibit negative MR at 5, 100, 200, 250 and 300K. It is reported that, nanostructured polycrystalline manganites show the low field MR (LFMR) at low temperature [19] which can be attributed to the SPT or SDS effect [8, 9]. The values of MR (LFMR and HFMR) at various temperatures for LCMO and NSMO samples are listed in Table 5.7.
Figure 5.22  MR vs. H isotherms collected at different temperatures for LCMO and NSMO manganites
Table 5.7  Values of D⁻¹, MR% (LFMR and HFMR) at 5K and HFMR at 100, 200, 250 and 300K obtained from MR-H isotherms

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface to Volume ratio D⁻¹ (nm⁻¹)</th>
<th>5K LFMR</th>
<th>HFMR</th>
<th>100K</th>
<th>200K</th>
<th>250K</th>
<th>300K</th>
</tr>
</thead>
<tbody>
<tr>
<td>LC7</td>
<td>0.025</td>
<td>35</td>
<td>57</td>
<td>N.A.</td>
<td>55</td>
<td>42</td>
<td>15</td>
</tr>
<tr>
<td>LC8</td>
<td>0.0125</td>
<td>35</td>
<td>55</td>
<td>N.A.</td>
<td>54</td>
<td>53</td>
<td>21</td>
</tr>
<tr>
<td>LC9</td>
<td>0.008</td>
<td>34</td>
<td>51</td>
<td>N.A.</td>
<td>48</td>
<td>56</td>
<td>31</td>
</tr>
<tr>
<td>LC11</td>
<td>0.00118</td>
<td>23</td>
<td>46</td>
<td>N.A.</td>
<td>48</td>
<td>56</td>
<td>48</td>
</tr>
<tr>
<td>NS7</td>
<td>0.00588</td>
<td>32</td>
<td>65</td>
<td>68</td>
<td>50</td>
<td>N.A.</td>
<td>09</td>
</tr>
<tr>
<td>NS8</td>
<td>0.004</td>
<td>31</td>
<td>58</td>
<td>56</td>
<td>52</td>
<td>N.A.</td>
<td>15</td>
</tr>
<tr>
<td>NS9</td>
<td>0.002</td>
<td>30</td>
<td>56</td>
<td>54</td>
<td>54</td>
<td>N.A.</td>
<td>17</td>
</tr>
<tr>
<td>NS11</td>
<td>0.00118</td>
<td>25</td>
<td>48</td>
<td>48</td>
<td>66</td>
<td>N.A.</td>
<td>21</td>
</tr>
</tbody>
</table>

Figure 5.23  MR vs. D⁻¹ plots (at 5K and RT) under 8T field for nanostructured LCMO and NSMO samples sintered at various temperatures
Fig. 5.23 shows the MR vs. $D^{-1}$ plots of LCMO and NSMO samples at 5K and RT under 8T field. It can be seen that HFMR (at 5K) increases with increase in $D^{-1}$ for both the samples suggesting the alignment of Mn-O dangling bonds at the surface of grains and grain boundaries under high applied magnetic field due to enhanced surface effect. However, at RT, HFMR decreases with $D^{-1}$, in both the samples, possibly due to extrinsic effect on MR becoming prominent over intrinsic MR. Hence, it can be seen that, there exist interplay between the MR at 5K and RT, induced due to surface to volume ratio effect in nanostructured manganites studied.

Fig. 5.24 depicts the dependence of MR at 5K and RT on the sintering temperature (TS) of the samples under high field (~ 8T) in LCMO and NSMO manganites. It can be observed that, MR% at 5K decreases with increasing TS in both the systems while at RT, it shows increasing behaviour. Also, due to large size disorder ($\sigma^2$) in NSMO manganites, leads to cation size mismatch resulting in large variation in scattering of charge carriers. Under large applied field, scattering is suppressed appreciably leading to large MR in NSMO as compared to LCMO having smaller disorder. At RT exactly opposite phenomenon of decreasing MR with TS is observed for

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NSMO samples, having smaller MR as compare to LCMO. The reason for this is as followed, all the NSMO samples have $T_P < 300K$ so around RT all the samples are in paramagnetic state due to that MR values are low as compared to LCMO samples.

