SYNTHESIS AND CHARACTERIZATION OF
NANOCRystALLINE COLOSSAL MAGNETORESISTIVE
MANGANITES

ABSTRACT
OF THE
THESIS
SUBMITTED FOR THE AWARD OF THE DEGREE OF
Doctor of Philosophy
IN
APPLIED PHYSICS
By
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Under the Supervision of
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DEPARTMENT OF APPLIED PHYSICS
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ALIGARH MUSLIM UNIVERSITY
ALIGARH – 202002 (INDIA)
2014
Abstract

The transition metal oxides [TMO's] with perovskite type (ABO$_3$) structure comprise one of the most interesting class of inorganic solids because of their rich physics as well as novel technological applications. These perovskites reveal exciting physical properties such as structural, electrical transport, magnetic and optical properties because of strong electron correlation effects in the systems. They have been attracting extreme attention because of their striking phenomena such as Metal to Insulator transition [MIT], Colossal Magneto Resistance [CMR] and Charge Ordering in manganites, High T$_c$ superconductivity in cuprate systems and ferroelectricity in titanates. Amongst these, the majority of the properties are due to the close relationship between electric and magnetic properties arising from the simultaneous presence of strong electron-electron interaction potential within the ample hopping interaction between the transition metal -d and oxygen-p orbitals.

Since the discovery of CMR effect in perovskite mixed valence manganites RE$_{1-x}$AE$_x$MnO$_3$ (RE = rare-earths such as La, Nd, Pr etc, AE = Alkaline-earths such as Ca, Sr, Ba, Pb etc), the magnetic, electronic and transport properties of these materials and their relations to microstructures have attracted much interest. Because of the large magnetoresistance effect and strong spin polarization at the Fermi level, these oxides can be used in magnetoresistive devices, such as magnetic random access memory (MRAM) and sensors. However, for a great number of these possible industrial applications, these materials have to be prepared in the form of thin films and because of this reason many research works are being carried out to get the best structural and physical properties of these thin films. Composition of thin films, oxygen content, film thickness, lattice strains induced by the lattice mismatch, and so on, have a crucial role in determining their magnetic and transport properties.

La$_{1-x}$Sr$_x$MnO$_3$ (LSMO) is the characteristic class of Mn perovskites which displays an extremely high degree of spin polarization, making them possible candidates for magnetic-based devices which exploit spin polarized electron transport. The transport properties of these ferromagnets appear to be related to strong interactions among charge, spin and lattice degrees of freedom. The electronic properties of LSMO, as described by band theory, are nearly half-metallic. The concept of half metallic ferromagnetism means that the conduction electrons are 100% spin polarized. That is, only one of the two spin bands is partially occupied at
the Fermi level while the other has zero density of states across the Fermi level. The half-metallic properties of LSMO are of great importance for applications in spintronics. Due to the high spin polarization of carriers, the spin dependent tunneling between two ferromagnetic manganite electrodes across a thin insulating barrier should produce a large magnetoresistance response. Although, the magneto resistance seems to vanish at room temperature. In particular, the electronic structure of LSMO is determined by the competition of double exchange (DE) and superexchange (SE) interactions, charge/orbital ordering instabilities and strong coupling with the lattice deformations. Moreover, LSMO have high conductivity and good thermal stability with maximum Curie temperature (Tc) of 370K for 33% Sr doping. They may be employed as electrodes for ferroelectric and dielectric capacitors in future dynamic random access memory applications.

The electronic phase diagram of LSMO reveals that it has an antiferromagnetic and insulating behavior at high and low doping concentration (x) values and ferromagnetic metallic behavior in a certain range of concentrations centered around x ≈ 0.33. So it is considered for the use in various devices such as magnetic field sensors and hard disk read heads. Since the density of states at the Fermi level in LSMO is occupied mostly by the majority-spin electrons alone in the ferromagnetic (FM) and metallic states, attempts have been made to use this almost 100% spin polarization in the form of heterostructures such as tunnel junctions. Moreover, due to the hole doping in LSMO, many interesting device applications have been proposed based on LSMO.

Nanotechnology is regarded as one of the most inventive and revolutionary technologies in the present scenario. This technology enables the existing substances to reveal new properties. The potential applications of this new technology appear to be unlimited and offer several prospects to do advancement in the quality of life. Fundamentally, materials having dimensions in the nanometer range reveal the properties which are amazingly different from their bulk counterparts. Consequently, the scientists and researchers are motivated to monitor the variations in properties with decreasing size and explore the reasons behind the novel properties of nanomaterials. In the field of biomedical sciences these nanoparticles are used for MRI, cell separation, drug delivery and magnetic hyperthermia.
Previously cancer was treated by surgery, radiation or chemotherapies which cause disadvantages of losing organs, burning and damage of other healthy cells. Researchers are doing tremendous efforts to find the new material particles which are sensitive to tumor cells leaving the healthy cells unaffected i.e. selective heating and targeting. Magnetic nanoparticles appear to have such properties.

In this work, I was motivated to explore the synthesis of the doped manganite using solid state reaction and sol-gel methods with varying concentration of the dopants. The parent material LaMnO$_3$ is an antiferromagnetic insulator at room temperature. The material was studied long back ago and doped by divalent metals at the lanthanum site for a variety of device applications. Hereafter, it was observed that strontium (Sr) doped LaMnO$_3$ is an interesting manganite which shows ferromagnetism at room temperature with a rich phase diagram. This manganite is well-known for its CMR properties and suitable for applications in spintronics devices, but, at the present time researchers are concerned with LSMO nanoparticles for biomedical applications. This material is capable for the treatment of cancer because of adjustable Curie temperature. LSMO has the Curie temperature much above the room temperature and with suitable doping concentration; it can be tuned with a desired magnetization.

In the present work, I have doped zinc (Zn) and iron (Fe) as foreign atoms at Mn site in La$_{0.67}$Sr$_{0.33}$MnO$_3$ and La$_{0.33}$Sr$_{0.67}$MnO$_3$ manganites respectively. The partial substitution of Zn$^{2+}$ at the magnetic sublattice of mixed-valent manganese in La$_{0.6}$Sr$_{0.4}$MnO$_3$ induces a random potential fluctuation because the Zn$^{2+}$ ion has the completely filled 3d$^{10}$ electronic configurations, which is different from those of Mn$^{3+}$ and Mn$^{4+}$ configuration respectively. Secondly, the Zn$^{2+}$ ions do not carry any magnetic moment as they are also expected not to participate in the ferromagnetic (FM) interaction and hence dilute the magnetic sublattice.

The doping by Fe$^{3+}$ also seems to be very suitable since Fe$^{3+}$ is magnetic, but does not give rise to the Jahn–Teller effect and unlike Chromium (Cr), does not take part in DE. The influence of Fe doping on magnetic and electrical properties was mainly studied for hole doped La$_{1-x}$Ca$_x$Mn$_{1-y}$Fe$_y$O$_3$ ($x = 0.3$ and $y = 0.25$) systems.
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In view of the above, this research work has been carried out which is divided into 8 Chapters as:

Chapter 1 deals with the introductory idea about the status of present research work. Fundamentally it provides us a brief idea about the properties of perovskite materials with special reference to mixed valence manganites. The major aim of this chapter is to study the different phenomena shown by mixed valence manganites. The properties and dramatic behavior exhibited by these materials in nanodomain have also been studied. Importance has been given to manganites doped with divalent strontium.

Chapter 2 illustrates the theories, basic physical concepts and mechanisms which have been employed to explain a variety of phenomena attributed to the experimental results found in this work. It consists of: Variable-Range Hopping Model, Small Polaron Hopping Model and Zener Double-Exchange Polynomial Law for electron conduction, Super-Exchange and Double-Exchange Interactions, Jahn Teller mechanism and Complex Ordering.

Chapter 3 deals with the study of a variety of experimental techniques utilized in the present research work. Standard Solid State Reaction Route and Sol-Gel Route have been elucidated for the synthesis of the samples followed by different characterization techniques in brief such as XRD, Rietveld Analysis, SEM, TEM, Four-Probe Resistivity Measurement, Magnetoresistance Measurement, VSM and SQUID Magnetometer which have been utilized to characterize and evaluate the different properties of these perovskites.

Chapter 4 deals with the synthesis of Zinc doped La$_{0.67}$Sr$_{0.33}$MnO$_3$ manganites using conventional solid-state reaction-route followed by the study of structural, electrical and magnetic properties. In this chapter, we have carried out the comparative studies of 10 and 20% zinc doping at the Mn site in La$_{0.67}$Sr$_{0.33}$MnO$_3$ (LSMO), i.e. La$_{0.67}$Sr$_{0.33}$Mn$_{0.9}$Zn$_{0.1}$O$_3$ and La$_{0.67}$Sr$_{0.33}$Mn$_{0.8}$Zn$_{0.2}$O$_3$ systems using the resistivity and magnetization measurements. A considerable change in the metal to semiconducting (M–S) transition temperature ($T_P$) and Curie temperature ($T_C$) is observed with Zn doping.
Chapter 5 deals with the results of electrical transport properties of La$_{0.67}$Sr$_{0.33}$Mn$_{1-x}$Zn$_x$O$_3$ (x = 0.1 and 0.2) bulk samples prepared by solid-state reaction route over a wide temperature range from 5 to 300 K in the presence of different magnetic fields. In this chapter, temperature dependent resistivity data were fitted using Mott’s variable-range hopping (VRH) model for a limited range of temperatures to calculate the hopping distance (R$_h$) and the density of states near the Fermi level, [N(E_F)]. It was found that all the parameters vary systematically with the increase in Zn concentration. The temperature dependent resistivity data were also fitted using the small polaron hopping (SPH) model. The adiabatic SPH conduction is followed for 10% Zn doped sample at all fields while a non-adiabatic type of SPH conduction is followed for 20% Zn doped sample at all fields.

Chapter 6 deals with the synthesis of pure, 10% and 20% Zinc (Zn) doped at Mn site in La$_{0.67}$Sr$_{0.33}$MnO$_3$ manganite samples synthesized through sol-gel method followed by the study of microstructural and magnetic properties. The samples are found to have rhombohedral symmetry. SEM images reveal that the particles of all the samples seem to be agglomerated, well connected and nanofibres type of structure is formed with no clear grain boundaries. TEM images reveal the very clean surface of nearly spherical nanoparticles and the particle size distribution is almost uniform in all the samples which is analyzed by the Image J software. From M-H measurements, it has been observed that superparamagnetic behavior is present in all the samples due to the decreasing particle size.

Chapter 7 deals with the systematic investigations carried out on structural, electrical and magnetic properties of Fe doped La$_{0.33}$Sr$_{0.67}$MnO$_3$ manganites prepared through solid-state reaction-route. The samples are found to have rhombohedral crystal symmetry. The crystallite sizes obtained by XRD data are much smaller than the average grain size obtained by scanning electron microscope (SEM). Temperature dependent resistivity data were fitted using Mott's variable-range hopping (VRH) and small polaron hopping (SPH) models for obtaining different parameters. The adiabatic SPH conduction mechanism is followed almost for both samples in the absence of magnetic field but a switching from adiabatic to non-adiabatic SPH conduction mechanism is found in the presence of magnetic field. Temperature dependent magnetization (M-T) measurements confirm the decrease in Curie-temperature (T$_C$)
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with Fe doping. The samples exhibited ferromagnetic behavior at 10 K and 300 K with a small hysteresis loop and low coercivity.

Chapter 8 deals with the concluding remarks of the work carried out in this thesis followed by future plan. La$_{0.67}$Sr$_{0.33}$Mn$_{1-x}$Zn$_x$O$_3$ ($0.1 \leq x \leq 0.2$) and La$_{0.33}$Sr$_{0.67}$Mn$_{1-y}$Fe$_y$O$_3$ ($0 \leq y \leq 0.02$) manganite samples were prepared by Standard Solid-State Reaction-Route and Sol-Gel Route. Effects of doping on structural, microstructural, electrical transport and magnetic properties have been investigated. In future plan, emphasis is given on the further utilization of magnetic nanoparticles for magnetic hyperthermia applications.
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ALIGARH – 202002 (INDIA)
2014
Dedicated

to

My Abba
(Lacequi Ahmed Siddiqui)

&

My Amma
(Safia Begum)
CERTIFICATE

This is to certify that the thesis entitled "Synthesis and Characterization of Nanocrystalline Colossal Magnetoresistive Manganites", which is submitted by Mr. Hilal Ahmed bearing En. No.: CC-6641 for the award of the degree of Doctor of Philosophy in Applied Physics is a record of the bonafide research work carried out by him. He has worked under my guidance and supervision and has fulfilled the requirements for the submission of the thesis.

The results presented in this thesis have not been submitted in part or in full, to any other University or Institution for the award of any degree or diploma.

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CANDIDATE'S DECLARATION

I, Hilal Ahmed, Department of Applied Physics certify that the work embodied in this Ph.D. thesis is my own bonafide work carried out by me under the supervision of Dr. Shakeel Khan at Aligarh Muslim University, Aligarh. The matter embodied in this Ph.D. thesis has not been submitted for the award of any other degree.

I declare that I have faithfully acknowledged, given credit to and referred to the research workers wherever their works have been cited in the text and the body of the thesis. I further certify that I have not willfully lifted up some other's work, para, text, data, result, etc. reported in the journals, books, magazines, reports, dissertations, thesis, etc., or available at web-sites and included them in this Ph.D. thesis and cited as my own work.

Date: 09/10/2014

(Signature of the candidate)

Hilal Ahmed
(Name of the candidate)

Certificate from the Supervisor

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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COURSE/ COMPREHENSIVE EXAMINATION/ PRE-SUBMISSION SEMINAR COMPLETION CERTIFICATE

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Acknowledgements

All praise to the Almighty Allah, most gracious, most merciful and the creator of the universe, who enabled me to complete this research work successfully.

I feel obliged to my supervisor Dr. Shakeel Khan, Associate Professor and Chairman, Department of Applied Physics, Zakir Hussain College of Engineering and Technology, Aligarh Muslim University, Aligarh for his invaluable supervision and enthusiastic endeavors to complete my research work.

I put on my record of thanks to all the teachers of the department particularly to Dr. M. Wasi Khan and Dr. M. Mohsin Khan who have always rendered their utmost help.

I would also like to express my heartfelt gratitude to my family members especially my Amma, Abba, Khala, Khalu, my elder brother Junaid Bhai, my younger brothers Noor, Suboor and Salim, my very cute and loving sisters, Tanzeem Fatima, Shazia, Shahana, Nazia Fatima, Sadaf, my Brother-in-Law, Mr. Mohammad Aqil Khan, my so cute maternal nephew Anzar Aqil and my nephew Athar Jamshed for their patience, inspiration and regular support throughout this work.

I cannot forget the great help, patience, mutual understanding, moral support and time sparing of my beloved and angel wife Mrs. Farha Naaz during the course of my Ph. D. work.

I also pay the heartiest thanks to my friends, Razia Nongjai, Imran Khan, Faheem Ahmed (Al-Faisal University, Riyadh, Saudi Arabia), Mohammad Ashiq Malik (I.I.T. Kanpur), Azizurrahman Ansari (I.I.T. Kanpur), Haider Hasan Jafri, Mohammad Firoz Khan (J.N.U.), Mohammad Tayyab (Scientist D at RRCAT, Indore), Syed Mohammad Amir (Post Doctoral Fellow in Germany), Rajmani Gaur, Sartaj Alam Ansari, Mohammad Shoeb Khan for their kind help and creative suggestions and putting forward their helping hands always.

Hilal Ahmed

09/10/2014
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Introduction and Literature Survey
This Chapter deals with the current research status of the work carried out in proposed field of manganites. It gives a brief idea about the perovskite materials, their properties with special reference to mixed valence manganites. The main objective of the chapter is to discuss about different properties and phenomena exhibited by mixed valence manganites.

1.1. Introduction

Transition metal oxides (TMO's) comprise one of the most interesting classes of inorganic solids exhibiting inspiring physical properties such as structural, electrical transport, magnetic and optical occurring due to the strong electron correlation effect in the systems. Additionally, TMO's possesses some fascinating phenomena such as high Tc superconductivity in cuprates, metal-insulator transition (MIT), colossal magnetoresistance (CMR) in manganites. Manganites exhibit a variety of phases with unusual spin, charge, lattice and orbital ordering. Amongst these, most of the properties are due to the close relationship between electric and magnetic properties arising from the simultaneous presence of strong electron-electron interaction potential within considerable hopping interaction between the oxygen p and transition metal d orbitals.

Particularly, the existence of metal-insulator transition in lanthanum based manganites was established in early 1950's [1,2] and was extensively studied afterward. These types of perovskites present a very interesting group of materials because of tremendously rich variety of their electrical transport properties from a large gap insulator to metal transition and magnetic properties such as from non magnetism to magnetism, antiferromagnetism to ferromagnetism [3,4]. A few examples of these perovskites are LaCoO₃, LaFeO₃, LaNiO₃, LaCrO₃, LaMnO₃ and certain doped manganites. The magnetic and electrical transport properties of these materials are being investigated with respect to several factors such as the percentage of the divalent ions, the ionic radii of the metal ions and the method of preparation [3-5].

1.2. Perovskite Materials

Fundamentally, the name perovskite refers to a relatively rare mineral called as calcium titanium oxide (CaTiO₃) occurring in orthorhombic crystal symmetry and is
found in metamorphic rocks and related mafic intrusives nepheline syenites and rare carbonates. This was first invented in 1839 in the Russian Ural Mountains by Gustav Rose and named for Russian Mineralogist Count Lev Alexevich von Perovski. Generally, the perovskite is a name of more general group of crystals that acquire the same structure and is now used to refer to any member of a very large family of compounds that has resemblance with the basic chemical formula $\text{ABO}_3$ where A and B ions are cations of different size in which the B ion is surrounded by an octahedron of O ions. Perovskites ($\text{FeSiO}_3$ and $\text{MgSiO}_3$) are the most copious compounds in the Earth's crust. The compounds with the formula $\text{ABO}_3$, with A=rare-earth ion, B=transition metal ion and O=oxygen; are a subclass of the transition metal oxides that belong to the perovskite family. Table 1 provides a concise list of some well-studied $\text{ABO}_3$ type perovskites. Many of the perovskites are cubic or nearly cubic, but they often go through one or more structural phase transitions, particularly, at low temperatures. The idealized structure is a primitive cube but differences in the ratio between the A and B cations can distort the crystal structure to some extent and become orthorhombic or worse.

Table 1.1: List of $\text{ABO}_3$ type perovskites with their different properties.

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<th>Metallic</th>
<th>Insulating</th>
<th>Superconducting</th>
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<tr>
<td>$\text{PbCrO}_3$</td>
<td>$\text{ReO}_3$</td>
<td>$\text{WO}_3$</td>
<td>$\text{SrTiO}_3$ (n-type) $\text{Na}_x\text{WO}_3$ (t)</td>
</tr>
<tr>
<td>$\text{LaCrO}_3$</td>
<td>$\text{NaWO}_3$</td>
<td>$\text{NaTaO}_3$</td>
<td>$\text{K}_x\text{WO}_3$ (t)</td>
</tr>
<tr>
<td>$\text{CaMnO}_3$</td>
<td>$\text{KMoO}_3$</td>
<td>$\text{SrTiO}_3$</td>
<td>$\text{K}_x\text{WO}_3$ (h)</td>
</tr>
<tr>
<td>$\text{LaMnO}_3$</td>
<td>$\text{SrNbO}_3$</td>
<td>$\text{BaTiO}_3$</td>
<td>$\text{Rb}_x\text{WO}_3$ (h)</td>
</tr>
<tr>
<td>$\text{LaCoO}_3$</td>
<td>$\text{LaTiO}_3$</td>
<td>$\text{KTaO}_3$</td>
<td>$\text{Cs}_x\text{WO}_3$ (h)</td>
</tr>
<tr>
<td>$\text{LaFeO}_3$</td>
<td>$\text{LaWO}_3$</td>
<td>$\text{LiNbO}_3$</td>
<td>$\text{Li}_x\text{WO}_3$ (h)</td>
</tr>
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$t$ = tetragonal; $h$ = hexagonal

The general perovskite structure may be considered as a body centered cube (BCC) lattice with 'A' ion of valency +2 at the center surrounded by eight 'B' ion of valency +4 each at the corner of 12 O ions each occupies the edge as shown in Figure 1.1.
Likewise, the perovskite structure may also be considered as face centered cube (FCC) lattice with ion ‘B’ at the center surrounded by six ‘O’ ions, each at a face center and eight ‘A’ ions, each located at the corners as shown in Figure 1.2.

The perovskite oxides are enormously interesting and extensively studied because of the gigantic varieties of solid-state phenomena they display. These perovskites are broadly studied due to the exhilarating and charming physical properties such as semiconducting, insulating, antiferromagnetism, ferromagnetism, colossal magnetoresistance, spin glass, spin/charge density wave transitions, superconductivity and ferroelectricity in different states and phases.
Many of these phenomena take place in materials with lattice matching within a few percent of one another, giving rise to the possibility of heteroepitaxial structures using perovskite oxides, accessing these multiple degrees of freedom. In general, the electrical and magnetic properties of these perovskites depend on the choice of element A, B and the doping element either at A or B site [6] or by departures from ideal stoichiometry. The electronic energy bands of the perovskites are very strange that they exhibit two-dimensional behavior which corresponds to the unique structure in various properties such as the dielectric function, Fermi surface, density of states, phonon spectra and the photoemission spectra. A few perovskites have delocalized energy-band states; some have localized electrons and some display transitions between these two types of behavior. Many of the perovskites are magnetically ordered and a large variety of magnetic structures may come into existence.

Moreover, perovskite structure has the unique property that the central atom does not touch its coordination neighbors in violation of Pauling’s rules. This type of structure shows the property of piezoelectricity and sometimes ferroelectricity and the perovskite oxides such as LaFeO$_3$, BaTiO$_3$, LaNiO$_3$, LaMnO$_3$, etc are the representative compounds. These materials also present a broad variety of phase transitions like ferroelectric, antiferroelectric or purely structural transitions. The majority of the transitions come across in the perovskite crystal involve only a minute change in the atomic position parameters, which leaves the important structural topology unchanged. These changes are frequently tough to detect directly and are detected indirectly by the changes or discontinuities in physical properties which are associated to the changes of atomic position parameters. The perovskites oxides are also significant in several technological areas and can be employed in electrochromic, photochromic and image storage devices. The ferroelectric and piezoelectric properties of perovskite oxides are utilized in other device applications such as switching, filtering and surface acoustic wave signal processing. Investigations on these interesting perovskites are being carried out since decades. Although in recent years the theoretical and experimental information on the electronic structure become available [7]. Neutron diffraction and inelastic scattering data, energy band calculations, optical spectra and transport data etc. are presently available for materials such as ReO$_3$, WO$_3$, NaWO$_3$, SrTiO$_3$, BaTiO$_3$, KMnO$_3$, KTaO$_3$, LaMnO$_3$, LaCoO$_3$, and a variety of other perovskites [7]. Surface studies of single-crystal...4...
perovskites using photoelectron spectroscopic technique point out that the surface properties are very complex and interesting [7].

1.3. Mixed valence manganites

Manganites have their significant place in the material science research because of their rich phase diagram and ample applications owing to the several properties shown by them in changeable conditions. Manganites are very fascinating and attractive systems due to their striking features in different varied environments. These are strongly correlated electrons systems wherein the correlations among electrons assign a variety of interesting properties to this class of materials. Being an interestingly class of materials, colossal magnetoresistive manganites have always been investigated by a considerable part of the condensed matter community and their popularity had touched the heights of the high-temperature superconducting cuprates. A massive interest in the study of colossal magnetoresistive manganites has been grown among the researchers working in this area because of their interconnected properties and possibilities of device applications. Mixed valence manganites with perovskite structure have been studied more than last 6 decades. They provide a degree of chemical flexibility which allows the relation between the structural, electrical and magnetic properties of these systems to be examined in a systematic way.

More recent work has been motivated by a desire to understand the large negative magnetoresistance effects which appear in the neighborhood of Curie temperature to realize the low field magnetoresistance (LFMR) effect at low temperature used by the grain boundary effects. Research on the mixed-valence manganites has exposed new phenomena; for instance colossal magnetoresistance (CMR) [8] and dense granular magnetoresistance [9] which led to the understanding of a variety of physical concepts such as Zener double exchange (ZDE) [10,11] and the Jahn-Teller (JT) effect etc. [12,13]. They may change stoichiometrically in time/space in an impressive manner as a result of small changes in conditions.

Therefore, it can be realized that there are minimum five reasons which put together manganites an essential area for theorists and experimentalists aiming to get better understanding of the behavior of electrons in manganites.
1. The rich phase diagrams of manganites exhibiting different phases with unusual spin, charge, lattice and orbital order. Phase competition at the boundaries between these phases produce remarkable results.

2. The unpredictably large magnetotransport properties of these compounds.

3. Field and Temperature dependent intrinsic and extrinsic magnetoresistance (MR) in nano regime depending upon the grain boundaries and grain morphology of the manganites.

4. Inhomogeneous nature of manganites which infers that these compounds are found to show simultaneous presence of clusters of competing phases. These phases may or may not have a different electronic density, but usually have different patterns of symmetry breaking.

5. Manganites have astonishing potential for a variety of applications in various fields for example; catalysts, sensors, solid electrolytes, biomedical sciences and novel electronic materials.

Thus, the interplay of experiment, theory and applications of these compounds which in turn arise as the essential aspects of condensed matter physics research deserves careful experimental and theoretical attention.

Manganese oxides with general formula RE$_{1-x}$AE$_x$MnO$_3$ where RE is a trivalent rare earth cation (RE = La$^{3+}$, Pr$^{3+}$, Nd$^{3+}$, Sm$^{3+}$, Eu$^{3+}$, etc.) and AE is divalent alkaline earth cation (AE = Ba$^{2+}$, Sr$^{2+}$, Ca$^{2+}$, etc.) with a structure similar to that of perovskite ABO$_3$ type structure are usually known as mixed valence manganites since in these compounds when divalent alkaline-earth ions have been substituted at the place of trivalent rare-earth ions on the site A, a portion of Mn$^{3+}$ cations is converted into Mn$^{4+}$ valence state to preserve the charge neutrality of the system. In stoichiometric oxides, the fractions of Mn$^{3+}$ and Mn$^{4+}$ cations correspond to 1-x and x, respectively. As one of the specific significant class of modern materials, these manganites have drawn an enormous amount of awareness due to their outstanding structural, magnetic and electronic properties, governed by the (competitive or cooperative) interplay of lattice, charge, orbital and spin degrees of freedom. These materials have long been the subject of study because they display amazing properties such as CMR effect, colossal magnetocapacitance (CMC), ...

...6...
multiferroic behavior, metal-insulator transition (MIT), complex phase transitions, giant magnetoresistance (GMR) effect etc. [14,15].

Because of the invention of CMR effect in mixed valence manganites, the magnetic, electronic and transport properties of these systems with their relationship to microstructures have attracted a large amount of interest [16,17]. Different striking properties of CMR manganites have been extensively discussed and described in review papers [18,19]. Due to the strong spin polarization and large magnetoresistance effect at the Fermi level, they can be used in magnetoresistive devices, such as magnetic random access memory (MRAM) and sensors [20,21]. However, for a large number of these possible industrial applications of these materials, the thin films have to be prepared and because of this reason much research work is being carried out to get the best structural and physical properties of these thin films. Composition of thin films, oxygen content, film thickness, and lattice strains induced by the lattice mismatch, and so on, have crucial role in determining the magnetic and transport properties [22-24].

The $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSMO; $x$ is the fraction of doping) is the characteristic class of Mn perovskites manganites which exhibit an extremely high degree of spin polarization, making them eligible candidates for the application of magnetic-based devices which utilize spin polarized electron transport. The transport properties of these systems appear to be related to strong interactions between spin, charge and lattice degrees of freedom. The electronic properties of LSMO, as described by band theory, are approximately half-metallic [25,26]. The concept of half metallic ferromagnetism means that the conduction electrons are 100% spin polarized i.e. only one of the two spin bands is partially occupied at the Fermi level while the other has zero density of states across the Fermi level. The half-metallic properties of LSMO make it very important material for applications in spintronics. Since the spin polarization of carriers is high, so the spin dependent tunneling among two ferromagnetic manganite electrodes across a thin insulating barrier should produce a large magnetoresistance response. Tunnel junction of LSMO/SrTiO$_3$/LSMO displays the magnetoresistance in excess of 1800% at a temperature of 4K which corresponds to a tunnel spin polarization of 95%. On the other hand, the magnetoresistance disappears at the room temperature [27]. Particularly, the electronic structure of LSMO is determined by the competition between double exchange and
superexchange interactions, charge/orbital ordering instabilities and strong coupling with the lattice deformations. Besides, they have high conductivity and good thermal stability with maximum Curie temperature (Tc) of 370K with Sr doping concentration, \( x = 0.33 \) [28]. They may be used as electrodes for ferroelectric and dielectric capacitors in the upcoming dynamic random access memory applications [29,30].

Doped manganites have new interest because they exhibit a variety of distinctive magnetic, electronic and transport behaviors such as colossal magneto resistance (CMR), spin/charge/orbital ordering and high degree of spin polarization and so on [31-33]. Ferromagnetic materials displaying half metallic behavior appear as potential candidates for spintronic devices and enormous amount of work is under progress to synthesize magnetic oxides, such as \( \text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3 \) (LSMO) [34-37]. The electronic phase diagram of LSMO reveals that it has an anti-ferromagnetic and insulating behavior at low and high doping concentration (x) values while ferromagnetic metallic behavior is shown in a certain range of doping concentrations centered around \( x \approx 0.33 \) [28] making its use in a variety of devices such as hard disk read heads and magnetic field sensors. In LSMO, since the density of states at the Fermi level (N(E_F)) is occupied frequently by the majority of the spin electrons only in the ferromagnetic (FM) metallic states, therefore efforts have been made to use this almost 100% spin polarization in the form of heterostructures such as tunnel junctions [38-40]. Additionally, many appealing device applications have been proposed based on LSMO due to the hole doping in it [41].

1.4. Physical properties exhibited by mixed-valence manganites

1.4.1. Crystal structure

The crystal structure of \( \text{RE}_{1-x}\text{AE}_x\text{MnO}_3 \) perovskite manganites is displayed in Figure 1.3, in which the large rare-earth (RE) and alkaline-earth (AE) ions occupy the A sites with 12-fold oxygen coordination whereas the small Mn\(^{3+}\) and Mn\(^{4+}\) ions occupy the B sites positioned at the center of the oxygen octahedra. The crystal structure of \( \text{RE}_{1-x}\text{AE}_x\text{MnO}_3 \) manganites is in the vicinity of the cubic perovskite.
Fig. 1.3: Schematic view of the cubic perovskite structure.

A typical orthorhombic/rhombohedral distorted perovskite lattice of manganite with A = La/Sr and B = Mn/Zn/Fe is shown in Figure 1.4 (a, b and c).

Fig. 1.4: Distorted orthorhombic/rhombohedral structure of perovskite manganite LaMnO₃.

1.4.2. Goldschmidt Tolerance Factor

The ratio between the A-O and B-O bond lengths should be equal to $\sqrt{2}$ in the ideal ABO₃ type perovskite structure. Infact, due to the dissimilarity in size between the rare-earth and alkaline-earth cations and due to the Jahn-Teller effect, the crystal structure of the doped manganites is generally distorted. Goldschmidt [42] in 1926 first observed this octahedral tilting type of distortion in ABO₃ types of perovskites and the degree of distortion between the A-O and B-O bond lengths can be characterized by Goldschmidt's tolerance factor 't' [43] expressed as

$$t = \frac{(r_A + r_0)\sqrt{2} (r_B + r_0)}{(r_A + r_0)\sqrt{2} (r_B + r_0)}$$

(1.1)
where $<r_A>$, $<r_B>$ and $r_0$ denote the average A-site cation, average B-site cation and the anion ionic radii respectively (only ionic bonding is presumed). Basically ‘t’ is a geometrical parameter which deals with the deviation from the perfect cubic structure. When $t = 1$ with B-O-B bond angle $180^\circ$, the structure is perfectly cubic. The system becomes strained and is driven towards the lower symmetry space group, away from its perfect cubic symmetry when $t<1$ or $t>1$. Cubic perovskite structure is stabilized for the $t$ values between $0.89 < t < 1.02$ [44]. The rhombohedral symmetry is observed for ‘t’ values in between 0.96 and 1 whereas the orthorhombic symmetry is observed for the value of ‘t’ below 0.96 which sets the critical limit on cationic radii $<r_A>$ and $<r_B>$ respectively. The perovskite structure adjusts to $t<1$ by a cooperative rotation of the BO$_6$ octahedra around, 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), a cubic [001] axis as in tetragonal. The B-O-B bond angle is bent from $180^\circ$ to $180^\circ-\varphi$ by these cooperative rotations. The application of hydrostatic pressure has the same influence on the physical properties as an increase in the tolerance factor [45], indicating the more compressibility of the B-O bond than the A-O bond in the paramagnetic phase. The tolerance factors for some of the manganites are given in table 2;

**Table 1.2: Tolerance factors of some of the manganites.**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compound</th>
<th>Tolerance factor (t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>LaMnO$_3$</td>
<td>0.889</td>
</tr>
<tr>
<td>2.</td>
<td>PrMnO$_3$</td>
<td>0.868</td>
</tr>
<tr>
<td>3.</td>
<td>NdMnO$_3$</td>
<td>0.864</td>
</tr>
<tr>
<td>4.</td>
<td>SmMnO$_3$</td>
<td>0.858</td>
</tr>
</tbody>
</table>

The orthorhombic structure of LaMnO$_3$ is illustrated in Figure 1.5 which is the parent compound of the mainly investigated manganites for potential application by partial substitution of La by divalent alkaline-earth ions like Ca, Sr, Ba etc.
**Fig. 1.5: Orthorhombic structure of LaMnO$_3$.**

### 1.4.3. Average Cationic Radius of A-site ($<r_A>$)

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

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

(1.2)

where, $x_i$ is the fractional occupancy of the $i^{th}$ cation and $r_i$ is the ionic radii of $i^{th}$ cation. The difference in $<r_A>$ at A-site cation in ABO$_3$ perovskite has same effect as an external pressure which makes an enhancement in the B-O-B transfer integral (Mn-O-Mn transfer integral in case of La$_{1-x}$Sr$_x$MnO$_3$) through a change in B-O-B bond angle and a measure of the degree of radial distortion of the BO$_6$ octahedra [46]. A linear relationship is found in between Tc and $<r_A>$, and both of them having inverse correlation with magnetoresistance [5]. A minor change in $<r_A>$, gives rise to the structural distortion at B-O-B bond angle up to a large amount 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 [47]. In case of manganites, the variation in A-site cationic radius affects the following:

- Decrease in the Mn-Mn distances
Distortion of the octahedral cage of MnO₆

Reduction in Mn-O-Mn bond angle

1.4.4. Density of carriers

In the mixed valence manganites, doping determines the carrier concentration and sign of the charge carriers (i.e. positively charged holes or negatively charged electrons). The variation in the valence of the transition metal cations i.e. Mn³⁺/Mn⁴⁺ in manganites which is responsible for the ferromagnetic Zener Double Exchange (ZDE) is decided by the carrier density. [48]. These compounds exhibit very rich phase diagrams at a certain level of doping as a function of magnetic field, external and internal chemical pressure and temperature, etc. which consecutively governs their physical properties.

1.4.5. Stoichiometry of Oxygen

The stoichiometry of oxygen is an important factor which determines the magnetic and transport properties due to its influence on the Mn³⁺/Mn⁴⁺ ratio and the Mn-O-Mn bond angles [49-55]. Taking into consideration the valence states of all the ions, the chemical formula of mixed-valence manganites can be written as RE₁₋ₓAEₓ₂⁺Mn₁₋₃yMn₂₄⁺O₃₋₄z. From this equation, a deviation from the stoichiometric value, δ, in the oxygen content definitely changes the concentration of Mn⁴⁺ ions (y) to satisfy the charge neutrality condition. Therefore, the oxygen deficiency in the mixed-valence manganites results in the decrease of hole concentration which in turn weakens double-exchange interaction, lowers conductivity, magnetization and the Curie temperature.

1.4.6. Electronic structure

The electronic configuration of Mn atom is 1s²2s²2p⁶3s²3p⁶3d⁵⁴s² with incomplete d-shell. In the RE₁₋ₓAEₓMnO₃ lattice, Mn ions are arranged in octahedral oxygen coordination and the 5-fold orbital degeneracy of the 3d levels of Mn ion is split into the lower-lying triply degenerate t₂g states and the higher-lying doubly degenerate e₈ states by the octahedral crystal field as shown in Figure 1.6. For the MnO₆ octahedron, the splitting between the lowest t₂g level and the highest e₈ level is ~ 1.5 eV. According to the Hund's first rule (maximum multiplicity S), the d-
electrons have the same spin orientation for the Mn$^{3+}$ and Mn$^{4+}$ ions (parallel spin alignment) assured by the intra-atomic correlations. Mn$^{3+}$ ion has an electronic configuration 3d$^4$ with three electrons at the t$_{2g}$ level and one electron at the e$_g$ level (S=2) where as Mn$^{4+}$ ion has an electronic configuration 3d$^3$ with three electrons at the t$_{2g}$ level and no electron at the e$_g$ level (S=3/2). The degeneracy of the t$_{2g}$ and e$_g$ levels can be further removed as a result of the Jahn-Teller distortion (details explained in chapter 2) in a crystal field of symmetry lower than cubic for an axial elongation of the oxygen octahedron as displayed on the right side of Figure 1.6. It is observed that the energy of the Mn$^{4+}$ ion having no electrons in the e$_g$ state remains unchanged by such a distortion but the energy of Mn$^{3+}$ ion with occupied e$_g$ state is lowered due to the Jahn-Teller distortion at the cost of the lattice energy.

![Diagram](image)

**Fig.1.6**: Crystal-field splitting of the 5-fold degenerate atomic 3d levels of Mn$^{4+}$ and Mn$^{3+}$ into lower t$_{2g}$ (triply degenerate) and higher e$_g$ (doubly degenerate) levels (in the middle). The Jahn-Teller distortion of the MnO$_6$ octahedron further lifts each degeneracy. Splitting of the t$_{2g}$ and e$_g$ levels and distortion of the MnO$_6$ octahedron with axial elongation due to the Jahn-Teller effect is shown on the right side.

Thus, Mn$^{3+}$ ions have a marked tendency to distort its octahedral environment rather than Mn$^{4+}$. This Jahn-Teller distortion is relatively more effective in the lightly doped manganites, i.e. with a large concentration, 1-x, of Mn$^{3+}$ ions [56]. The MnO$_6$ octahedra are strongly elongated within the ab plane in a regular way leading to a doubling of the unit cell which is illustrated by the structure of LaMnO$_3$ (Figure 4). As the Mn$^{4+}$ content increases, the Jahn–Telller distortions get reduced and the $3z^2 - r^2$ e$_g$ orbital becomes less stabilized. However, in a large number of manganites, the e$_g$
orbitals of two types, $3z^2-r^2$ and $x^2-y^2$ are not randomly occupied by the $e_g$ electrons of Mn$^{3+}$ and an orbital order is achieved.