5.8 Discussion

During the course of present work on the structure-property correlation studies in LCMO and NSMO manganites, it has been observed that Mn - O$_1$ - Mn bond angle increases toward $180^\circ$ with increase in TS and Mn - O$_2$ - Mn bond angle remain almost constant $\sim 180^\circ$ which supports the ZDE to become prominent in higher sintered samples (Table 5.4). The reduced difference between Mn - O - Mn bond angles and hence suppressed distortion in MnO$_6$ octahedra results into better transfer integral of itinerant $e_g$ electrons through the Mn - O – Mn. Similarly, the large difference between bond lengths in MnO$_6$ octahedra, observed in lower sintered samples of LCMO and NSMO systems, reveals the presence of strong Jahn - Teller (JT) effect. This bond length difference decreases with TS, and at higher TS; the JT effect becomes less effective where the ZDE is prominent mechanism due to the reduced distortion in MnO$_6$ octahedra (Table 5.4 and 5.5). As a consequence, the overall reduction in MnO$_6$ octahedral distortion results into the ZDE mechanism which becomes apparent over the JT effect in the samples sintered at higher TS and hence resistivity is largely suppressed and $T_P$ increases.

Moreover, it has been reported that, in nanostructured manganites, an increase in $T_P$ and reduction in resistivity can be attributed to the grain morphology in the system [13, 20 - 24]. SEM study on LCMO and NSMO reveals that, the grains are evenly distributed in the samples. In addition, with increase in TS the porosity decreases while the connectivity between grains increases. Further, it has been observed that, the average grain size in both the systems increases with increase in TS resulting in the reduction in grain boundary density. Grains are more crystalline while the grain boundaries are amorphous or less crystalline depending upon the nature of the grain boundaries. Hence, in the samples sintered at higher temperatures, the large grain size and lower grain boundary density results in the better crystallinity in the samples and hence better transport. With increase of TS, the grain size increases as a result grain boundary density
is reduced resulting in the suppression of scattering of charge carriers at the grain boundaries. With increase in TS, and hence reduction in grain boundary density number of Mn - O - Mn broken bonds is reduced [20, 22]. Hence overall grain boundary effects decrease from LC7 (NS7) to LC11 (NS11), which results in to the control over JT effect and supports the ZDE mechanism. Thus, it can be seen that, with increase in grain size, decrease in number of grain boundaries and hence decrease in broken Mn - O - Mn bonds at the grain boundaries result into the decrease of scattering of $e_g$ electrons, excess of electron conduction, reduction in spin disorder and hence enhancement in the value of $T_P$. The sharpness of the electrical transition is increased with TS which may be attributed to the grain structure of the samples [19]. In lower sintered samples, the grains are loosely connected or connected through the less crystalline necks as also visible in the SEM micrographs of LCMO and NSMO samples resulting into the broader metal - insulator transition.

In the presently studied nanostructured LCMO and NSMO manganites, the LFMR increases on decreasing the sintering temperature because of enhanced spin-polarized tunneling (SPT) through the increased number of grain boundaries as the sintering temperature decreases.

In both the nanostructured manganite systems, the reason behind the prominence of extrinsic MR over the intrinsic MR sintered at lower temperatures can be explained as: with increase in TS, the grain size increases and hence the grain boundary density decreases resulting into the decrease in scattering of the charge carriers at the grain boundaries on application of magnetic fields ($\leq 1T$). This promotes the suppression in the total SPT at the grain boundaries resulting into the decreasing MR values at low temperature with increase in TS. Furthermore, the variation in MR observed for LCMO indicates that, the constant MR region is only possible for the sample sintered at 700$^\circ$C (LC7) while in NSMO sample it is possible in all the samples except NS11 indicating the most prominent role of grain morphology in NSMO as compared to LCMO samples.
5.9 Conclusions