1.4.7. Exchange interaction

The exchange interactions between the Mn ion spins are responsible to govern the magnetic properties of the manganites. These exchange interactions are comparatively large between two Mn spins separated by an oxygen atom and are controlled by the overlap between the Mn d-orbitals and the O p-orbitals. The subsequent superexchange interactions (discussed in detail in Chapter 2) depend on the orbital configuration following the rules of Goodenough–Kanamori. In general, for Mn$^{4+}$–O–Mn$^{4+}$ network, the interaction is antiferromagnetic (AF) in nature, while for Mn$^{3+}$–O–Mn$^{3+}$ network, it may be ferro- or AF [57], like in LaMnO$_3$ where both F and AF interactions exist simultaneously. An interesting and peculiar case is to consider the Mn$^{3+}$–O–Mn$^{4+}$ network in which the Mn ions may switch their valence by a simultaneous jump of the $e_g$ electron of Mn$^{3+}$ on the O p-orbital and from the O p-orbital to the empty $e_g$ orbital of Mn$^{4+}$. This mechanism of double-exchange (DE) (discussed in detail in Chapter 2) was originally proposed by Zener [11] assures a strong ferromagnetic-type interaction. The probability of the $e_g$ electron transfer from Mn$^{3+}$ to neighboring Mn$^{4+}$ is $t_0 \cos(\theta/2)$ as shown by Anderson and Hasegawa [58], where $\theta$ is the angle between the Mn spins, in the case of strong Hund’s coupling (Figure 1.7). The degeneracy of the configurations Mn$^{3+}$–O–Mn$^{4+}$ and Mn$^{4+}$–O–Mn$^{3+}$ networks leading to two energy levels $E_{\theta=0} = t_0 \cos(\theta/2)$ is lifted by the process of electron transfer. The energy gain of the parallel spin configuration where $\theta = 0$, maximizing $t_0$, with respect to the antiparallel one where $\theta = \pi$, reveals the ferromagnetic character of the DE interaction. Though, the DE angular dependence of $\cos(\theta/2)$ is reasonably different from $\cos(\theta)$ of the usual exchange interaction. This difference in angular dependence in conjunction with the competition between DE ferromagnetism and superexchange (SE) antiferromagnetism is at the origin of the complex magnetic phase diagram of manganites versus the doping level, $x$. Particularly, canted AF phases at small ‘$x$’ were predicted early on by de- Gennes [48]. They result from the energy gain of first-order in the canting angle for DE which overcomes the energy increase of second-order in the canting angle for the AF superexchange.

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Ferromagnetic metallic (FM) phases are mandatory for potential applications with high Curie temperature, $T_C$. The $\text{Mn}^{3+}$-$\text{Mn}^{3+}$ interaction can be neglected in the first approximation because it is either F or AF depending on the orbital configuration while at present both F and AF interactions exist simultaneously in the same compound such as in LaMnO$_3$. Then, assuming the same magnitude of $\text{Mn}^{4+}$-$\text{Mn}^{4+}$ AF superexchange and $\text{Mn}^{3+}$-$\text{Mn}^{4+}$ F DE interaction, the mean field approximation leads to $T_C \sim 2x(1−x)−x^2$, which is maximum for $x = 1/3$. Therefore, the fact that the FM phases are generally found around $x = 0.33$ in manganites is in agreement with this crude model.

\[ t = t_0 \cos \left( \frac{\theta}{2} \right) \]

\[ \text{Figure 1.7: Schematic view of the double-exchange (DE) mechanism.} \]

1.4.8. Half metallic behaviour

The basic mechanism of electrical conduction in the manganites is the transfer of $e_g$ electron from $\text{Mn}^{3+}$ ion to $\text{Mn}^{4+}$ ion via an intermediate oxygen ion by DE (Figure 1.7). In strong DE systems, for a certain range of doping centred approximately at $x \approx 0.33$, the $e_g$ electrons become delocalized in the ferromagnetic phase and a FM state is established at low temperature. The electronic structure of such a FM phase is schematically shown in Figure 1.8. In contrast to the 3d ferromagnetic metals such as Ni or Fe where the up- and down-spin bands are both occupied, they are separated by 1 eV or more and the upper band is empty, leading to a half-metallic behaviour. The conduction band of such a half-metallic ferromagnet is thus fully spin-polarized and is of large potential interest for spin electronics [59]. The theoretical interpretation for the electronic structure of $\text{La}_{1-x}\text{AE}_x\text{MnO}_3$ (AE = Ca, Sr, ...15...
In contrast to the insulating state, the ferromagnetic phase is a first order phase transition accompanied by an abrupt change in the electronic structure. This transition is associated with a change in the magnetic moment of the system. At the critical point, the electronic structure undergoes a Peierls transition, resulting in a metal-insulator transition. The critical point is characterized by a divergence of the magnetic susceptibility and a change in the electronic band structure.

The magnetic and electronic properties of this system are governed by the interplay between magnetic and electronic interactions. The magnetic ordering is driven by the exchange interaction, while the electronic structure is determined by the band structure. The competition between these two interactions leads to a rich phase diagram with a variety of phases.

The figure shows the band structure of the system, with the conduction and valence bands indicated. The Fermi level is shown to be at the center of the band structure, indicating a metallic state.

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**Chapter 3**

**Introduction**

The band structure of the system is shown in the figure. The conduction and valence bands are indicated, with the Fermi level positioned at the center of the bands. The magnetic ordering is driven by the exchange interaction, while the electronic structure is determined by the band structure. The competition between these two interactions leads to a rich phase diagram with a variety of phases.
is also closely related to the orbital ordering through the Jahn–Teller effect of Mn$^{3+}$ [68,69].

1.4.9. Metal–insulator transition

The simple manganites such as La$_{1-x}$AE$_x$MnO$_3$ (AE = Ca, Sr, Ba) exhibiting strong DE, with $x \approx 0.33$, make a transition from a high temperature paramagnetic (P) semiconducting or insulating (I) phase to a low temperature FM phase. An example is displayed in Figure 1.9 for a single crystal of La$_{1-x}$Sr$_x$MnO$_3$ ($x = 0.175$). In the P phase, the electrical resistivity generally exhibits strong temperature dependence. Different $\rho(T)$ laws are used to fit the experimental data in which the most popular ones are: (i) simple thermal activation law $\rho = \rho_0 \exp(E_0/k_B T)$, with a typical gap value of about 0.1 eV; (ii) hopping of adiabatic polarons $\rho \sim T \exp(E_0/k_B T)$; (iii) Mott variable range-hopping (VRH), $\rho = \rho_0 \exp[(T_0/T)^{1/4}]$. Each of these laws have some physical origins, which are respectively: (i) the existence of a pseudo gap at the Fermi level in the P phase [62]; (ii) the local lattice distortion accompanying the moving charge carrier (Jahn–Teller polaron); (iii) the localization of the charge carriers by the magnetic disorder [70]. It is practically impossible to differentiate between these different $\rho(T)$ laws in a constrained temperature range. A delocalization of the $e_g$ electrons, corresponding to a low resistivity FM phase with $\rho \approx \rho_0 + aT^2$ for $T \ll T_C$, takes place by the spontaneous alignment of the Mn spins below the Curie temperature, $T_C$. This alignment of the Mn spins can be reinforced for $T \leq T_C$ or, induced for $T \geq T_C$, with the application of an external magnetic field. The maximum effect is observed near $T_C$ (Figure 1.9) since the initial magnetic susceptibility diverges as $T \to T_C$. Therefore, these manganites have a rather large negative magnetoresistance, the so-called CMR, which peaks around $T_C$. At the Curie temperature, the change from insulating to metallic behaviors of the material causes a peak in the resistivity at a temperature $T_P$ close to $T_C$. The effect of an applied magnetic field is maximized due to the large spin disorder and magnetic susceptibility, which gives rise to a peak value of the CMR at a temperature slightly lower than $T_P$.

In general, the high values of CMR peak are generally found when $T_P$ and $T_C$ are low and the peak resistivity at $T_P$ is high. The CMR becomes larger at phase transitions at lower temperatures, because with decreasing temperature, the metallic
resistivity decreases while the semiconducting resistivity increases, thereby generating a larger difference between the two states at lower temperatures.

\[ \text{Fig. 1.9: Resistivity in zero field and in 8 T applied field versus temperature, of a single crystal of } \text{La}_{0.825}\text{Sr}_{0.175}\text{MnO}_3. \text{ In inset, magnetoresistance ratio versus temperature. The array indicates the Curie temperature, } T_C. \]

1.5. Magnetoresistance (MR), Giant Magnetoresistance (GMR) and Colossal Magnetoresistance (CMR)

The relative change in the electrical resistivity of a material created by the applied magnetic field is referred as Magnetoresistance (MR). In general, it is defined as-

\[ \text{MR}\% = \frac{\Delta \rho/\rho(0) - [\rho(H) - \rho(0)]/\rho(0)} \times 100 \quad (1.3) \]

where \( \rho(0) \) and \( \rho(H) \) are the values of resistivity at a given temperature in the absence and presence of a magnetic field respectively.

MR may be positive or negative depending on the rise or fall in the resistivity with the application of magnetic field. Most of the metals show a small amount of MR (only a few %). In non-magnetic pure metals and alloys, MR is usually positive and has a quadratic dependence on \( H \). Because of the suppression of the spin disorder by the magnetic field MR may be negative in magnetic materials. During last 50 years, the magnetoresistance have been studied in the following forms having their origin in different physical aspects.
i. Anisotropic magnetoresistance (AMR)

ii. Ordinary magnetoresistance (OMR)

iii. Granular and tunneling magnetoresistance (TMR)

iv. Giant magnetoresistance (GMR)

v. Colossal magnetoresistance (CMR)

Giant magnetoresistance (GMR) was first observed on the application of magnetic field to atomically engineered magnetic super lattices (e.g.-Fe/Cr) [71] and in magnetic semiconductors. Moreover, some of the bimetallic or multi-metallic layers, comprising of ferromagnetic and antiferromagnetic or nonmagnetic metals, GMR are also found in ferromagnetic granules dispersed in paramagnetic metal films. An ample attention has been drawn with the discovery of negative GMR in rare-earth manganites $\text{RE}_{1-x}\text{AE}_x\text{MnO}_3$.

Fig. 1.10: Variation of resistivity of multilayers [(001) Fe 30 angstroms/(001) Cr 9 angstroms]$_{50}$ as function of the magnetic field at 4.2K. The specimen is a super lattice of 60 bilayers in which the current flows along the (110) direction and the magnetic field is applied in the layer plane (001) along the current direction. At the magnetic field $B_s$ (in the saturated state; $B_s = 2T$) the resistivity drops to almost half its zero field value.
There is a variety of applications of GMR for these types of materials in device applications, for example; (i) actuators (ii) sensors and (iii) magnetic recording (memory storage). The first observation regarding GMR was made in respect of Fe/Cr multilayers [72] with thin Cr layers; prepared by molecular beam epitaxy (MBE) technique. For Cr layers of 9 angstroms thickness, the resistivity was found to drop by almost a factor of 2 in a magnetic field of 2 Tesla at 4.2 K as shown in Figure. 1.10, giving a negative GMR of about 50 percent.

1.5.1. Colossal Magnetoresistance (CMR)

After the work of Von Helmolt et al. [73] and Charara et al.[74] in 1993, reporting a huge negative magnetoresistance, a modern family of materials \( RE_{1-x}AE_xMnO_3 \) (\( RE = \) trivalent rare earth cation, \( AE = \) divalent cation) having perovskite type of structure has drawn a wide attention. In 1994 S. Jin et al. [8] found ~ 100% MR in manganites and the phenomenon is named as "Colossal Magnetoresistance (CMR)" drawing a new interest in these materials because the origin of MR in manganites is pretty different from that observed in other forms of MR. CMR effect being an intrinsic property of crystal structure, has its origin in the spin disorder of conduction electron which can be suppressed by the applied magnetic field resulting in huge magnetoresistance [73,74]. At its earliest, it was recognized in 1950 that, the perovskite compound LaMnO\(_3\) with the characteristic structure, usually is in antiferromagnetic state. If rare-earth La\(^{3+}\) ions were replaced with divalent ions like Ca\(^{2+}\), Sr\(^{2+}\), Pb\(^{2+}\) or Ba\(^{2+}\) in between 20% and 40%, the resistance reduces drastically leading to the ferromagnetic character of the material. The replacement of a trivalent cation with a divalent cation in such type of materials compels a nearby Mn to alter from Mn\(^{3+}\) to Mn\(^{4+}\). Each time Mn\(^{3+}\) and Mn\(^{4+}\) are on adjacent Mn-sites, there exists a chance of conduction by electrons hopping from the Mn\(^{3+}\) to Mn\(^{4+}\) via the intermediate oxygen anion (O\(^{2-}\)) which requires the spin polarized character of hopping current. This hopping process seriously depends on the relative alignment of the neighboring Mn core spins. As a result, the electrical resistivity is extremely sensitive to the external magnetic field, giving rise to CMR.

CMR is often used to describe the extremely strong influence of the magnetic field. The CMR is defined as
\[
\text{CMR\%} = \frac{\Delta \rho}{\rho} = \frac{\{\rho(H) - \rho(0)\}}{\rho(H)} \times 100
\] (1.4)

The CMR reaches its maximum (in access of \(10^6\) percent) at 110 K with the magnetic field at 6 Tesla as shown in Figure 1.11. The peak occurs just below the Curie temperature. For films thicker than 2000 angstroms, the MR is reduced by orders of magnitude. The presence of grain boundaries corresponding to lattice strain is disadvantageous to achieve large MR. The MR improves further on heat treatment.

The two most prominent features of the GMR-CMR effects in manganites are as under:

(i) Firstly, by adjusting the processing parameters, the MR peak can be shifted to occur at room temperature.

(ii) Secondly, the resistivity can be manipulated by magnetic field to change by orders of magnitude.

1.6. Phase Diagrams and Phase Separation in Manganites

The properties of the perovskite manganites like \( \text{La}_{1-x}\text{AE}_x\text{MnO}_3 \) (\( \text{AE} = \text{Ca}, \text{Sr}, \text{Ba} \) etc) depend on the concentration (\( x \)) of the dopants and the temperature. These systems show different phases of conduction and complicated magnetic phase transitions depending on the doping level (\( x \)) and the temperature. The changes in the magnetic and electronic characteristics of the manganites with the change in composition have been investigated in several systems. Characteristic phase diagrams for Ca and Sr doped systems of \( \text{LaMnO}_3 \) are displayed in Figure 1.12 (a) and 1.12 (b) respectively on the basis of these measurements. The material is always paramagnetic above the transition temperature. The undoped compound is insulating and a layered antiferromagnet. On the small doping concentration (\( x<0.2 \)) with divalent alkaline elements like Ca, Sr, Ba, the structures become complicated and the material may be a ferromagnetic metal under certain conditions.

![Phase diagrams](image)

*Fig. 1.12: The phase diagrams of (a) \( \text{La}_{1-x}\text{Ca}_x\text{MnO}_3 \) and (b) \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \).*
The material becomes ferromagnetic below the Curie temperature with the increasing doping concentration and the ferromagnetic coupling reaches its strongest level at $x = 0.3-0.4$, where the Curie temperature has maximum value. At the doping level $x > 0.2$, the material behaves like a semiconductor, showing an increase in resistivity as the temperature is lowered. However, there is an inclination towards metallic conductivity, as observed for $La_{0.67}Sr_{0.33}MnO_3$ in the paramagnetic phase for increased doping. In the region of high doping ($x > 0.5$), an antiferromagnetic and insulating charge ordered state is formed. The paramagnetic state to the ferromagnetic state transition is also accompanied by a sudden drop in the resistivity. Such a drop is well known in other ferromagnetic metallic systems and is caused by the transition from a spin disordered state to one with ordered spin. Disorder causes charge carriers with different spin orientations to scatter from each other, increasing the resistivity. The loss of resistivity is observed in an applied magnetic field because of the alignment of the electrons spins since the magnetic field prevents the scattering caused by spin disorder.

A triplet state is formed by three of the electrons in the 3d orbital of the manganese ions at a lower energy. These electrons are considered as localized electrons that remain bound to the ion and because their spin points in the same direction, they have an overall magnetic moment of $3/2$. An energy band extending throughout the solid is formed by the sharing of electrons in the highest energy level with the oxygen ion. The width of this energy band largely controls the motion of charge carriers and hence the conductivity of the material. This is estimated by the overlapping of the manganese and oxygen orbitals, which in turn depends on the geometrical arrangement of the ions. A large overlap increases the width of the band and the overlap is largest when the Mn-O-Mn bond angle is $180^\circ$ for a given distance between manganese and oxygen ions. Such an arrangement is displayed by an ideal perovskite structure in which manganese and six oxygen ions form a regular octahedron. But if the lanthanum ion is replaced by a smaller ion, the distortion of the octahedron takes place making the bond angle smaller which reduces the overlap between the orbitals and the energy band becomes narrow. Materials with narrow energy bands show weaker ferromagnetism, corresponding to a lower value of Curie temperature.
The effective bandwidth of mixed valence manganites is modified by the alignment of electron spins. The alignment of localized moments in neighbouring ions makes the electrons hopping easier between Mn$^{3+}$/Mn$^{4+}$ sites. Therefore, when the material becomes magnetically ordered below the Curie temperature, an increment in the effective bandwidth takes place favoring the motion of charge carriers making the conductivity larger. Therefore, in these types of materials, the ferromagnetism is transmitted via mobile carriers. When the charge carriers are not free for movement, the system is insulating and the interaction between the localized electrons induces antiferromagnetic order below the Néel temperature.

Electrical transport, magnetic and other measurements on La$_{1-x}$AE$_x$MnO$_3$ systems have revealed certain extraordinary features with respect to charge carriers. For instance, the manganites exhibit very high resistivity particularly at low temperatures (<100 K) and the values of resistivity are noticeably higher than Mott’s maximum value of resistivity [75,76]. The resistivity value of $10^3$-$10^4$ ohm-cm corresponds to the metallic state.

In the ferromagnetic regime of manganites, the resistivity has been investigated by a number of researchers. Just below $T_C$, it varies rapidly with temperature. For $T < 0.5 T_C$, the variation is less rapid and is different from what is generally seen in a metallic ferromagnet. In general, for $T < 0.2 T_C$, a $T^2$ dependence makes an important contribution.

1.7. Nanostructural Manganites and their size dependence

Nanomaterials form an astonishing attention of scientists, in the material science group world over in the present scenario. Because of their unique properties, the structure on the nanometer scale always sparks the attention. The particle size or the grain size in nanometer range (1-100nm) in a material causes the important changes in the electronic band structure as well as in the crystal structure which in turn affect the electrical, magnetic, mechanical, optical and thermal properties dramatically. These properties are associated to the low density of grain boundaries and interfaces that result from their nanoscale structure (characteristic length scale below 100 nm) [77]. In order to predict the performance of a particular component or device based on nanomaterials, it is important to recognize the way in which a variety of structural
properties change with particle size in nano systems. This lets us to know that with a
decrease in the particle size, how the variation in the crystal structure of a material
takes place. The effects determined by size, related to the advancement of structural,
thermodynamic, electronic, spectroscopic, electromagnetic and chemical properties of
nanomaterials are known as size effects which composed of attractive aspects of these
materials. The structural properties of nanomaterials appreciably differ from those of
bulk materials. Physics and chemistry play a crucial role in the synthesis and
characterization of nano building blocks. Thus in present scenario, the instant
objectives of the science and technology of nanomaterials are:

i. Completely mastering the synthesis of isolated nanostructures and their
   assemblies with the desired features.
ii. Generating novel class of materials with high performance.
iii. Establishing and exploring the concepts of nanodevice and systems
    architectures.
iv. To establish the connection of nanoscience with molecular electronics.
v. Improving known tools while discovering better tools of analysis of
   nanostructures.

In the current work, focus is given on the CMR manganites with
ferromagnetic character at room temperature have been emphasized which display
unique magnetic properties at nanoscale. These properties make them very interesting
both from theoretical and technological point of view. The magnetism of
nanomaterials lies between atomic-scale magnetism and bulk material magnetism.
There exist two types of magnetic properties: intrinsic and extrinsic. The intrinsic
properties include Curie temperature, magnetization and magnetocrystalline
anisotropy, and the extrinsic properties include coercivity. When the grain size is
reduced to nano scale, both intrinsic and extrinsic properties behave differently and
the extrinsic properties are affected more than the intrinsic at nano scale. However,
the large surface to volume ratio of the particles corresponds to strong dependence on
diameter of the intrinsic properties such as magnetization and anisotropy. At high
temperatures superparamagnetic behavior is shown by them [78]. Also, the
competition between dramatically different phases is extremely important in case of
manganites. This is a common factor of strongly correlated electron systems and is
difficult to avoid. In several materials, stable states are induced by this phase competition where the carriers are not equally distributed but form a variety of unequal patterns. It may be argued that, in manganites, these inhomogeneities are the origin of the unusually huge MR. There is a evidence that in manganites, the large resistivity of the paramagnetic insulating phase is related with nanoscale inhomogeneities. Manganites come out to form “nanoscale phase-separated” states, where two competing phases reach to cooperation by forming inhomogeneous patterns. These days, nano manganites have been proven to be an attractive class in biomedical application for diagnosing cancerous cells without destroying the healthy cells. The nano-structure of a material exclusively depends upon the synthesis method. The synthesis of these materials have the following basic challenges: (i) With decreasing particle size the agglomeration of powders increases and the characteristic length scales are defined by the size of the agglomerates rather than the size of the nanopowders in sintering and the final microstructure. (ii) Final stage sintering is accompanied always by quick grain growth which has increasing driving force with decreasing grain size, making it hard to sustain the microstructure while improving density. (iii) While there are conventional ceramic methods to improve densification kinetics and suppress grain growth; they either depend on additives, which might unfavorably alter the physical properties, or resort to “bruit force” such as large amount of applied pressure, which makes an increment in the expenditure and restricts the process flexibility. Therefore, novelty is required to prevail over these troubles in order to accomplish the proficient fabrication of nanoceramics.

Manganites have different transport and magnetic dependent phases which may or may not have different carrier densities but generally display different structural symmetries corresponding to ferromagnetic, spin ordered/ charge ordered antiferromagnetic phases. In certain manganites, an enormously diverse range of unusual electronic and magnetic phases can exist simultaneously at different locations within a single crystal due to their strong electronic, magnetic, and crystal structure interactions. An early idea was made by Gorkov [79] that two phase separation might govern the colossal magnetoresistive regime. Uehara et al. [80] have convincingly revealed the presence of intrinsic mixed phase tendencies in their study of La\textsubscript{0.625-y}Pr\textsubscript{y}Ca\textsubscript{0.375}MnO\textsubscript{3} manganites using transport, magnetic and electron microscopy techniques and demonstrated phase separation in these particular...
manganites. It is well known and general belief that the interior of each grain has the crystalline nature having ferromagnetic phase displaying metallic behavior and large transfer integral while the grain boundary have amorphous like nature having paramagnetic phase displaying insulating behavior and negligibly small transfer integral in granular manganites. A very small magnetic interaction results between well separated ferromagnetic islands without application of magnetic field at each step of the paramagnetic to ferromagnetic transformation (means from grain boundary to interior of the grain transformation). Over the ferromagnetic region, the magnetization is uniform which vanishes unexpectedly at the interface with the paramagnetic phase. In the presence of a magnetic field, these islands are supposed to interact with each other. At the grain boundaries the unsystematically arranged spins become systematic and \( e_g \) itinerant electrons can move from one grain to another in presence of an applied magnetic field and as the applied magnetic field increases, the transfer integral increases. This is the basis of the CMR effect and favoring evidence to the earlier statement that, the CMR effect in manganites originates from phase separation [79]. Three fundamental transport and magnetotransport properties of manganites are affected by the nanoscale regime, which are (i) resistivity, (ii) transition temperatures, \( T_c \) and \( T_p \), and (iii) magnetoresistance (MR) [56].

Two very important parameters play a very crucial role in nanostructural manganites; namely

a) Extrinsic and Intrinsic Magnetoresistance (MR) components

b) Effects caused by grain boundaries

\( a) \). **Extrinsic and Intrinsic Magnetoresistance (MR) Components**

Depending upon the nature of the grain boundaries and grain morphology as well as temperature at which MR behavior is exhibited; two types of CMR effects are observed in mixed valence manganites as shown in Figure 1.13.
Fig. 1.13: Types of magnetoresistance exhibited by CMR materials.

b). Effects caused by grain boundaries

The grains separated by grain boundaries in different nanomaterials are shown in Figure 1.14. Grain boundaries critically affect the physical properties of these materials. In general, the effects caused by grain boundaries come into existence because of large number of atoms are located at the grain boundaries having different behaviors from that of bulk having similar chemical composition. The nanoscale effect occurs because many elementary processes in crystals are associated with length scales around few nanometers. The exceptional physical and chemical properties of nanocrystalline materials are highly sensitive to their structural stability. A grain growth process which destroys the nanocrystalline state is capable of causing a dramatic degradation of these properties. On a variety of length scales, the structures of nanophasic materials have an important attitude on their physical and chemical properties [81,82]. These properties are dominated by their ultrafine grain sizes and the large number of interfaces linked with their small grains. During the past several years, it has become gradually clearer that all of these structural aspects must be carefully considered to have complete understanding of the properties of nanophasic materials.
**Fig. 1.14:** Different nanocrystalline materials showing grains separated by grain boundaries.

Grain-growth is the familiar phenomenon which is responsible for an increase in average grain size during annealing due to grain boundary movement. This movement of grain boundaries is because of annealing at a definite temperature for some time. The motivating force for this growth is the reduction in the area of grain boundary and hence the total grain boundary energy of the system is reduced.

**Fig. 1.15:** (a) and (b) Schematic representations of nanocrystalline solids and (c) isolated nanosized particles. Light and dark shaded circles stand for the atoms at the interfaces and in the core of the grains respectively. Dashed lines indicate the grain boundaries.

The growth in grains is a cooperative process which involves many individual grains of various sizes and shapes at the same time [83,84]. Numerous properties of manganites such as structural, transport, magnetotransport, magnetic, etc depend on grain size and this requires a theoretical understanding of grain size [83] to provide further approach into future applications in nanosystems as well. Figure 1.15 (a) shows the schematic diagram of nanocrystalline solids having the disordered grain
boundaries in which the atoms are not located on lattice sites demonstrating the non-crystalline nature of the grain boundaries. This enhances the non-crystallinity in the materials (especially in manganites) and hence makes a reduction in the intensity of the XRD peaks causing an enhancement in the full width of half maximum (FWHM) of the XRD peaks. Due to the large number of the non-crystalline grain boundaries the transport is reduced and hence the resistance of the manganites is enhanced on suppression of the transfer integral of itinerant $t_g$ electrons from Mn$^{3+}$ site to Mn$^{4+}$ site. Figure 1.15 (b) shows the schematic diagram of nanocrystalline solids having the disordered grain boundaries wherein the atoms are located at lattice sites indicating that the atoms at the interfaces make an enhancement in the crystallinity of the manganite nanomaterials. This results into the large intensity of XRD peak causing low values of FWHM, better transport and hence the enhancement in the transfer of itinerant charge carriers through the oxygen site from Mn$^{3+}$ site to Mn$^{4+}$ reduces the value of resistivity. An illustration of isolated nanosized particles is shown in Figure 1.15 (c) which may have the grain boundaries having the size equivalent to the grain diameter.

1.8. Applications of Mixed Valence Manganites

Based on their different physical and chemical properties, perovskite manganites have a great potential for applications [85-87]. The strong metal-insulator (M-I) transition near Curie- temperature, the polarizability of the material by electric field, the magnetic field sensitivity of the transport properties and its consequent effects on the transport properties, the half metallic behavior of the electronic bands, etc., are properties of the rare earth manganites that could be utilized in various devices. Numerous device approaches are being investigated based on these properties, out of which some of them are depicted below.

1. The magnetoresistance property of manganites can be utilized in magnetoresistive read-write heads, magnetic sensors and magnetoresistive random access memory (MRAM). Magnetic sensors prepared from either single crystals or thin films can be utilized for sensing the magnitude of a magnetic field either in one or several directions by choosing the right crystal form and de-magnetizing factor. However in manganite samples having high grain boundary density and in tunnel spin valve structures, a low field...
magnetoresistive (LFMR) behavior can be observed. Sun et al. [88] prepared one of the first operational devices of this type which consists of two layers of ferromagnetic \( \text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3 \), separated by a \( \text{SrTiO}_3 \) spacer layer and displays a decrement in resistance by a factor of 2 in a field of less than 20 milli Tesla. Based on ferromagnetic tunneling junctions or on grain-boundary magnetoresistance, the major disadvantage of devices is that large magnetic field sensitivities are only achieved at temperatures below 200 K.

2. The mixed valence manganites become very fascinating materials for spintronics due to their large spin polarization of carriers and as a result large tunnel magnetoresistance (TMR) ratios. Presently, \( \text{La}_2\text{SrMO}_3 \) based magnetic tunnel junctions (MTJs) show the best figure of merit among manganite based tunnelling structures. However, the TMR ratio of these MTJs decays rapidly with temperature, vanishing completely well below \( T_c \).

3. The electric field effect has also been observed in manganites. In this case, the bottom layer is a CMR material and the top layer may be of ferroelectric layer (\( \text{PbZr}_0.2\text{Ti}_0.8\text{O}_3 \)) or a paramagnetic (\( \text{SrTiO}_3 \)) [89] but the variations are more intense in the case of \( \text{PZT} \) in which over a time period of 45 minutes, only a change of 3% in the channel resistance is evaluated at room temperature which makes this material appealing for the applications in nonvolatile ferroelectric field-effect device [90,91].

4. These CMR materials become very fascinating for use in bolometric detectors [92-94] because of their large temperature coefficient of resistance (TCR, calculated as \( (1/R) (dR/dT) \)) just below the peak resistivity. Bolometer is a device to detect and measure the radiations. In fact, the TCR can reach 15% per degree at 300K [95] which is about one order of magnitude larger than that of \( \text{VO}_2 \), the material commonly used in bolometers.

Some of the CMR materials have been shown in Table-3 having remarkably high values of TCR in the temperature range 200 K - 300 K.
<table>
<thead>
<tr>
<th>S. No.</th>
<th>Composition</th>
<th>Peak Temperature (T_p) (K)</th>
<th>Temperature Coefficient of Resistance TCR (%/K)</th>
<th>Peak Resistivity (mΩ-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Nd_{0.7}Sr_{0.3}MnO_3</td>
<td>235</td>
<td>32</td>
<td>40</td>
</tr>
<tr>
<td>2.</td>
<td>Nd_{0.6}Sr_{0.4}MnO_3</td>
<td>215</td>
<td>7</td>
<td>60.5</td>
</tr>
<tr>
<td>3.</td>
<td>La_{0.8}Sr_{0.1}MnO_3</td>
<td>277</td>
<td>5</td>
<td>14</td>
</tr>
<tr>
<td>4.</td>
<td>La_{0.8}Ca_{0.2}MnO_3</td>
<td>298</td>
<td>8</td>
<td>12</td>
</tr>
<tr>
<td>5.</td>
<td>La_{0.7}Ba_{0.3}MnO_3</td>
<td>330</td>
<td>4</td>
<td>17.5</td>
</tr>
<tr>
<td>6.</td>
<td>La_{0.37}Pr_{0.30}Ca_{0.33}MnO_3</td>
<td>230</td>
<td>58</td>
<td>200</td>
</tr>
<tr>
<td>7.</td>
<td>La_{0.7}Sr_{0.3}MnO_3</td>
<td>380</td>
<td>2.5</td>
<td>0.5</td>
</tr>
<tr>
<td>8.</td>
<td>Pr_{0.7}Sr_{0.3}MnO_3</td>
<td>320</td>
<td>11</td>
<td>8</td>
</tr>
<tr>
<td>9.</td>
<td>Ag-doped La_{0.7}Ca_{0.3}MnO_3</td>
<td>285</td>
<td>18</td>
<td>8</td>
</tr>
</tbody>
</table>

5. Since at low temperatures i.e. below 100 K, the properties of the CMR materials are quite impressive, so the combination CMR manganites and superconducting cuprates thin films of high-T_c may correspond to hybrid high temperature superconductivity (HTSC)–CMR structures at these low temperatures [96,97]. These HTSC–CMR structures not only lead to potentially new spin-injection devices but also may serve as a useful medium for understanding some of the forefront theoretical ideas.

6. Chemical applications involve catalysis such as catalysts for oxygen sensors, automobile exhausts and solid electrolytes in fuel cells. The catalytic activity is related with the Mn^{3+}-Mn^{4+} mixed valence and the chance of forming oxygen vacancies in the solid [98,99].

7. Due to their higher magnetic entropy near T_c, magnetocaloric effect in doped manganites has been reported for potentially enabling high temperature and low magnetic field refrigerators [100,101].

8. Manganites nanocomposites have been deployed for low field magnetoresistive (LFMR) devices. For example LSMO + TiO_2 nanocomposite where MR increases significantly at low field at 77K and TiO_2 does not enter...
the LSMO grains so does not alter the LSMO phase and stoichiometry with in grain. Moreover, as doping increases, $T_p$ shifts towards lower temperature [102].

9. In the frequency range of 8-12 GHz, manganite nano-composites have also a significant application in wide-band and super-thin electromagnetic (EM) absorbers. Recently, the rapidly expanding business of communication devices, such as mobile telephones and radar systems causing severe electromagnetic interference pollution have attracted great interest in developing efficient EM-wave absorption materials with properties of wide frequency range, low density and strong absorption. Specifically, for the purpose of the microwave absorber used as coating on the exterior surfaces of military aircraft and vehicles, Carbonyl Iron P/LSMO composites exhibit outstanding micro-wave absorption properties in the frequency range of 8–12GHz with the thickness of 0.8mm.

1.9 Motivation

Perovskite manganites are complex functional materials and an immense interest has been developed in the investigation of mixed valence manganites because of their variety of interconnected properties like structural, electrical transport and magnetic. Early research was motivated by a need to develop insulating ferromagnets with an ample magnetization for high-frequency applications. More recent work has been determined by a desire to understand and develop the large negative magnetoresistance effects which occur in the vicinity of the Curie temperature. Research on the manganites has exhibited new phenomena such as colossal magnetoresistance (CMR) and dense granular magnetoresistance which correspond to the understanding of numerous physical concepts such as Zener double exchange and the Jahn-Teller effect.

The aim of this work is to study the physical properties like structural, electrical and magnetic of the perovskite manganite $\text{LaMnO}_3$ with doping of Strontium (Sr) at La site followed by zinc (Zn) and iron (Fe) at manganese site prepared mainly through solid-state reaction route along with sol-gel method and characterized through various techniques. Strontium at A site i.e. $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (x = 0.33) is chosen because it is half metallic at room temperature corresponding to a
variety of applications in spintronics devices and it shows the ferromagnetic metallic (FMM) character along with the large MR value at room temperature. Curie temperature is also well above the room temperature. The variation in strontium content reduces the MR both at low and high temperatures and modifies the grain boundary contribution to the electrical transport and magnetotransport properties. In recent times, the Mn-site substitution has drawn more attention and a group of researchers synthesized the doped nanoparticles of $La_{1-x}Sr_xMnO_3$ and observed electrical and magnetic properties in detail. They observed smaller particle size in 33% Sr doped sample with good magnetoresistance [103]. The maximum magnetoresistance was observed in Ni doped $La_{0.67}Sr_{0.33}Mn_{1-x}Ni_xO_3$ ($x=0\leq x\leq 0.25$) at low temperature for the highest doping concentration along with a decrease in magnetization. [104].

The partial substitution of $Zn^{2+}$ at the magnetic sublattice of mixed-valent manganese in $La_{0.6}Sr_{0.4}MnO_3$ induces a random potential fluctuation because the $Zn^{2+}$ ion has the completely filled 3d$^{10}$ electronic configurations, which is different from those of Mn$^{3+}$ and Mn$^{4+}$ configuration respectively. Secondly, the Zn$^{2+}$ ions do not carry any magnetic moment as they are also expected not to participate in the ferromagnetic (FM) interaction and hence dilute the magnetic sublattice [105].

The doping by Fe$^{3+}$ also seems to be very suitable since Fe$^{3+}$ is magnetic, but does not give rise to the Jahn–Teller effect and unlike Chromium (Cr), does not take part in DE. The influence of Fe doping on magnetic and electrical properties was mainly studied for hole doped $La_{1-x}Ca_xMn_{1-y}Fe_yO_3$ ($x = 0.3$ and $y = 0.25$) systems [106-108].
References:


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Chapter 2

Theoretical Models for Manganites
This Chapter deals with the fundamental physical concepts, mechanism and theories which have been utilized to elucidate different phenomena. It includes: charge conduction mechanism, super-exchange and double-exchange interactions, Jahn-Teller (J-T) distortion and the complex charge ordering in manganites.

2.1. Mechanism of Charge Conduction

A remarkable behavior has been found in Ln_{1-x}A_xMnO_3 (where Ln is a lanthanide and A is a divalent cation) on doping of divalent cations like Sr^{2+}, Ca^{2+} or Ba^{2+} etc. at Ln site in LnMnO_3 insulator which has been explained on the creation of Mn^{3+} state in the compound with the interplay between Mn^{3+} and Mn^{4+} due to the hopping of electron from one site to another corresponding to electronic transport in them. Two types of transitions are exhibited by the doped manganites. First one is the electrical transition from insulating/semiconducting state to metallic state occurring at peak temperature (T_p) and the second one is the magnetic transition from paramagnetic state to ferromagnetic state occurring at Curie temperature (T_c). At room temperature, most of the manganites are in paramagnetic insulating/semiconducting (PMI/PMS) state and they show signs of increase in electrical resistivity with decreasing temperature; but when cooled below T_c, metal-insulator (M-I) transition occurs in the vicinity of paramagnetic to ferromagnetic transition. At low temperature below T_p, in the half doped manganites (0≤x≤0.5), an enhancement in the resistivity is observed along with reduction in magnetization at a temperature T_N known as Neel's temperature (a temperature below which a compound is antiferromagnetic and above which it is paramagnetic). In the low temperature regime T < T_N, a real space ordering of all Mn^{3+} and Mn^{4+} ions is occurred which causes the increment in resistivity and reduction in magnetization. The doped manganites with doping level x = 0.33 display a transition from high temperature PMI/PMS state to a low temperature ferromagnetic metallic (FMM) state as the temperature is decreased. The resistivity decreases abruptly particularly in the region of metal-insulator transition (T_p) as the material is kept in the applied magnetic field. Since the decrease in resistivity may be almost 100% and hence, the use of the term colossal seems appropriate while we refer to the magnetoresistance in these types of materials. The transport and magnetotransport properties may be directly affected by a variety of parameters like doping, average ionic radius, size variance, grain morphology, heat treatment, etc. Previously in Mn oxides, the foundation for the theoretical understanding of the variation in resistivities
was generally the concept of the double exchange (DE) that considers the exchange of electron between neighboring Mn$^{3+}$ and Mn$^{4+}$ sites with strong on-side Hund’s coupling. Perturbative calculations carried out by Millis et al. [1,2] demonstrated that DE alone could not explain the experimental data of Mn oxides and suggested that a strong Jahn-Teller (J-T) distortion should be accountable for the transport properties. Later on it was suggested that based on non-perturbative behaviors, the localization effect [3,4] in the double exchange model might be able to account for the novel properties of manganites.

But, to understand the resistivity in a better way in semiconducting or insulating and metallic region, several models have been proposed and some of them are:

i. Variable Range Hopping (VRH) Model
ii. Small Polaron Hopping (SPH) Model
iii. Zener Double Exchange Polynomial law

Hopping conduction is described as electrical conduction where the carriers are transported via electrons hopping from one localized state to another. Electron transport through localized state (shallow level states or deep level states) within the band gap of a semiconductor comprises the following (as shown in Fig. 2.1) [5].

1. Electron hops from a state to another state which has higher energy. This movement requires a thermal energy. The energy difference is symbolized by $E_{hop}$ in Figure 2.1. This process is thermally supported tunneling and depends on temperature.

2. Electron hops from a state to another state of equal energy. This type of transport is a tunneling process and is independent of temperature.

3. Electron hops from a state to another state that has a lower energy. This type of transport is a tunneling process with the emission of a phonon(s) and is independent of temperature.

The essential conditions for the hopping to occur are:

(i) There should be an overlapping of wave function of the two localized states.
(ii) Empty and occupied states must be present for the occurrence of hopping. This condition needs the hopping should take place between states close to the Fermi level.