In summary, in this chapter, the successful synthesis of nanophasic polycrystalline La_{0.7}Ca_{0.3}MnO_3 (LCMO) and Nd_{0.7}Sr_{0.3}MnO_3 (NSMO) manganites using Sol-Gel route has been reported and the results of the studies on sintering temperature dependent modifications in structural, microstructural, transport and magnetotransport properties of both the systems have been discussed in detail. The main objective behind selecting these two manganites systems having $<r_A> \sim 1.2\AA$ is, to understand the effect of the size variance (which is 20 times larger in NSMO as compared to LCMO) on the MR behaviour of samples. It is observed that, using Sol-Gel route of synthesis, the phase formation takes place at comparatively lower temperature (~ 700°C). Microstructural studies using SEM shows that, grain size increases with TS and the necking between grains reduces using increasing TS with samples sintered at 1100°C having necks fully suppressed. The suppression in the mismatch between the bond lengths and bond angles due to the TS lead the reduction in the octahedral distortion which supports ZDE mechanism to provide the better transport in samples sintered at higher TS. It has been found that, low temperature LFMR (extrinsic MR) decreases and intrinsic MR increases with increase in TS. The enhancement in LFMR for small size particles is attributed to SPT between the loosely connected grain boundaries at lower TS. The cause for resistivity upturn phenomenon can be attributed to electrostatic blocking of the itinerant $e_g$ electrons at the grain boundaries. Finally, the fine tuning between the extrinsic MR, intrinsic MR and electrostatic blocking effect has been studied with an effect of $D^{-1}$ in the nanostructured LCMO ad NSMO manganites. Thus, the transport and magnetotransport in nanostructured LCMO and NSMO manganites is appreciable affected by the size variance effect and a sintering temperature dependent interplay between the intrinsic and extrinsic MR behaviour exists in the manganite systems studied.
References


Scope for the Future Work

During the present research work, an attempt has been made to study structure-property correlations in the bulk polycrystalline charge ordered (CO) manganites using temperature dependent Neutron Diffraction (ND) technique. The emergence of magnetic peaks at low temperature, resulting in the coexisting A-type antiferromagnetic and CE-type antiferromagnetic phases in \( \text{La}_{0.325}\text{Tb}_{0.125}\text{Ca}_{0.30}\text{Sr}_{0.25}\text{MnO}_3 \) (LTCSMO) sample has been understood using detailed analysis of the neutron diffraction data taken at various temperatures. To understand the effect of individual substitution of smaller \( \text{Ca}^{2+} \) and larger \( \text{Sr}^{2+} \) ion at La-site along with magnetic \( \text{Tb}^{3+} \) ion, two different systems namely \( \text{La}_{0.375}\text{Tb}_{0.125}\text{Ca}_{0.5}\text{MnO}_3 \) (LTC) and \( \text{La}_{0.375}\text{Tb}_{0.125}\text{Sr}_{0.5}\text{MnO}_3 \) (LTS) have been studied using temperature dependent ND and magnetization measurements. Both the systems exhibit different low temperature magnetic behavior which needs further in depth investigations using ND and magnetic measurements. Attempt has also been made to study the effect of structure, grain size and grain morphology on transport and magnetotransport of \( \text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 \) (LCMO) and \( \text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3 \) (NSMO) nanostructured manganites synthesized using novel Sol-Gel route.

It is proposed that below mentioned investigations and studies need to be carried out to resolve few unsolved issues evolved during the present course of work -

- The effect of simultaneous divalent cation and \( \text{Tb}^{3+} \) doping having different concentration at La-site in the charge ordered \( \text{La}_{0.5}\text{Mn}_{0.5}\text{O}_3 \) manganite needs to be understood using temperature dependent ND under various applied fields and magnetic measurements under similar conditions.

- The understanding of the phenomenon of kinetic arrest and magneto-structural correlations in \( \text{(LaTb)(Ca/Sr)MnO}_3 \) charge ordered manganites using various magnetic measurement protocols at low temperatures.