(iii) An energy is required for the hopping of electron from a localized state to another localized state with a higher energy level.

\[
\text{Conduction Band} \\
E_{\text{hop}} \downarrow \hspace{1cm} \rightarrow \hspace{1cm} \rightarrow \hspace{1cm} \rightarrow \\
\text{(1)} \hspace{2cm} \text{(2)} \hspace{2cm} \text{(3)} \\
\text{Valence Band}
\]

*Fig. 2.1: Electron transport between localized states: (1) thermally-supported tunneling; (2) tunneling but independent of temperature; (3) tunneling with the emission of a phonon(s) and independent of temperature.*

**(i) Variable Range Hopping Conduction**

When the temperature is sufficiently low, the probability of the electron thermal activation between states which are close in space but far in energy becomes smaller than that of electron hopping between some more remote states whose energy levels happen to be very close to each other. In this case, the characteristic hopping distance \(d_v\) increases with decreasing temperature. Therefore, this kind of hopping is called variable-range hopping (VRH). [5]

Figure 2.2 displays the nearest neighbor hopping and variable range hopping in which \(d_{nn}\) and \(d_v\) corresponds to the average distance between the neighbors and the variable range hopping distance respectively.

\[
\text{Conduction Band} \\
E_{\text{hop}} \downarrow \hspace{1cm} \rightarrow \hspace{1cm} \rightarrow \hspace{1cm} \rightarrow \\
\text{\hspace{1cm} \hspace{1cm} \hspace{1cm} d_{nn} \hspace{1cm} d_v} \\
\text{Valence Band}
\]

*Fig. 2.2: Nearest neighbor hopping and variable range hopping.*
Few years later the invention of the transistor effect in the second half of the forties by Brattain, Bardeen and Shockley, it has been observed as early as 1950, a break in the behaviour of conductivity of doped Germanium at low temperatures. Gliessman and Hung pointed out this behaviour to a different mechanism from usual conduction that governs doped semiconductors. A few years after in 1956, Conwell and Mott suggested a model for a "new" process of conduction in which charge carriers conduct the electric current by thermally activated tunnelling from an occupied state to an empty state. This process has been known as phonon assisted hopping and was the starting point of a number of transport theories as, the model of Miller and Abrahams developed in 1960. This model became the most broadly accepted theory of conduction between localized states in the 60's decade and was the source of inspiration for the variable range hopping theory of Mott [6].

The variable range hopping theory has been extensively used these last years to elucidate the electric conduction process in some biological systems as DNA. On the other hand, the experimental measurements on some systems disclose that the density of states varies strongly near Fermi level. This observation suggests that the theoretical concept of "constant density of states" near Fermi level is certainly inadequate to justify the observation of the $T^{-1/4}$ conductivity in some systems. [6]. The resistivity can be explained in semiconducting or insulating regions by using Mott's variable range hopping (VRH) model for uncorrelated carriers [7-9] and can be given as:

$$\rho = \rho_0 \exp \left( \frac{T_0}{T} \right)^{1/(1+d)}$$

(2.1)

where 'd' is the dimensionality and for 3D systems, $d = 3$, so it becomes

$$\rho = \rho_0 \exp \left( \frac{T_0}{T} \right)^{3/4}$$

(2.2)

In doped manganites the randomness in spins and fluctuations in Coulombic potential are generated due to the increase in the size disorder with doping level $x$. That's why, beyond the Mn-O distances, the carriers experience some potential difference 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 is known as characteristic temperature and can be related to the carrier localization length by the

...44...
expression, \( T_0 = 18/k_bN(E_F)L^3 \), where \( k_b \) is the Boltzmann constant, \( L \) is the carrier localization length and \( N(E_F) \) is the density of states at Fermi level, the values of the localization length should be comparable to Mn-O distances for the VRH type of conduction [10].

(ii) Small Polaron Hopping (SPH) Model

The small polaron hopping mechanism appears to be most appropriate for manganites with rare earth ions of smaller ionic radii since the small polarons are created due to the structural distortions because of the lower ionic radii. In general, it is recognized that the presence of small polarons plays a very important role in the peculiar transport properties of manganites, the true nature and the exact transport process of small polarons is still an open question and a matter of clash and necessitates more investigations.

Adiabatic nearest neighbor hopping model of small polaron conduction [11,12], according to which the resistivity may be given as

\[
\rho = \rho_a \exp \left( \frac{E_F}{k_bT} \right)
\]

where \( E_F \) is the activation energy and \( k_b \) is the Boltzmann’s constant and \( T \) is the absolute temperature.

(iii) Zener-Double Exchange (ZDE) Polynomial Law

The cause of resistivity in the metallic region and the electron transport mechanism 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 \( \rho_0 \) and \( \rho_2 \) are respectively the residual resistivity and the resistivity contributed by an electron-electron and electron-phonon scattering mechanism, \( n \) is a higher order term and may take values; \( n = 2.5, 3, 4.5 \) and 7.5 and \( \rho_n \) is the corresponding resistivity coefficient [13-18]. In this law, \( n = 2.5 \) and 3 correspond to the one magnon scattering phenomenon while \( n = 5, 4.5 \) and 7.5 correspond to two magnon scattering process.
2.2. The Physics for Magnetic Interactions

To recognize the different phenomena including antiferromagnetism, ferromagnetism and magnetic long range order etc., the understanding of magnetic interactions is necessary. Generally, the exchange interactions are electrostatic interactions which in turn determine the nature of the magnetic material. The exchange interactions in manganites can be generally divided into following two types: one is the direct exchange corresponding to the interactions between neighbouring magnetic ions and other is indirect exchange corresponding to the interactions between non-neighbouring magnetic ions.

![Diagram of MnO crystal structure]

*Fig. 2.3: The crystal structure of MnO. Nearest neighbour pairs of Mn$^{2+}$ (manganese) ions are connected via O$^{2-}$ (oxygen) ions.*

Nearest neighbour magnetic ions of Mn$^{2+}$ are displayed in Figure 2.3 which are connected to O$^{2-}$ ions in MnO crystal structure. Alternatively, indirect exchange appreciably depends upon the kind of the magnetic material and is again depicted in terms of superexchange and double exchange mechanism.

2.3. Superexchange and double exchange interactions

2.3.1. Superexchange Interaction

The interactions in which the oxygen ion plays an important role may be achieved by the two mechanisms which are called superexchange and double exchange interactions. There is a strong dependence of both effects on the magnetic moments of Mn ions, the overlap integral between orbitals of Mn and O ions and the Mn-O-Mn bond angle in the manganites. Since the bonding in oxides is mostly ionic, the oxygen...
ion with a full 2p shell has an inert gas electronic configuration and its interaction in this ground state with metallic ions is small. The superexchange interaction has been suggested for the case in which there is a mechanism of excitation from this ground state. By considering the following example of ferric ions in an oxide, the superexchange interaction can be understood. According to Hund’s rule, in ground state of these ferric ions, all the five 3d electrons are aligned. The six 2p electrons of the oxygen ions from three pairs in which each of the pairs have canceling spins. For the time being, one of the p electrons becomes one of the d electrons of the iron ion by considering the interaction in excited state. The transfer process in which we have one ferric ion on one side of the oxygen and another ferric ion on the other side of oxygen, the one ferric ion now converts into a ferrous ion. Now, there may be an interaction between the unpaired electron of the oxygen p orbital and the unpaired ferric ion on the other side in a negative way. Including some oxides and fluorides, number of ionic solids has magnetic ground states e.g. MnO and MnF₂ are both antiferromagnets, even if this observation becomes visible at first sight rather amazing due to absence of direct overlap between the electrons on Mn²⁺ ions in each system. The exchange interaction is usually very short-ranged so that the longer ranged interaction that is operating in this case must be in some sense 'super'. Infact, the exchange mechanism which is active here is known as super-exchange [19].

2.3.2. Double exchange interaction

A large amount of the early reported theoretical work on manganites was centered 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. No more work was dedicated to the magnitude of the magnetoresistance effect itself. The states of manganites were supposed to be identical and double exchange (DE) was suggested by Zener in 1951 in terms of indirect magnetic exchange interaction between adjacent ions of parallel spins through a neighbouring oxygen ion in which ferromagnetic interactions are favored when the magnetic ions are fairly well separated and conduction electrons are present [20]. This model is more restraining than the superexchange interaction and necessitates the presence of ions of the same element with different valence states i.e. in manganites, the presence of Mn³⁺ and Mn⁴⁺ ions. The theory was applied to the manganese perovskites with the motive of explaining the strong correlation between conductivity and ferromagnetism. Starting
from the insulating antiferromagnetic $\text{LaMnO}_3$ parent compound in which electrons are localized on the atomic orbitals, Zener explained how the system progressively becomes more ferromagnetic upon hole doping (introduction of $\text{Mn}^{4+}$ ion). He considered the case of the exchange between $\text{Mn}^{3+}$ and $\text{Mn}^{4+}$ ions via an oxygen ion and established the concept of simultaneous transfer of an electron from the $\text{Mn}^{3+}$ ion to the oxygen ($\text{O}^{2-}$) ion and from the oxygen ion to the neighboring $\text{Mn}^{4+}$ ion as displayed in Figure 2.4 (a). The double exchange mechanism appears to be a contributing part to the observed ferromagnetic interactions in these manganites and cobaltites. Additionally, in the case of the strong coupling, limited with $J_H \gg t$, the inter-site hopping parameter ‘$t$’ of the $e_g$ electron between neighbouring sites can be roughly estimated by

$$t = t^0 \cos \left( \frac{\theta}{2} \right)$$

(2.5)

where $\theta$ is the relative angle between the neighbouring spins and $t^0$ is the value of ‘$t$’ when $\theta = 0^\circ$ as schematically shown in Figure 2.4 (b). Moreover, all the spins of $\text{Mn}^{3+}$ and $\text{Mn}^{4+}$ ions have the same direction for the ferromagnetism below the Curie temperature $T_c$ as displayed in Figure 2.4 (c). Hence the single $e_g$ electron of $\text{Mn}^{3+}$ ion can hop back and forth between $\text{Mn}^{3+}$ and $\text{Mn}^{4+}$ ions via oxygen 2p states. As a result, the FM metallic ground state appears. All spins are completely disordered energetically with an increase in temperature up to the ideal paramagnetic regime as shown in Figure 2.4 (d) which hinders electron hopping, creating the paramagnetic insulating (PMI) state.

---

**Fig. 2.4:** (a) Double exchange mechanism showing ferromagnetic coupling between $\text{Mn}^{3+}$ and $\text{Mn}^{4+}$ ions participating in electron transfer via $\text{O}^{2-}$ (b) intersite hopping parameter (c) Ionic state of $\text{Mn}$ ions below $T_c$ (d) Ionic state of $\text{Mn}$ ions above $T_c$. 

...48...
However, at temperatures in the vicinity of $T_c$, the spins can be easily aligned by an applied magnetic field. This makes a more or less enhancement in the effective electron hopping due to which the resistivity decreases and consequently, the CMR effect is generated.

Therefore, the FM interaction of $e_g$ electrons can be produced by the double exchange only at lower temperatures in some mixed-valence manganites. Based on the double exchange mechanism and Hund's coupling, the CMR effect could be explained qualitatively but not quantitatively [20].

The pure LaMnO$_3$ shows the semiconducting property. When some of the La$^{3+}$ ions are replaced by divalent ions like Sr$^{2+}$ or Ca$^{2+}$ ions, it is essential that a corresponding number of Mn$^{3+}$ ions are replaced by Mn$^{4+}$ ions to preserve the charge neutrality.

Then, if we define $\Psi_1$ and $\Psi_2$ as follows

\[
\Psi_1: \text{Mn}^{3+}\ O^2-\ \text{Mn}^{4+}
\]

\[
\Psi_2: \text{Mn}^{4+}\ O^2-\ \text{Mn}^{3+}
\]

Since $\Psi_1$ and $\Psi_2$ are degenerate wave functions, more exact waveforms can be found by taking their linear combinations.

\[
\Psi^+ = \Psi_1 + \Psi_2 \quad ; \quad \Psi^- = \Psi_1 - \Psi_2
\]  \hspace{1cm} (2.6)

The energy difference of these two linear combinations is given by $2\epsilon$ where $\epsilon$ being the exchange energy, represented explicitly by

\[
\epsilon = \int \Psi_1^*(H - \epsilon_0) \Psi_2 \, dt
\]  \hspace{1cm} (2.7)

where $H$ is the Hamiltonian of the whole system and $\epsilon_0$ is the energy associated with the initial states $\Psi_1$ and $\Psi_2$. The above integral which can extend over the coordinates and the spins of all the electrons is generally known as the exchange integral. The integral in equation (2.7) will be non vanishing only if spins of the two d-shells are aligned parallel. Therefore, the lowest energy of the system corresponds to a parallel alignment of electron spins in Mn$^{3+}$ and Mn$^{4+}$ ions. It can be concluded that the lining up of the spins adjacent to incomplete d-shells of the Mn ions will be accompanied by an increase in the rate of migration of Mn$^{4+}$ ions and hence resulting an increase in the open circuit voltage.
electrical conductivity. Furthermore, it should be recognized that a stationary state is represented neither by $\Psi_1$ nor by $\Psi_2$ but by either of the two linear combinations as shown in equation (2.6).

Depending upon the sign of the exchange integral in equation (2.7), the double exchange raises the energy associated with $\Psi^+$ and lowers the energy associated with $\Psi^-$ or vice-versa. Hence, the double exchange lowers the energy of one of these two stationary states which takes place when the spins of the d-shell are parallel. However, apart from of the sign of the exchange integral, the energy of the system will be lowered by a parallel alignment of spins at lower temperatures. The rate at which electron jumps from a Mn$^{3+}$ ion through an intervening O$^{2-}$ ion to an adjacent Mn$^{4+}$ ion is given by the frequency;

$$\nu = 2\varepsilon /h$$

(2.8)

Therefore, the diffusion coefficient for the Mn$^{4+}$ ion is given by

$$D = a^2 \varepsilon /h$$

(2.9)

where 'a' is the lattice parameter. From Einstein relation

$$\sigma = ne^2 D /kT$$

(2.10)

where $\sigma$ = electrical conductivity

$D$ = diffusion coefficient

$n$ = no. of ions (Mn$^{4+}$) per unit volume

Electrical conductivity can be written as

$$\sigma = xe^2 \varepsilon /ahk_B T$$

(2.11)

Here x is that fraction of Mn ions which have 4+ charges.

The Curie temperature $T_C$ is approximately given as

$$kT_C \approx \varepsilon$$

(2.12)
From (2.11) and (2.12)

$$\sigma = (xe^2/ah) (T_c/T)$$  \hspace{1cm} (2.13)

This relation correlates the conductivity ($\sigma$) and Curie temperature ($T_c$) for manganites.

2.4. Jahn-Teller (J-T) Effect

The simple perovskite compounds are insulators. Out of a possible ten, the Mn$^{3+}$ ion has four electrons in its outermost 3d shell. If this shell were completely filled, five electrons would be spin up while other five would be spin down. According to Hund's rule the four electrons in a manganese ion should point in the same direction to minimize the electrostatic repulsion. The spin-up and spin-down states are thus well separated in energy and the four electrons occupy the spin state with the lowest energy. Electrostatic interactions between these four electrons and the neighbouring oxygen ions cause this single spin state to split into two sub-energy levels as shown in Figure 2.5. Out of these four electrons, three of the electrons form a triplet state at a lower energy while remaining single electron occupies a doublet state at a higher energy. However, this single electron is unstable in nature and the energy of the system is lowered by the splitting of the doublet state into another two hyperfine energy levels. This well-known phenomenon is called the Jahn-Teller effect.

As in a pure manganite, both the triplet and singlet energy levels are fully occupied, the solid material is an insulator. On the other hand, the electronic properties can be modified by substituting a rare-earth ion with a divalent alkaline element such as Sr$^{2+}$ or Ca$^{2+}$ at $La^{3+}$ sites. And as a consequence some of the Mn$^{3+}$ ions changes into Mn$^{4+}$ ions and holes are created in the singlet energy state. By altering the doping concentration of charge carriers in perovskites such as $La_{1-x}A_xMnO_3$ ($A = Ca, Sr, Ba$ etc) where $x$ is the fraction of doping, a variety of structural, electrical transport and magnetic have been investigated.
Fig. 2.5: The four electrons in the manganese ion have the same spin state—three occupy the low-lying triplet state and one occupies a doublet state.

The tendency of electron pairs to occupy positions as far as possible from each other determines the shape of transition metal complexes. Additionally, the shape of transition metal complexes is influenced by whether the d orbitals are symmetrically or asymmetrically filled. Electrons are localized in a partially filled cation shell 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 J-T ion. The elucidation of $e_g$ and $t_{2g}$ orbitals are displayed in Figure 2.6.

Fig. 2.6: Representation of $e_g$ and $t_{2g}$ orbitals of Mn ion.
In an octahedral complex, repulsion by six ligands splits the d orbitals on the central metal into $t_{2g}$ and $e_g$ levels which causes repulsion between the d electrons and the ligands. If the d electrons are symmetrically arranged, they will repel all six ligands equally but if the d electrons are asymmetrically arranged, they will repel some ligands in the complex more than others. Thus the structure is distorted some ligands are prevented from approaching the metal as others. The $e_g$ orbitals point directly at the ligands. Therefore asymmetrical filling of $e_g$ orbitals results in some ligands being repelled more than others which causes considerable distortion of the octahedron. The distortion caused by asymmetric filling of the $t_{2g}$ orbitals is too small to measure because $t_{2g}$ orbitals do not point directly at the ligands rather they point in between the ligand directions. The two $e_g$ orbitals $d_{x^2-y^2}$ and $d_{z^2}$ are normally degenerate and this degeneracy is destroyed if they are asymmetrically filled and now these two orbitals are not equal in energy. If $d_{z^2}$ orbital have one more electron than the $d_{x^2-y^2}$ orbital then ligands approaching along $+z$ and $-z$ directions will experience greater repulsion than the other four ligands. The octahedron is elongated along $z$ axis due to the distortion and repulsion. So whenever the $d_{z^2}$ and $d_{x^2-y^2}$ orbitals are unequally occupied, distortion occurs. This is known as Jahn-Teller (JT) distortion. The Jahn-Teller theorem states that "For a nonlinear molecule in an electronically degenerate state, distortion must occur to lower the symmetry, remove the degeneracy and lower the energy." In present case of mixed valence manganites, the electronic properties are closely associated to the lattice. Numerous interesting phenomena exhibited by them involve an intricate interplay between the spin, charge and orbital degrees of freedom accompanied with minor 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 $t_{2g}^{3}e_g^{1}$.

According to the JT theorem, Mn$^{3+}$ ion becomes a JT ion which makes a distortion in the structure and as a result the degeneracy of the $e_g$ orbitals is removed. In solids, the orbital degree of freedom of the Mn$^{3+}$ ion frequently shows long range ordering related with the cooperative JT effect. It is observed for the most widely studied compounds throughout the $Ln_{1-x}A_xMnO_3$ series, i.e. LaMnO$_3$, that below a transition temperature T$_{Tr}$, the 3d$_{3x^2-r^2}$ and 3d$_{3y^2-r^2}$ orbitals are ordered in the ab plane...
in an alternating fashion as in Figure 2.6. Figure 2.7 illustrates the effect of J-T effect on the energy band structure.

![Diagram of 3d orbitals and Mn^3+ ions](image)

**Fig. 2.7: Representation of energy band structure affected by Jahn–Teller effect.**

A quantitative evaluation of the magnitude of cooperative JT distortion is given by the octahedral distortion parameter $\Delta$ defined as:

$$\Delta = \left( \frac{1}{6} \right) \sum_{m=0}^{1} \left( \frac{d_m - <d>}{<d>} \right)^2$$  \hspace{1cm} (2.14)

where $d_m$ and $<d>$ are the six Mn-O bond lengths along six different directions and the mean Mn-O bond length respectively. Since a net lowering of the electronic energy can not be accomplished with a preservation of the gravity centre for all filled $t_{2g}$ states in octahedral geometry, it is interesting to understand that the JT effect is not shown by the Mn$^{4+}$ (3d$^3$) ion. As a result, the high concentration of Mn$^{4+}$ ions will discourage the distortions of MnO$_6$ octahedra while a high concentration of Mn$^{3+}$ ions tends to support such distortions. Different doping levels can modify the Mn$^{3+}$/Mn$^{4+}$ ratio. It has been observed that there are two types of distortions related with the JT effect which are Q2 and Q3. The Q3 is a tetragonal distortion which makes an elongation or contraction of the MnO$_6$ octahedron corresponding to the filled 3z$^2$-r$^2$ orbital or x$^2$-y$^2$ orbital, respectively [Figure 2.8 (a) and (b) respectively]. The Q2 is an orthorhombic distortion [Figure 2.8 (c)] obtained by a certain superposition of the 3z$^2$-r$^2$ and x$^2$-y$^2$ orbitals [21,22].
Fig. 2.8: (a) and (b) The Q3 distortion with oxygen displacements corresponds to the filled $3z^2-r^2$ and $x^2-y^2$ orbitals, respectively (c) The Q2 distortion which stabilizes a certain superposition of $3z^2-r^2$ and $x^2-y^2$ orbitals.