- The study of particle size and grain morphology on CO in manganites.
1. Grain Size Dependent Transport and Magnetoresistance Behavior of CSD Grown Nanostructured LSMO Manganite Thin Films

2. Transport and Magnetotransport Studies on Sol-Gel Grown Nanostructured La0.7Pb0.3MnO3 Manganites
   P.S. Solanki, R.R. Doshi, C.M. Thaker, Swati Pandya, V. Ganesan and D.G. Kuberkar

3. Magnetic Phase Coexistence in Tb3+ and Sr2+ doped La0.7Ca0.3MnO3 manganite: A Temperature Dependent Neutron Diffraction Study

4. Structural, Microstructural, Transport and Magnetotransport Properties of Nanostructured La0.7Sr0.3MnO3 Manganites Synthesized by Co-precipitation
   J. Mater. Res. (Accepted) (2010)
5. Grain Growth Dependent Transport and Magnetotransport of Nanostructured La$_{0.7}$Pb$_{0.3}$MnO$_3$ Manganites

P.S. Solanki, **R.R. Doshi**, Swati Pandya, V. Ganesan and D.G. Kuberkar

Indian J. Cryo. 33, 28 (2008)

6. Studies on Mixed Valant Manganites: Nanostructured Bulk, Thin Film Multilayer and Devices


J. Sci. 1, 7 (2010)

7. Structural and Magnetic Investigations on La$_{0.325}$Tb$_{0.125}$Ca$_{0.5}$MnO$_3$ and La$_{0.325}$Tb$_{0.125}$Sr$_{0.5}$MnO$_3$ Manganites


8. Substrate Dependent Transport and Magnetotransport in Manganite Multilayer

P.S. Vachhani, P.S. Solanki, **R.R. Doshi**, N.A. Shah, S. Rayaprol and D.G. Kuberkar

Communicated to Physica B (2010)

9. Thickness and Microstructure Dependent Transport and MR in La$_{0.7}$Pb$_{0.3}$MnO$_3$ Manganite films

P.S. Solanki, **R.R. Doshi**, U.D. Khachar and D.G. Kuberkar

Communicated to Ceramic Int. (2010)
10. Thickness Dependent Transport and Magnetotransport in CSD Grown La$_{0.7}$Pb$_{0.3}$MnO$_3$ Manganite films

P.S. Solanki, R.R. Doshi, U.D. Khachar, Ram Choudhary, S. Rayaprol and D.G. Kuberkar


11. Enhancement in TCR of La$_{0.5}$Pr$_{0.2}$Ba$_{0.3}$MnO$_3$ manganite thin film by swift heavy ion irradiation

P.S. Vachhani, R.R. Doshi, R.N. Parmar, J.H. Markna, J.A. Bhalodia, Ravi Kumar and D.G. Kuberkar,


12. Influence of 200 MeV Ag$^{+15}$ Ion Irradiation on Low Frequency 1/f Noise in La$_{0.5}$Pr$_{0.2}$Ba$_{0.3}$MnO$_3$ (LPBMO) Manganite Thin Films

R.R. Doshi, R.N. Parmar, P.S. Solanki, R.J. Choudhary, Ravi Kumar and D.G. Kuberkar

Solid State Physics (INDIA) 52, 833 (2007)

13. Microstructural Dependent Transport and Magnetotransport Behavior of Pb-doped LaMnO$_3$ Manganite

P.S. Solanki, R.R. Doshi, R.N. Parmar, C.M. Thaker, Swati Pandya, V. Ganesan and D.G. Kuberkar

Solid State Physics (INDIA) 52, 835 (2007)

14. Structural and Microstructural Dependence of Transport and Magnetotransport properties of Sol - Gel Grown Nanostructured La$_{0.7}$Ca$_{0.3}$MnO$_3$ Manganites

R.R. Doshi, U.D. Khachar, P.S. Solanki and D.G. Kuberkar

15. Strain and Microstructure Dependent Transport and Magnetotransport in Pb - Doped LaMnO₃ Manganite Films


16. Temperature Dependent I-V Characteristics of Manganite Based p-n Junction Diodes

U.D. Khachar, P.S. Vachhani, P.S. Solanki, R.R. Doshi, N.A. Shah, R.J. Choudhary, D.M. Phase and D.G. Kuberkar

Solid State Physics (INDIA) 54, 821 (2009)

17. Magnetic Properties of Co-doped ZnO: Role of Grain Morphology

M.V. Vagadia, P.S. Solanki, R.R. Doshi, A.B. Ravalia and D.G. Kuberkar

Solid State Physics (INDIA) 54, 993 (2009)

18. Size Dependent Magnetotransport in Nanostructured Manganites


Proceeding of International Conference on Nanoscience and Nanotechnology - 2010 (ICONN - 2010), February 24 - 26 (2010)

19. Structural, Microstructural and Magnetic Properties of Co:ZnO Nanoparticles

M.V. Vagadia, U.D. Khachar, A.B. Ravalia, R.R. Doshi, P.S. Solanki and D.G. Kuberkar

Proceeding of International Conference on Synthesis, Characterization, Consolidation and Modeling of Nanomaterials - 2010 (ICON - 2010), March 05 - 06 (2010)
List of Awards Achieved at International / National Conferences / Symposia

- 1st Prize for Oral: R.R. Doshi et. al. (Presented by: U.D. Khachar)
  Recent Advances in Condensed Matter and Materials Physics - 2009 (RACMMP - 2009), Baroda
  February 28, 2009

- 1st Prize for Oral: R.R. Doshi et. al. (Presented by: R.R. Doshi)
  Symposium on Nanomaterials and their Applications - 2009 (SNMA - 2009), Pune
  March 04 - 06, 2009

- 1st Prize for Oral: R.R. Doshi et. al. (Presented by: R.R. Doshi)
  International Conference on Nanoscience and Nanotechnology - 2010 (ICONN - 2010), Chennai
  February 24 - 26, 2010

- Best Poster Award: P.S. Solanki et. al. (Presented by: P.S. Solanki)
  December 27 - 31, 2007

- 1st Prize for Poster: P.S. Solanki et. al. (Presented by: P.S. Solanki)
  International Conference on Nanoscience and Nanotechnology - 2008 (ICONSAT - 2008), Chennai
  February 27 - 29, 2008
1. Workshop on “Operation, Maintenance and Utilization of Electronic Instruments” held at Saurashtra University, Rajkot during October 7 - 13, 2002
2. Seminar on “Current Trends in Materials Research” held at Saurashtra University, Rajkot on February 28, 2005
3. National Workshop on “Nanotechnology: Opportunities & Challenges” held at Saurashtra University, Rajkot on October 17, 2005
4. Course Module on “Ion Beams in Material Science” held at IUAC, New Delhi during September 26 - October 20, 2005
5. Course Module on “Instrumentation and Control” held at IUAC, New Delhi during October 25 - November 18, 2005
6. Course Module on “Data Reduction and Error Analysis” held at IUAC, New Delhi during April 10 - 27, 2006
7. Course Module on “Engineering Drawing” held at IUAC, New Delhi during April 10 - 27, 2006
10. One day Seminar on “Recent trends in materials science” held at Department of Physics, Saurashtra University, Rajkot on March 25, 2007.

15. One day seminar on “Advances in Materials Research - 2008” (AMR - 2008) held at Saurashtra University, Rajkot on February 15, 2008


17. Advanced School on “Applications of High Resolution X-Ray Techniques” held at ITC Hotel The Sonar Bangla, Kolkata during March 3 - 4, 2008


19. “Symposium on Nanomaterials and their Applications - 2009” (SNMA - 2009) held at Fergusson College, Pune during March 5 - 6, 2009

20. “Conference on Neutron Scattering and Mesoscopic Systems” held at Goa University, Goa during October 12 - 14, 2009


22. 54th National symposium “DAE - SSPS - 2009” (DAE - 2009) held at M.S. University of Baroda, Baroda during December 14 - 18, 2009

23. “21st Annual General Meeting Materials Research Society of India - 2010” (21st AGM MRSI - 2010) held at Sardar Patel University, V.V. Nagar during February 09 - 11, 2010


25. “International Conference on Nanoscience and Nanotechnology - 2010” (ICONN - 2010) held at SRM University, Chennai during February 24 - 26, 2010