The oxygen framework is portrayed in Pbnm [space group No. 62] symmetry by two oxygen positions: the O1 position located on the mirror plane and attributed to the out-of-plane oxygens; the O2 position attributed to the in-plane oxygens as shown in Figure 2.9.

Fig. 2.9: Schematic diagram of MnO$_6$ octahedral with epical (O1) and equatorial (O2) oxygen positions.
The rotations of the octahedra are reflected in the deviation of the Mn-O-Mn bond angle from 180°. 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 Figure 2.10 (b). The deviation in medium bond length 'm' from the average bond length, such that \( m < (l + s)/2 \), demonstrating that the JT distortion is not of a pure Q2 type. A contribution of the Q3 distortion is also present. Therefore, the JT effect obviously combines the magnetic, electron orbital and lattice degrees of freedom in manganites, thus playing considerable roles to affect the orbital degeneracy and governing the electronic properties, e.g. ferromagnetism, charge and orbital ordering, phase separation, the CMR effect, etc. and hence opens a channel to study the contributing effect in such systems.

![Diagram](image)

**Fig. 2.10:** (a) The JT distorted perovskite structure (the rotation is not indicated). The cubic and orthorhombic unit cells are indicated by thin and thick contours respectively. (b) The ab plane highlighting the alternation of the short and long Mn-O distances in a and b directions.

### 2.5. The Complex Ordering Phenomenon

The electrons that usually localize on specific atomic sites, often demonstrate cooperative electronic ordering phenomenon due to the strong correlation effect, i.e. spin ordering, charge ordering, orbital ordering and lattice ordering represented pictorially in Figure 2.11.
These new quantum collective behaviors are usually accompanied by related structural, magnetic and metal insulator phase transitions and so on so forth. Therefore they are trusted to play considerable roles in controlling these interesting physical properties in manganite perovskites.

### 2.5.1. Spin ordering

In manganites, the strong coupling between spin, charge, orbital and lattice degrees of freedom results in various long-range magnetic spin ordering phenomena. Most of them can be explained in a well manner based on the double-exchange and super-exchange interactions as well as the interplay between them. Figure 2.12 portrays some common types of spin-ordering. There is a strong dependence of the strength of spin interactions on the temperature and doping level in manganites. Nd$_{1-x}$Sr$_x$MnO$_3$ shows the FM state for $0.3 < x < 0.5$ at room temperature. For further doping, within the range $0.5 < x < 0.7$, the compounds show the A type AFM state and the C-type AFM state comes into view as the doping level goes beyond 0.7. Above 77 K, YVO$_3$ displays C-type AFM spin ordering followed by a transition to the G-type AFM spin ordering below 77 K. In manganites, the incompletely filled 3d level can display both localized spin and orbital moment, which, in general, are strongly coupled through the super exchange interaction.
Fig. 2.12: Different types of spin ordering in manganites.

The coupling concerns not only the spins but also the orbitals at neighbouring sites in the case of orbital degeneracy. This can be explained as if there is a direct overlapping between the orbitals of two electrons. The exchange between the two electrons is strong and AFM, otherwise, the exchange is weak and FM. The strength of super-exchange interaction strongly depends on the bond angle of TM ion-intermediate ligand-TM ion. For example, the 180° super exchange concerning two 3d $e_g$ orbitals linked by an oxygen 2p orbital is strongly AFM but if the angle gets closer to 90°, the strength of super-exchange interaction decreases at a large extent and at 90°, the exchange becomes much weaker and FM in nature.

2.5.2. Charge ordering

In the doped manganites when cations having different oxidation states are situated on specific lattice sites, forming a long-range ordered structure, a phenomenon is observed known as charge ordering (CO) [23-25] which arises due to the interactions taking place in between the charge carriers and phonons. It occurs at low temperatures when mobile electrons can be localized on certain Mn ions to form a regular lattice or long-range order through-out the crystal structure. Charge ordering is motivated by interatomic Coulomb interactions and possibly takes place in the RE$_{1-x}$AE$_x$MnO$_3$ compounds when proportions of Mn$^{3+}$ and Mn$^{4+}$ ions are rational fractions.

...58...
Fig. 2.13: (a) Charge ordering of Mn$^{3+}$ and Mn$^{4+}$ in a mixed crystal with doping concentration $x=0.5$ (b) Orbital ordering of the $dz^2$ orbitals of Mn$^{2+}$ when doping concentration $x=0$ (c) Combined charge and orbital ordering when doping concentration $x=0.5$.

Electrons are localized as a result of the ordering of Mn$^{3+}$ and Mn$^{4+}$ ions on specific lattice sites in a charge-ordered lattice, as displayed in Figure 2.13 (a) [26]. Hence, the charge ordering encourages antiferromagnetic and insulating behavior of a material [25]. The CO phenomenon represents one of the most fascinating issues due to the strong interactions among the spin, charge, orbital and lattice degrees of freedom in these types of materials and has been studied rigorously.

2.5.3. Orbital ordering

At definite carrier concentrations when the d electrons occupy an asymmetric orbital, the orbital ordering can take place. The driving force is partially direct electrostatic repulsion of the charge clouds, but coupled Jahn-Teller distortions of adjacent octahedral stabilize the effect. Goodenough suggested that this ordering would involve displacements of the Mn$^{4+}$O$_6$ octahedra. In accord with Goodenough's hypothesis, the super structure is described by a large J-T distortion of the Mn$^{3+}$O$_6$ octahedra while the Mn$^{4+}$O$_6$ octahedra remain approximately undistorted. Moreover, orbital ordering takes place by a displacement of the Mn$^{4+}$O$_6$ octahedra mostly along the [001] direction. The Mn$^{3+}$ $e_g$ orbitals ($3dz^2$) and the coupled lattice distortions (long Mn-O bonds) also develop long-range order, leading to the orbital ordering.
(Figure 2.13b) Figure 2.13 (c) demonstrates the coupled charge and orbital ordering [26]. Therefore, the rare-earth manganites are antiferromagnetically ordered (AFM) with CE or A type ordering at low temperatures, but only the former takes place in the charge-ordered materials where the $e_g$ electrons are localized. The CE-type spin ordering is illustrated by the alternate ordering of Mn$^{3+}$ and Mn$^{4+}$ ions.
References:


Chapter 3

Synthesis and Characterization Techniques
This chapter deals with different experimental techniques which are explored and utilized for the current research work. There are two major objectives considered in this chapter: First one is to explore the synthesis routes for the preparation of perovskite manganite samples and the second is to understand various characterization techniques utilized to investigate and evaluate a variety of properties of these perovskite manganites.

3.1. Introduction

In the experimental condensed matter physics and material science, the synthesis and characterization of high quality material with desired properties is of supreme importance. The quality of samples depends highly on the synthesis method used. Additionally, to carry out the desired properties in the samples to be characterized along with desired potencies have been facilitated by the proper selection of the synthesis parameters. Structure, surface morphology, grain growth, transport of electrons within a material and magnetic properties depend on material synthesis. The solid samples can be synthesized in variety of particle shapes and sizes depending upon their necessities, such as, single crystals, amorphous solids, polycrystalline powder, etc. There are different methods available for the synthesis of polycrystalline bulk materials like solid state reaction route (SSRR) for preparing bulk manganite samples and sol-gel route, co-precipitation method, solvo-thermal method, micro-emulsion route, citrate route, nitrate route, etc for synthesizing the nanostructured manganites. For characterization, various techniques are available depending on the properties and analysis of the sample to be carried out. Techniques exploited for structural analysis of the samples are X-ray Diffraction (XRD), while for microstructural characterizations Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) have been utilized. For transport and magnetoresistance studies, four probe resistivity measurements have been performed. Magnetic properties measurements have been done by using Vibrating sample magnetometer (VSM) and a Magnetic Properties Measurement System (MPMS). A brief introduction to different synthesis routes and characterization techniques used in material science research is depicted in the forthcoming sections.
3.2. Experimental Techniques for Material Synthesis

In the present work, the bulk materials of manganites with different dopant concentration have been synthesized by solid state reaction route and sol-gel method and described in the following sections.

3.2.1. Solid State Reaction Route

Solid state reaction route (SSRR) is the most commonly used method for synthesizing the bulk materials (powders) with direct reaction of a mixture of solids as starting materials. This technique of synthesis is also known as ceramic method and has supremacy over other methods such as co-precipitation or hydrothermal technique due to the involvement of simple steps of the process. Since, solids do not generally react together at room temperature over normal time scale; hence it is necessary to heat them at much higher temperature for long time duration for reaction to occur at an appreciable rate. There are two important factors in solid state reaction, namely thermodynamic and kinetic in which 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]. To form a stable compound of minimum free energy, the atoms diffuse through the material. Different compounds or phases might have the lowest free energy at different 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 and time for the reaction are required to be varied according to the phase requirements in the sample. The mapping of all variables has to be made to find the conditions which are best for each material and phase. The main steps in the solid-state reaction route for synthesizing bulk polycrystalline samples are shown in the flow chart of Figure 3.1.
Fig. 3.1: Typical flow chart of Solid-State Reaction-Route.
3.2.2. Sol Gel Method

With controlled size, shape and structure, the nanostructured perovskite manganites can be synthesized using physical, chemical and biological routes. Among a variety of synthesis techniques, chemical methods for the synthesis of nanoparticles have become more popular and achieved broad acceptance. Further, for synthesizing polycrystalline manganites in the chemical methods, sol-gel (SG) is the cost-effective method, easy to handle and produces stoichiometric compounds. It recommends a range of starting materials as precursors to choose. Sol-Gel is a chemical solution based process for synthesizing ample range of materials especially mixed oxides which is used due to its advantages of flexible nature, low temperature synthesis etc. Sol-gel has become an alternate method to the conventional solid state reaction route, allowing more accurate control over the phase formation, desired stoichiometry, homogeneity and uniformity in particle size with the monodispersive nature of the particles. In sol-gel technique, material is obtained from the chemical solution via gelation; hence for synthesizing polycrystalline materials, it is more convenient technique. It is necessary to have control over grain size and also on the phase formation at much lower temperature for nanomaterials synthesis which can be achieved by using such chemical methods. Unlike the solid state reaction route, another advantage of sol-gel method is that it does not require any grinding process to achieve homogeneous single phasic ceramics and as a result potential source of contamination is avoided. In this way, the sol-gel process has become an excellent method for making high purity materials along with the purity of the precursors. Figure 3.2 depicts the schematic steps involved in the synthesis of crystalline oxides using sol–gel method. In sol-gel, the precursors are mixed in solvent and through hydrolysis and condensation reactions connect them with each other to form a sol. The intimate mixing of the elements in gel form results in very short diffusion and thereby allows formation of the target material to occur at considerably lower temperatures.

The sol-gel process has a potential advantage over the other methods not only for achieving homogeneous mixing of the components on the atomic scale but also for the possibility of forming films or fibers from gels which are of technological importance.
Fig. 3.2: Schematic steps used in Sol-Gel synthesis.

In Sol-Gel Method, we have adopted the following steps [3] to synthesize the polycrystalline samples of Zn doped La$_{0.67}$Sr$_{0.33}$MnO$_3$ manganites.

- The aqueous solution of high purity La(NO$_3$)$_3$·6H$_2$O, Sr(NO$_3$)$_2$ and Mn(NO$_3$)$_2$·4H$_2$O and Zn(NO$_3$)$_2$·6H$_2$O have been taken in the desired stoichiometric proportions.

- An equal amount of ethylene glycol has been added to this solution with continuous stirring.

- After this, the solution is heated on a hot plate at a temperature of $\sim$100–140 $^\circ$C to get a dry thick brown colour sol. At this temperature, ethylene glycol polymerizes into polyethylene glycol due to which the cations disperses homogeneously forming a cation–polymer network.

- The as obtained sol is further decomposed in an oven at a temperature of $\sim$300 $^\circ$C to get a polymeric precursor in the form of a black resin-like material.

- To get phase pure completely crystalline samples, the polymeric precursor thus obtained is sintered at 600$^\circ$C for 4 hours.

Figure 3.3 shows the typical flow chart of sol-gel method used for the synthesis of manganites polycrystalline samples.
Fig. 3.3: Typical flow chart of Sol-Gel method.

3.3. Characterization Techniques

The development of materials, processes and advanced devices for various applications necessitates a huge effort in the field of the characterization techniques. Various experimental techniques have been utilized to characterize structural, electrical and magnetic properties of the samples. All the manganites samples in this work are usually characterized using X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Four Probe Resistivity Measurement Technique, Magnetoresistance Measurement Technique and...
Magnetic Properties using Vibrating Sample Magnetometer (VSM) and Magnetic Properties Measurement System (MPMS).

3.3.1. X-ray Diffraction

X-ray diffraction is one of the most frequently used non-destructive materials characterization technique for investigating the crystallographic arrangement of powder samples. This technique can be used for phase identification, particle and unit cell volume determination. When an electromagnetic wave enters a crystal, it will be scattered by the electrons inside. From certain angles of incidence, there will be constructive interference between the different scattered beams, but for most of the angles, destructive interference will cancel the diffracted beams. By measuring at which angles the constructive interference takes place, it is possible to study about the geometrical ordering of the atoms inside the crystal [4-6].

In normal 0-20 scan mode, a beam of monochromatic x-rays is made to incident on the sample, making an angle θ with the sample surface. The detector motion is coupled with that of the x-ray source so that it is always kept in a position at an angle of 2θ with the incident direction of the x-ray beam. The spectrum is recorded as intensity versus 2θ. The schematic of the x-ray diffractometer is given in Figure 3.4.

![Schematic diagram of x-ray diffractometer.](image)

**Fig. 3.4: Schematic diagram of x-ray diffractometer.**

The interaction of x-ray radiation with crystalline sample is governed by Bragg's law, which demonstrates a relationship between the diffraction angles, x-ray wavelength and interplanar spacing of the crystal planes. According to Bragg's law, the x-ray diffraction can be visualized as x-rays reflecting from a series of crystallographic planes as shown in Figure 3.5. The path differences introduced between a pair of waves travelled through the neighboring crystallographic planes are determined by the
interplanar spacing. If the total path difference is equal to \( n\lambda \), the constructive interference will occur and a group of diffraction peaks can be observed which give rise to x-ray diffraction patterns. The Bragg's law can be quantitatively expressed as:

\[
2d_{hk\ell} \sin \theta = n\lambda
\]  

(3.1)

Fig. 3.5: Geometrical illustrations of crystal planes and Bragg’s law.

The employment of X-ray diffraction for structural characterizations of samples is a Rigaku, MiniFLEX-II at Centre of Excellence in Material Science, Department of Applied Physics, Aligarh Muslim University (AMU), Aligarh and Bruker D8 Advance Diffractometer at Inter University Consortium (IUC), Indore, having Cu-K\(\alpha\) radiation (\(\lambda = 1.5418 \ \text{Å}\)) at room temperature as shown in Figure 3.6 (a) and (b) respectively. The diffraction method is based on the effect of broadening of reflections associated with the size of the crystallites. All types of defects cause displacement of the atoms from the lattice sites. One equation has been derived from the intensity of the Bragg reflections from a crystal defect, which enabled all the defects to be derived conventionally into two groups [7].

The defects in the first group only lower the intensity of the diffraction reflections but do not cause the reflection broadening.
Fig. 3.6: (a) Rigaku Miniflex -II (b) Bruker D8 Advance X-ray diffractometer.

The broadening of the reflections is caused by the defects of the second group. These defects are micro-deformations, inhomogeneity (non uniform composition of the substance over their volume) and smaller particle size. The size of nanomaterials can be obtained from the peak broadening and can be estimated by using the following Scherrer equation, provided that the nanocrystalline size is less than 100 nm.

\[ D = \frac{k\lambda}{\beta \cos \theta} \]  

(3.2)

where D is the average crystalline dimension perpendicular to the reflecting phases, \( \lambda \) is the x-ray wavelength, k is the Scherrer’s constant which equals 0.9 whose value depends on the shape of the particle (crystallite, domain) and on diffraction reflection indices (hkl) and \( \beta \) is the full width at half maximum (FWHM) of the peaks. The Scherrer formula is quite satisfactory for small grains (large broadening) in the absence of significant micro strain. A micro strain describes the relative mean square deviation of the lattice spacing from its mean value. Based on the grain size dependence of the strain, it is reasonable to assume that there is a radial strain gradient, but from x-ray diffraction only a homogeneous, volume-averaged value is obtained.
3.3.2. Rietveld Analysis

There are six factors which affect the relative intensities of the diffraction lines on a powder pattern, namely, i) structure factor, ii) polarization factor, iii) multiplicity factor, iv) Lorentz factor, v) temperature factor and vi) absorption factor. A very important technique for analysis of powder diffraction data is the fitting method of whole pattern proposed by Rietveld (1969) [8]. The Rietveld method is a tremendously powerful tool for the structural analysis of virtually all types of crystalline materials which are 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 2θ. The analysis can be divided into many separate steps. While some of these steps rely on the correct completion of the previous one(s), they usually comprise 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 [9]. The parameters refined in the Rietveld method fall into mostly three classes: peak-shape function, profile parameters, atomic and structural parameters. The peak shapes observed are function of both the sample (e.g. domain size, stress/strain defects) and the instrument (e.g. radiation source, geometry, slit sizes) and they vary as a function of 2θ. The profile parameters comprise the lattice parameters and those describing the shape and width of Bragg peaks (changes in FWHM and peak asymmetry as a function of 2θ, 2θ correction, unit cell parameters). Particularly, the peak widths are smooth function of the scattering angle 2θ. 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 essential 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 make changes in magnitudes of structure factor and consequently in relative peak intensities, whereas atomic displacements (thermal) parameters have the effect of highlighting the high angle region (smaller thermal parameters) or de-emphasizing it (larger thermal parameters). The scale, the thermal parameters and the occupancy parameters are greatly 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 consistent and even anisotropic refinement is sometimes possible. Occupancy

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parameters are correspondingly difficult to refine and chemical constraints should be applied whenever possible [10].

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 [11].

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

$$R_{wp} = 100 \left[ \frac{\sum_{i=1}^{n} w_i | y_{i} - y_{c,i} | ^2}{\sum_{i=1}^{n} w_i y_{i}^2} \right]^{1/2}$$  \hspace{1cm} (3.3)

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

$$R_{exp} = 100 \left[ \frac{n - p}{\sum_i w_i y_i^2} \right]^{1/2}$$  \hspace{1cm} (3.4)

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),

$$\chi^2_v = \left[ \frac{R_{wp}}{R_{exp}} \right]^2 = S^2$$  \hspace{1cm} (3.5)
An R value is observed and calculated structure factors, \( F_{\text{obs}} \), can also be calculated by distributing the intensities of the overlapping reflections according to the structural model,

\[
R_p = 100 \cdot \frac{\sum_h |F_{\text{obs},h} - F_{\text{calc},h}|}{\sum_h |F_{\text{obs},h}|} \tag{3.6}
\]

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

\[
R_B = 100 \cdot \frac{\sum_h |I_{\text{obs},h} - I_{\text{calc},h}|}{\sum_h |I_{\text{obs},h}|} \tag{3.7}
\]

R values are useful indicators for the evaluation of refinement, particularly in the case of small improvements to the model, but they should not be over interpreted. The most important criteria for evaluating 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. Therefore the technique is mainly 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.

### 3.3.3. Scanning Electron Microscopy (SEM)

Electron microscopes are scientific instruments which utilize a beam of energetic electrons to study objects on a very fine scale. Electron microscopes came into existence due to the limitations of Light Microscopes which are limited by the physics of light. In the early 1930's this theoretical limit had been reached and there was a scientific aspiration to see the well details of the interior structures of organic cells such as nucleus, mitochondria. This needed 10,000X plus magnification which was not possible using accessible optical microscopes. The first Scanning electron microscope (SEM) came into view for the first time in 1938 invented by Von Ardenne

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with the first commercial instrument available around 1965. Its development was delayed due to the electronics involved in "scanning" the beam of electrons across the sample. Scanning electron microscopy (SEM) can give a highly magnified image of the surface and the composition information on near surface regions of a material [12]. Figure 3.7 (a) and (b) display the typical schematic diagram and photographic view for SEM equipment.

![SEM Diagram](image)

**Fig. 3.7:** (a) Schematic diagram of SEM equipment. (b) Photographic view of SEM.

The resolution of SEM can move towards a few nanometers and the magnifications of SEM can be easily adjusted from about 10 times to 300,000 times. In SEM, electron beam, accelerated by a relatively low voltage of 1 - 20 kV, is scanned on the sample surface. As the electron beam hits the surface, a large number of signals are produced through or from the surface in the form of photons or electrons. These signals emitted from the sample are collected by detectors to form images and the images are displayed on a cathode ray tube screen. Three types of images are generated in SEM: secondary electron images, backscattered electron images and elemental x-ray maps. Secondary electrons (SE) are regarded as to be the electrons resulted from inelastic scattering with atomic electrons and with the energy less than 50 eV. The secondary emission of electrons from the sample surface is generally confined to an area near the beam impact zone that allows images to be obtained at high resolution. These images, as seen on a cathode ray tube screen, give a
three dimensional appearance because of the large deepness of field of the SEM as well as the shadow release of the secondary electrons contrast. Backscattered electrons (BSE) are regarded as the electrons resulted from elastic scattering with the atomic nucleus and with the energy more than 50 eV [12]. The backscattering will likely take place in a material of higher atomic 50 numbers, so the contrast caused by elemental differences can be built up. After the collision of primary electron beam with an atom in the sample and ejection of a core electron from the atom, the excited atom then decomposes to its ground state and emits either a characteristic x-ray photon or an Auger electron [13].

3.3.4. Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) has been used to study the grain shape, size and distribution of particles at nanoscale. Figure 3.8 (a) and (b) display respectively, the typical schematic diagram and photographic view for TEM equipment. In TEM, a thin solid specimen (< 200 nm) is bombarded in vacuum with a highly focused, mono energetic beam of electrons. The high resolution results from the smaller de Broglie wavelength correlated with high-energy electron beam and its capability to focus the electron beam. For example, electrons having energy of 100 keV corresponds to a de Broglie wavelength of 3.7×10⁻⁹ nm. In general, TEM operates with the electron beams having energy in the range of 20-200 keV. The spatial resolution is large for higher energy electron beam. The beam has adequately high energy to propagate through the specimen. The transmitted electron signals are magnified by a series of electromagnetic lenses [14]. There are two modes offered by TEM to study a desired specimen i.e. image and diffraction.

The image mode contrast must be induced in order to produce image for analysis. Many contrast-forming mechanisms exist and the interpretation of images is complicated due to the interplay of the different mechanisms. The most common imaging techniques in TEM are mass-thickness imaging, phase contrast imaging and diffraction imaging. In the diffraction mode, the diffracted electrons pattern is obtained from the sample illuminated by electrons. As the electron beam is incident on the sample, scattering events occur because all the illuminated parts of the sample act as scattering sources. Interference causes coherently scattered beams when Bragg’s law is fulfilled. The coherently scattered beams are recorded as a “spot”. This
spot pattern of the diffracted electron beam from the selected area of the sample is called the selected area electron diffraction (SAED) pattern. It provides the information about the crystalline structure and crystal orientation. A key requirement for TEM sample is the electron transparency since in a thick sample too many interactions would take place which leaves no intensity in the transmitted beam. A thick sample also increases the risk that an electron is scattered on multiple occasions and the resulting image would be difficult to interpret. In the present work, TEM samples are prepared by dispersing powder sample in iso-propanol using sonification in an ultra sonic bath (20 kHz, 300 W) for half an hour.

Fig. 3.8: (a) Schematic diagram of TEM (b) Photographic view of TEM.

One drop of the well-dispersed sample solution is deposited on to a carbon coated copper grid with 400 meshes and was used for microscopy. In the present study, TEM has been used to analyze shape, size and particle size distribution of doped manganites.

3.3.5. Four Probe Resistivity Measurement

Resistivity measurement is a pretty easy and straightforward way to provide much useful information about the electrical properties of the sample. The measurement of electrical resistance as a function of temperature provides information about the temperature dependent electronic phase transitions along with the value of critical
temperature as well as the quality of the sample. A low contact resistance is advantageous due to the small resistance of the samples.

To achieve this requirement, standard four probe method was used for measuring resistance of the samples [15]. 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 paste 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. Because of very less resistance, very thin copper wires were connected with silver paint as shown in Figure 3.9 and the whole assembly was put onto a sample holder where the wires were connected with leads to the measuring instruments.

![Four probe contacts diagram]

**Fig. 3.9: Four probe contacts of current and voltage supplies to the sample during the resistivity measurements.**

Since samples have low resistance at room temperature, therefore a precise current source is used which can pass a current of few microamperes and a voltmeter used has a measuring range from nano volts to a few volts. As displayed in the figure, current is passed through the outer two probes (+I & -I) and resultant potential difference developed between two points is measured using the inner two 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 essential to keep the voltage probes between the current probes in a linear way. Using dimensions, shown in figure 3.9, the exact resistivity (\( \rho \)) of the sample can be calculated using the relation...
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/N\(_2\). The samples were then heated in a controlled way by using a heater and resistance was measured with slowly increasing temperature.

The block diagram of four-probe setup used for measuring the resistivity is shown in Figure 3.10.

![Block diagram of four-probe resistivity setup](image)

**Fig. 3.10: Block diagram of Four-Probe Resistivity Setup.**

### 3.3.6. Magnetoresistance Measurements

For studying magneto resistive properties 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. At a constant applied field, resistance was measured as a function of temperature in the temperature range from 5-300K.

Magnetoresistance is a very significant property of manganite based materials. Manganite materials show enormous changes in resistance under application of magnetic field around transition temperature (\( T_P \)). To study the magnetoresistive properties of manganite bulk samples, magnetoresistance (MR) versus temperature
plots in the presence of an external magnetic field were recorded using the standard four probe method.

Figure 3.11 displays the photographic view of the setup, showing the electromagnet, probes and reservoirs arranged in it.

Fig. 3.11: Laboratory Setup of the Magnetoresistance Measurement.

3.3.7. Vibrating Sample Magnetometer

Magnetic properties of the materials can be measured by using numerous techniques such as Physical Property Measurement System (PPMS), Superconducting Quantum Interference Device (SQUID) and Vibrating Sample Magnetometer (VSM) [16]. VSM is the most common instrument since it presents the best combination of performance capabilities and can put up a large range of samples with broadly different properties. A VSM can measure the magnetic properties of the magnetic materials. The principle of VSM is the measurement of the electromotive force (emf) induced by a magnetic sample when it is vibrated at a constant frequency in the presence of time varying DC magnetic field. On the other hand, VSM simply 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 information about the changing magnetic field. When a sample is placed within a time varying DC magnetic field and made to undergo sinusoidal motion (i.e. mechanically vibrated), there is some change...

...80...
in magnetic flux. Because of this, a voltage is induced in the pick-up coils which is proportional to the magnetic moment of the sample. The block diagram of a typical VSM setup is shown in Figure 3.12. A VSM operates by first placing the sample to be studied in a constant magnetic field. If the sample is magnetic, the constant magnetic field will magnetize the sample by aligning the magnetic domains, or the individual magnetic spins, with the field. The higher value of the constant applied magnetic field will make the magnetization higher. The magnetic dipole moment of the sample will produce a magnetic field around the sample which 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 pickup coils. According to Faraday's law of induction, the alternating magnetic field will cause an induced electric field in the pick-up coils. 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 interfaced with a computer. Using controlling and monitoring software, the system can provide information about the magnetization value of the 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 starts vibrating at a frequency of 72 Hz.
- 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 received from the probe again gets translated into a value for the magnetic moment 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.
In the present study, the Vibrating Sample Magnetometers, model EV7-VSM from the company Micro Sense placed at IIT Kanpur, India and LakeShore 7304, placed in a Laboratory at NPL, New-Delhi, India, have been used to measure the magnetic property of all the samples. Figure 3.13 illustrates the photographic view of VSM.

The characteristic of this setup is that the magnetic measurement of a sample in the temperature range from ambient temperature up to 1100 K can be performed. A weighed amount of powder sample (~50 mg) is taken and make tight to avoid movements inside the sample holder. The magnetic measurement in the high temperature regime is performed by flowing an inert gas (argon) into the sample chamber. It can be operated up 1.2 T at a vibration frequency of 72 Hz. The calibration of magnetic moment is carried out using a Ni standard (sphere) with known saturation magnetization (Ms=6.92 emu at 5 kOe) at room temperature. The temperature calibration is performed using a Ni standard with a Curie temperature of the value 627 K.
3.3.8. Magnetic Properties Measurement System (MPMS)

Magnetic Property Measurement System (MPMS) is a highly integrated instrument system, designed to be a primary research tool in the complex study of magnetism in matter. The magnetic signature of a material reflects its intrinsic spin and orbital angular momentum. In the case of a material that would normally be identified as strongly magnetic, (the ferromagnets used in electric motors or the material used on magnetic recording tape), determining a "magnetization curve" over a range of applied magnetic fields, will set up its commercial value for a particular application [17].

The principal components of this measurement system comprise the following:

(1) Temperature Control System

(2) Magnet Control System

(3) Superconducting SQUID Amplifier System
(4) Sample Handling System

(5) Computer Operating System

At present, MPMS sample magnetometer is used in research laboratories worldwide, and is specified for experimental and materials characterization tasks that require the highest detection sensitivities over a broad temperature range and in applied magnetic fields up to seven teslas.

The MPMS system consists of the following different superconducting components.

1. A Superconducting Quantum Interference Device (SQUID) connected to the detection coil.

2. A superconducting magnetic shield surrounding the SQUID.

3. A superconducting detection coil which couples inductively to the sample.

4. A superconducting magnet to generate large magnetic fields.

1. Superconducting Quantum Interference Device (SQUID)

A SQUID utilizing the Josephson junction is the most sensitive device available for measuring magnetic fields. Although the SQUID in the MPMS is the source of the instrument’s remarkable sensitivity, it does not directly detect the magnetic field from the sample. Instead, the sample moves through a system of superconducting detection coils which are connected to the SQUID with superconducting wires, allowing the current from the detection coils to inductively couple to the SQUID sensor. When configured properly, the SQUID electronics generates an output voltage which is strictly proportional to the current flowing in the SQUID input coil.

A measurement is performed in the MPMS by moving a sample through the superconducting detection coils, which are located outside the sample chamber and at the center of the magnet. As the sample moves through the coils, an electric current is induced in the detection coils because of the magnetic moment of the sample. Since the detection coils, the connecting wires and the SQUID input coil form a closed superconducting loop, any change of magnetic flux in the detection coils produces a...
change in the persistent current in the detection circuit, which is proportional to the change in magnetic flux. Since the SQUID operates as a highly linear current to voltage converter, the variations in the current in the detection coils produce corresponding variations in the SQUID output voltage which are proportional to the magnetic moment of the sample.

2. Superconducting Magnetic Shield

Due to the SQUID's extreme sensitivity to fluctuations in magnetic fields, the sensor itself must be shielded both from fluctuations in the ambient magnetic field of the laboratory and from the large magnetic fields produced by the superconducting magnet. The required magnetic shielding is provided by the superconducting shield which provides a volume of relatively low magnetic field in which the SQUID and its coupling transformers are situated. As a result, the superconducting shield serves the two purposes in the MPMS.

1. To shield the SQUID detector from the magnetic field generated by the superconducting magnet.

2. To trap and stabilize the ambient laboratory magnetic field present when the SQUID and the superconducting shield are first cooled to liquid helium temperature.

3. Superconducting Detection Coil

The detection coil is a single piece of superconducting wire wound in a set of three coils configured as a second order gradiometer. In this configuration, as shown in Figure 3.14, the upper coil is a single turn wound clockwise, the center coil includes two turns wound counter-clockwise and the bottom coil is a single turn wound clockwise.

When installed in the MPMS, the coils are situated at the center of the superconducting magnet outside the sample chamber in such a manner that the magnetic field from the sample couples inductively to the coils as the sample is moved through them.

It is very important to note down that small differences in the area of the counter wound coils will make an imbalance between the different coils, causing the
The NMR/DS system utilizes a superconducting magnet wound in a solenoidal configuration. Instead of a conventional detection coil, the coil is outside of the sample space within the superconducting bore. The configuration and the location of a second order quadrupole detection can compensate for some spatial sensitivity to the magnetic field from the sample and characterization techniques.
persistent current is already flowing, the closed superconducting loop must be electrically opened by using a persistent current switch, formed by wrapping a small heater around a short segment of the magnet’s superconducting wire. When the heater is energized, the segment of wire within the heater becomes normal (no longer superconducting), thereby electrically opening the closed superconducting loop. By attaching a power supply (which essentially functions as a current source) to each side of the switch, it becomes possible to change the current in the superconducting magnet [17].

While the current in the magnet is being provided by the power supply, the SQUID detection system in the MPMS will display a high level of noise. The detection system noise takes place from fluctuations in the magnetic field of the magnet created by current fluctuations in the current source.

**Modes of Operation for the Magnet**

The MPMS uses three different modes of operation for the magnet: *no-overshoot*, *oscillate* and *hysteresis*. In the *no-overshoot* mode, the magnetic field is changed monotonically from the initial field set point to the desired field set point. The ramping in the field is rapid in the beginning of the field change, but in the final approach, the field changes very slowly to avoid overshooting the target value. In the *oscillate mode*, the magnetic field value alternately overshoots and undershoots the desired field with the amplitude of the overshoot and undershoot decreasing in every cycle. The purpose of the oscillate mode is to minimize the amount of magnetic flux “settling” characteristic of a field change in any superconducting magnet. High sensitivity measurements can be run more quickly (with a minimal delay time for magnet settling) after using the oscillate mode; however, oscillate mode should not be used with samples exhibiting irreversible (hysteretic) magnetic behavior. Lastly, in the *hysteresis mode*, the persistent current switch is left *ON* at all times. In this case the magnet is not in persistent mode, and the current supply is constantly part of the magnet circuit. This mode is particularly useful for making rapid measurements of the magnetization as a function of field (“hysteresis loops”) of a sample. However, it can only provide good results on samples with moments of about $10^{-5}$ emu and larger and therefore is not advised for high sensitivity measurements. The boil off rate of liquid helium is also higher during the operation of hysteresis mode [17].
Figure 3.15 displays the photographic view of the equipment.

*Fig. 3.15: Photographic view of the MPMS system from Quantum Design.*
References:


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Chapter 4

Study of structural, electrical and magnetic properties of Zn doped $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ manganite synthesized through Solid-State Reaction-Route
This chapter deals with the synthesis of Zinc doped La$_{0.67}$Sr$_{0.33}$MnO$_3$ manganites using conventional solid-state reaction-route followed by the study of structural, electrical and magnetic properties. In this chapter, we have carried out the comparative studies of 10 and 20% zinc doping at the Mn site in La$_{0.67}$Sr$_{0.33}$MnO$_3$ (LSMO), i.e. La$_{0.67}$Sr$_{0.33}$Mn$_{0.9}$Zn$_{0.1}$O$_3$ (onwards said as Z1) and La$_{0.67}$Sr$_{0.33}$Mn$_{0.8}$Zn$_{0.2}$O$_3$ (onwards said as Z2) systems using the resistivity and magnetization measurements. We observed a considerable change in the metal to semiconducting (M–S) transition temperature ($T_P$) and Curie temperature ($T_C$) with Zn doping.

4.1. Introduction

The rare-earth doped manganites with the general formula of R$_{1-x}$A$_x$MnO$_3$ (R = Rare earth, A = divalent alkaline earth) have attracted much attention in the last decade or so, due to their unique and versatile properties, such as colossal magnetoresistance (CMR) [1,2], gas sensing [3] and fuel cell [4]. Nevertheless, several factors such as the requirement of large magnetic fields, to observe the CMR effect, make the realization of their full potential a rather slow process, and therefore, there are intensive efforts ongoing to optimize the properties of these manganites [5].

The physics of CMR is also closely related to the bad metal features which are ubiquitously observed in the conducting transition metal oxides with strong electron-electron (electron correlation) or electron–lattice interactions. The correlated electrons which are almost localized on the respective atomic sites bear three attributes, namely, charge, spin and orbital degrees of freedom [6,7]. The conduction electrons with an orbital degree of freedom (3d eg orbitals) are scattered not only by the strong electron correlation effect but also by the strong electron–lattice coupling termed as Jahn–Teller interaction [8]. The collective or local Jahn–Teller (JT) distortions, as described by the displacement of the oxygen ions surrounding Mn sites, are observed everywhere when the compound shows the dramatic resistive (metal to semiconducting) or magnetic (antiferromagnetic to ferromagnetic) transitions.

The changing of Mn$^{3+}$/Mn$^{4+}$ ratios in the CMR materials are essentially related to the doping mechanism to control the effective Mn valency [9,10]. This is achieved by either substitution or by changing overall oxygen contents, which determines the value of metal to semiconducting transition temperature, $T_P$. In addition, most of these
compounds go through a structural phase transition often coupled with the para to ferromagnetic transition and accompanied with a change in sign of charge carriers at $T_P$ [11,12]. The static and dynamic magnetic properties of LaMnO$_3$ bulk and nanocrystalline materials were studied by Chandra et al. [13]. They observed ferromagnetic and antiferromagnetic phases coexisted in these samples. The nature of the ferromagnetic but insulating state for $0.1 < \kappa < 0.17$ in La$_{1-x}$Sr$_x$MnO$_3$, and perhaps up to $x \sim 0.3$ for other narrower-$W$ manganites (e.g. Pr$_{1-x}$Ca$_x$MnO$_3$), is still puzzling and under investigation. Unlike the other elements, e.g. Fe, Co, Ni and Cu, the mechanism of Zn doping at Mn site is different and only few reports on this system are available about the transport properties of bulk and thin films [14,15]. Some researchers observed the effect of Zn substitution on para to ferromagnetic transition temperature in La$_{0.67}$Ca$_{0.33}$Mn$_{1-x}$Zn$_x$O$_3$ [16,17]. Whereas, Ghosh et al. [18] studied the effects of transition elements (Cr, Fe, Co, Ni, Cu, Zn) doping in La$_{0.7}$Ca$_{0.3}$MnO$_3$ for a fixed (5% at Mn site) dopant concentration. These authors pointed out metal-insulator transition temperature, the Curie temperature, and the maximum value of magnetoresistance (MR), with respect to lattice parameter and the ionic radii of dopants.

The partial substitution of Zn$^{2+}$ at the magnetic sublattice of mixed-valent manganese in La$_{0.6}$Sr$_{0.4}$MnO$_3$ induces a random potential fluctuation because the Zn$^{2+}$ ion has the completely filled 3d$^{10}$ electronic configurations, which is different from those of Mn$^{3+}$ and Mn$^{4+}$ configuration respectively. Secondly, the Zn$^{2+}$ ions do not carry any magnetic moment as they are also expected not to participate in the ferromagnetic (FM) interaction and hence dilute the magnetic sublattice [19].

4.2. Experimental details

The La$_2$O$_3$, SrCO$_3$, MnO$_2$ and ZnO materials were taken as 2.6810, 1.1967, 1.9216 and 0.2007 grams respectively for 10% Zn doped sample, while for 20% doped sample these amounts were 2.6868, 1.1993, 1.7117 and 0.4022 grams respectively. The polycrystalline bulk samples of La$_{0.67}$Sr$_{0.33}$Mn$_{0.9}$Zn$_{0.1}$O$_3$ (Z1) and La$_{0.67}$Sr$_{0.33}$Mn$_{0.8}$Zn$_{0.2}$O$_3$ (Z2) were prepared by mixing and grinding of ingredients La$_2$O$_3$, SrCO$_3$, MnO$_2$ and ZnO powders (all of AR-grade with purity > 99.9% and purchased from CDH) in stoichiometric ratio, heated at 1000°C for 12 h [7,20]. After this heat treatment samples were ground thoroughly in agate mortar and again heated...
at 1250°C for 24 h. For final preparation, samples were ground with polyvinyl alcohol (PVA), pelletized and calcined at 1300°C for 24 h.

All the samples were characterized by X-ray diffraction (XRD) (Bruker D8 Advance) using Cu-Kα radiation (λ≈1.5406Å) in the 2θ range 20–80° with scan speed 0.2°/min and step size is 0.02°. The resistivity of samples was measured by using standard four-probe technique in the temperature range 5–300 K in a cryostat assembly (VTI or magnet system). Four contacts of indium were made on a well sintered pellet using conductive solder of low melting point. Fine enameled copper wires were used to pass the constant current of the order of few microamperes through the outer two leads using a constant current source (KEITHLY, Model- 2400). The voltage developed across the two inner leads was measured using the sensitive digital multimeter (KEITHLY, Model-182) as a function of temperature. The temperature was controlled using the temperature controller (Lakeshore-DRC-93CA). The magnetization measurements were carried out using Vibrating Sample Magnetometer (VSM, Model-MTS-XL) in the temperature range 100–400 K.

4.3. Results and Discussion

4.3.1. Surface and morphological studies

The representative XRD patterns of Z1 and Z2 are shown in Fig. 4.1. At room temperature, the XRD patterns show that both the samples are formed in a single phase with orthorhombic crystal symmetry with Pnma space group.

![XRD patterns of Z1 and Z2 samples.](image-url)
Average crystallite size using most intense peak (1 2 1) has been determined from XRD patterns by using Debye–Scherrer’s formula [21,22]. The unit cell volume increases with increase in Zn concentration, since the ionic radius of Zn$^{2+}$ is larger than that of Mn$^{3+}$, so the Zn substitution can of course make the volume larger as the doping level goes from 10% to 20%. The lattice parameters, unit cell volumes and the crystallite size have been tabulated in Table 4.1. The lattice parameters changed considerably as compared to parent compound LSMO. The as-obtained crystallite sizes (D) are 27.48 nm and 24.32 nm for the samples Z1 and Z2 respectively.

SEM micrographs for Z1 and Z2 samples are displayed in Fig. 4.2. The particles can be clearly distinguished and all the observed particles connect with each other. The particles of the sample Z2 are in better and clear shape than those of the Z1 sample, revealing that increase in Zn doping could improve the crystallization of the sample. In addition, the particle sizes for the two samples are comparable, which are estimated to be mostly within 200 nm range. Obviously, the particle sizes observed by SEM are several times larger than the crystallite sizes calculated by XRD [23].

![SEM micrographs of Z1 and Z2 samples.](image)
Table 4.1: Lattice parameters, Unit Cell Volume and Crystallite Size for Z1 and Z2 samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Symmetry</th>
<th>Lattice Parameters (Å)</th>
<th>Unit Cell Volume (Å³)</th>
<th>Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a</td>
<td>b</td>
<td>c</td>
</tr>
<tr>
<td>Z1</td>
<td>Orthorhombic</td>
<td>5.742</td>
<td>7.668</td>
<td>5.532</td>
</tr>
<tr>
<td>Z2</td>
<td>Orthorhombic</td>
<td>5.537</td>
<td>7.695</td>
<td>5.743</td>
</tr>
</tbody>
</table>

4.3.2. Electrical transport properties

Fig. 4.3 (a) and (b) shows the temperature dependence of resistivity for both the samples Z1 and Z2, which exhibit metal-semiconducting (M–S) transition. The M–S transition temperature (T_P) decreases with increase in Zn concentration. The observed values of T_P for doped LSMO are lower than that of undoped sample (LSMO) which is 295 K near room temperature, reported elsewhere [24].

![Graph showing temperature dependence of resistivity for Z1 sample.](image)

*Fig. 4.3(a): Temperature dependence of resistivity for Z1 sample.*
Fig. 4.3(b): Temperature dependence of resistivity for Z2 sample.

It is also observed that resistivity drops with the application of magnetic fields from 0.734 ohm-cm at 0 T to 0.369 ohm-cm at 5 T for 10% zinc doped sample while from 4.75×10^4 ohm-cm at 0 T to 4.45×10^3 ohm-cm at 5 Tesla for 20% zinc doped sample at T_p. The value of T_p and the resistivity of doped samples show the dramatic change as the concentration goes from 10% to 20%. The values of T_p for 10% and 20% Zn doped samples are shown in Table 4.2 at different fields. Table 4.2 also exhibits the resistivity obtained at zero field and T = T_C/2, where T_C is the Curie temperature of sample. The doped samples have higher resistivity than undoped LSMO at zero field and T = T_C/2 (ρ~4.92×10^-3 ohm-cm). These results are predicted due to the fact that the destruction of the partial double exchange interaction would lead to a decrease of the electrons’ hopping at Mn-site substitution [25].

Table 4.2: Transport and Magnetic parameters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T_P</th>
<th>T_C</th>
<th>ρ^9 (Ω-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 T</td>
<td>1 T</td>
<td>2 T</td>
</tr>
<tr>
<td>Z1</td>
<td>176.88</td>
<td>180.08</td>
<td>182.29</td>
</tr>
<tr>
<td>Z2</td>
<td>57.14</td>
<td>66.82</td>
<td>70.89</td>
</tr>
</tbody>
</table>

*a At T = T_C/2 and zero field*
It is well known that the resistivity is mostly influenced by the presence of grain boundaries which act as a region of enhanced scattering for the conduction electrons [24]. Moreover, the resistivity in a magnetic field is smaller than that in zero field. The alignment of the core spin of Mn ions under the applied magnetic field can cause the reduction in the spin scattering of the itinerant electrons. As a result the resistivity should decrease with increasing the magnitude of the applied magnetic field. In Fig. 4.3 (a) and (b) the peak of M–S transition can be seen. Since the M–S transition is closely correlated with the FM transition, the position of the peak has same tendency as $T_C$ in doped samples. The tendency of the magnetic field to stabilize the FM state moves the M–S peak to the high temperature region [25].

4.3.3. Magnetoresistance

The CMR as a function of temperature, calculated using the formula $(\rho_{hl}-\rho_o)/\rho_h$ (here $\rho_{hl}$ and $\rho_o$ are the values of resistivity in the presence and absence of magnetic field) are shown in Fig. 4.4(a) and (b). In Fig. 4.4 (a) with $x=0.1$, MR peaks can be observed in the vicinity of experimental temperature range where the sample exhibits an M–S transition. Furthermore, a significant MR ratio appears in the low-temperature range, either metallic or insulating, and decreases monotonically with increasing temperature. It is noteworthy that the hump in the MR peaks is increasing with the increasing magnetic fields. In Fig. 4.4 (b), the CMR effect can be visualized only up to 150 K. The encircled portion of the figure indicates that the large MR difference can be clearly seen within the range 35–85 K at different fields. The MR values at different temperatures and different fields are displayed in Table 4.3. The presence of magnetically disordered regions increasingly affects the zero field resistivity $\rho_o$. This together with the change of resistivity ($\Delta \rho$) induced by applied field decreases due to the broadening of ferromagnetic transition, leading to the reduction in CMR ratio.
Fig. 4.4(a): Magneto-resistance of Z1 sample.

Fig. 4.4(b): Magneto-resistance of Z2 sample.
Table 4.3: MR ratios at different temperatures and fields.

<table>
<thead>
<tr>
<th>Sample</th>
<th>MR%</th>
<th>1 T</th>
<th>2 T</th>
<th>5 T</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z1</td>
<td>-34.49</td>
<td>-23.64</td>
<td>0.41</td>
<td>-49.11</td>
</tr>
<tr>
<td>Z2</td>
<td>-131.04</td>
<td>-13.70</td>
<td>0</td>
<td>-326.15</td>
</tr>
</tbody>
</table>

4.3.4. Magnetic properties

Fig. 4.5 shows the temperature dependence of dc-magnetization (M–T) of the Z1 and Z2 samples measured in a field of 5000 Oe during the warming up cycle from 100 K to 400 K. The inset of this figure shows the temperature dependent dc-susceptibility (χ–T) for both samples. The Curie temperature (T_C) values, determined from the maximum point in the dM/dT or dχ/dT are listed in Table 4.2. For the undoped LSMO sample, the T_C is 365 K [25]. These results are quite different as compared to the result observed by Markovich et al. [26]. There is a monotonous decrease in T_C with increasing zinc concentration. For the samples with x = 0.1 and 0.2, the paramagnetic (PM) state to FM state transition is narrow. This fact indicates a wider distribution of the magnetic exchange interactions in the Mn–O network. Moreover, for the Z1 and Z2 samples, a magnetization drop appears at certain low temperatures in the M–T curve. The reduction in T_C is also because of the fact that the double-exchange interaction between Mn^{3+}–O^{2–}–Mn^{4+} network has been destroyed by the substitution of dopants at Mn-site. It is also noteworthy that the increasing doping level leads to the more drop off of T_C.
Fig. 4.5: M–T curve for Z1 and Z2 samples. The inset shows d.c. susceptibility for the same.

4.4. Conclusions

In summary, the structural, electrical transport and magnetic properties of Zn doped La_{0.67}Sr_{0.33}MnO_3 samples were studied. XRD patterns confirm that the Zn ions are successfully substituted at Mn site. The resistivity data shows that both sample show metal to semiconducting (M–S) transition and the M–S transition temperature is shifted towards the higher temperature value with the effect of increasing magnetic field for both samples. The magnetoresistance is found to be negative in the entire temperature range for the Z1 sample except at 300 K (1 T) while for sample Z2 it can be seen only up to 150 K. Zn substitution on Mn site leads to a strong decrease of the Curie temperature because of suppression of ferromagnetism.
References:


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Chapter 5

Adiabatic to non adiabatic change in conduction mechanism of Zn doped \( \text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3 \) perovskite
This chapter deals with the results of electrical transport properties of La$_{0.67}$Sr$_{0.33}$Mn$_{1-x}$Zn$_x$O$_3$ ($x = 0.1$ and $0.2$) bulk samples prepared by solid-state reaction route over a wide temperature range from 5 to 300 K in the presence of different magnetic fields. In this chapter, temperature dependent resistivity data were fitted using Mott’s variable-range hopping (VRH) model for a limited range of temperatures to calculate the hopping distance ($R_h$) and the density of states near the Fermi level, [N(E_F)]. It was found that all the parameters vary systematically with the increase in Zn concentration. The temperature dependent resistivity data were also fitted using the small polaron hopping (SPH) model. The adiabatic SPH conduction is followed for 10% Zn doped sample at all fields while a non-adiabatic type of SPH conduction is followed for 20% Zn doped sample at all fields.

5.1. Introduction

The colossal magnetoresistance (CMR) effects in the manganite perovskite oxides La$_{1-x}$A$_x$MnO$_3$, where A is a divalent ion such as Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$ or Pb$^{2+}$, have attracted worldwide attention due to their potential applications [1]. The CMR effects can be explained by the double-exchange (DE) model qualitatively. In the DE scenario, the electron hopping between the Mn$^{3+}$ and Mn$^{4+}$ ions, with the help of intermediate oxygen ion, can produce a magnetic coupling among the ions [2,3]. The presence of Mn ions with different valences is essential to DE. One of the parent materials of these systems LaMnO$_3$ (Mn$^{3+}$ t$_{2g}$ e$_{g}^1$) is an antiferromagnetic insulator (AFMI) with a Néel temperature of 141 K [4,5] because of the absence of Mn$^{4+}$ ions [6]. Without DE in LaMnO$_3$, the superexchange (SE) between Mn$^{3+}$ ions is dominant, and the activation type conduction prevails due to the full occupation of the e$_{g}^1$ band and the complete emptiness of the e$_{g}^2$ band.

The substitution of a trivalent La ion by a divalent alkaline-earth ion causes the conversion of Mn$^{3+}$ to Mn$^{4+}$, which leads to a ferromagnetic metallic state, having a colossal magnetoresistance (CMR) near the metal–insulator (M–I) transition [7] which has been mediated by a long known phenomenon called as DE mechanism. Interestingly, the CMR effect has been found not only in a conventional ferromagnetic metal (FMM) system like La$_{0.67}$Sr$_{0.33}$MnO$_3$, but also in an FM insulator, [8] an AFM charge ordering compound [9] and even spin glass [10,11]. It is believed that corroborating a detailed relationship between the electrical transport and
different magnetic states is critically important to ascertain the micro-mechanism of the CMR effect. To meet this end, much work in the past few years has been centered on structurally tuning the double exchange, usually by doping at rare earth site. Another important feature of the manganites is that a Mn$^{3+}$ ion is a Jahn–Teller (JT) ion. It has been recently pointed out that the influence of the JT effects has to be taken into account to understand the transport as well as magnetic properties in the lightly doped manganese system [12]. Recently the Mn-site substitution has drawn much attention and group of researchers synthesized the doped nanoparticles of La$_{1-x}$Sr$_x$MnO$_3$ (0.3 ≤ x ≤ 0.4) and observed electrical and magnetic properties in detail. They found smaller particle size in 33% Sr doped sample with good magnetoresistance [13]. The maximum magnetoresistance was observed in Ni doped La$_{0.67}$Sr$_{0.33}$Mn$_{1-x}$Ni$_x$O$_3$ (x = 0 ≤ x ≤ 0.25) at low temperature for the highest doping concentration and a decrease in magnetization was found in the same [14]. XPS results of LSMO samples prepared by solution combustion techniques show that Mn ions have mixed valence states between +3 and +4 and presence of ferromagnetism [15] and high Curie temperature was observed for thin film samples prepared by PLD technique [16]. However, other researchers reported the electrical and magnetoresistance properties of La$_{0.67}$Sr$_{0.33}$MnO$_3$/BaZrO$_3$ composite. The metal-to-insulator (M–I) transition temperature, low-field magnetoresistance (LFMR) and high-temperature resistivity behavior were found remarkably changed, suggesting the importance of variation of the manganite composition due to ionic interdiffusion in the La$_{0.67}$Ca$_{0.33}$MnO$_3$/BaZrO$_3$ composite [17] and in SrBiMn$_{1.75}$Ti$_{0.25}$O$_6$ manganite, charge and orbital ordering CO/OO) temperatures are remarkably high concerning the important role of the Bi 6$s^2$ lone-pair in the CO/OO ordering [18]. The on-line ultra-sonic measurements on bulk and nano sized La$_{0.61}$Sr$_{0.39}$MnO$_3$ perovskite manganite samples, prepared by solid-state reaction route and sonochemical reactor methods respectively revealed that there is a shift in Curie temperature (T$_C$) from 368 to 361 K from bulk to nano sized perovskite samples as the grain size of bulk to nano perovskite samples changes from 0.65 nm to 60 nm respectively. This reduction in grain size corresponds to a decrease in transition from ferromagnetic (FM) to a paramagnetic (PM) state as reported in earlier results [19]. Castellano et al. [20] reported the formation of magnetic clusters in (Pr$_{0.35}$Ca$_{0.45}$)(Mn$_{1-y}$Cr$_y$)$_3$O$_3$ (y = 0.00, 0.03, 0.06) manganites analyzed by small angle neutron scattering (SANS) and found an enhancement in the ferromagnetic phase component rather than the
charge ordered insulating phase due to the doping of non-Jahn-Teller Cr\(^{3+}\) ion and the appearance of magnetic domains as a function of temperature and magnetic field is an evidence of nanophasic percolation. The dimensions of magnetic domains increase at lower temperature (at T < T\(_c\)) or by increasing the magnetic field. Magnetic clusters formation favoured by Cr\(^{3+}\) substitution is much softer than in standard CMR manganites.

Our comparative study of introducing nonmagnetic ions into the Mn–O plane hopefully can fill this gap. One of the most extensively studied system is (Ln\(_{1-\delta}\)A\(_{\delta}\))MnO\(_3\), where Ln is a rare-earth (Ln = La\(^{3+}\), Pr\(^{3+}\), Sm\(^{3+}\), and Nd\(^{3+}\)) and A is a divalent cation (A = Ca\(^{2+}\), Sr\(^{2+}\), Ba\(^{2+}\), and Pb\(^{2+}\)). It is beneficial to study this system by Mn-site substitution because Mn site doped ion takes the place of Mn ion, consequently the perfection of the Mn–O plane no longer exists, which will cause a considerable change in structural and transport properties [21]. We have chosen La\(_{0.67}\)Sr\(_{0.33}\)MnO\(_3\) to study the effect of Mn-site substitution by a non-magnetic Zn ion.

5.2. Experimental details

The synthesis and characterization of samples La\(_{0.67}\)Sr\(_{0.33}\)Mn\(_{0.9}\)Zn\(_{0.1}\)O\(_3\) (onwards said as MZ1) and La\(_{0.67}\)Sr\(_{0.33}\)Mn\(_{0.8}\)Zn\(_{0.2}\)O\(_3\) (onwards said as MZ2) have been explained in detail in chapter 4 under section 4.2.

5.3. Results and discussion

5.3.1. Structural behaviour

The XRD patterns (shown in chapter 4) of MZ1 and MZ2 samples indicate that the samples are in a single phase with a high degree of crystallinity. Average crystallite size of MZ1 and MZ2 samples estimated from line width of the most intense XRD peak using the well known Debye–Scherrer formula is 27.48 nm and 24.32 nm respectively [22,23].

5.3.2. Transport behavior

The electrical resistivity data in the semiconducting region were mostly fitted by Mott's variable-range hopping (VRH) and Mott and Davis’s small polaron hopping (SPH) models [24,25]. According to Mott’s VRH model, the expression for electrical resistivity in three dimensional hopping can be written as [26]
\[ \rho = \rho_0 \exp \left( \frac{T_0}{T} \right)^{1/4} \]  
\[ (5.1) \]

where To is the Mott characteristic temperature, which can be expressed as:

\[ T_0 = \frac{18}{k_B N(E_F) a^3} \]  
\[ (5.2) \]

where \( k_B \) is the Boltzmann's constant, \( N(E_F) \) is the density of states and ‘a’ is the localization length.

The mean hopping distance, \( R_h(T) \), and hopping energy, \( E_h(T) \), can be written at a given temperature \( T \), as [27]

\[ R_h(T) = \frac{3}{8} a \left( \frac{T_0}{T} \right)^{1/4} \]

\[ E_h(T) = \frac{1}{4} k_B T^{3/4} T_0^{1/4} \]  
\[ (5.3) \]

In order to understand the effect of disorder-induced localization on the electrical transport behavior, we have fitted our resistivity data using Mott's VRH model [28] by varying the parameters \( \rho_0 \) and \( T_0 \). The fitted data for MZ1 and MZ2 are shown in Figs. 5.1 (a) and (b). These plots reveal that the data fit very well with the VRH model in the limited range of temperature, suggesting that the conduction is governed by the disorder-induced localization of charge carriers.

\[ \La_{0.67}\Sr_{0.33}\Mn_{0.85}\Zn_{0.20}\O_3 \]

\[ \La_{0.67}\Sr_{0.33}\Mn_{0.85}\Zn_{0.20}\O_3 \]

**Fig. 5.1:** (a) Plots of \( \ln(\rho) \) versus \( T^{1/4} \) for sample MZ1 under different fields (b) Plots of \( \ln(\rho) \) versus \( T^{1/4} \) for sample MZ2 under different fields.
Using the fitted values of $T_0$ obtained from the above equations, we have calculated the values of $N(E_F)$, $R_h$ and $E_h$ at room temperature (300 K) by taking the localization length, $a = 4.5 \, \text{Å}$, as reported by Viret et al. [29] for such type of materials. The above parameters estimated for MZ1 and MZ2 characterized under different magnetic fields are tabulated in Table 5.1.

Table 5.1: The values of density of states at the Fermi level, $N(E_F)$, the hopping distance, $R_h$, and the hopping energy, $E_h$, at room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Field (Tesla)</th>
<th>$\rho$ (300K) (mΩ-cm)</th>
<th>$\rho_0$ (mΩ-cm) $\times 10^{-16}$</th>
<th>$N(E_F)$ (eV$^{-1}$-m$^{-3}$) $\times 10^{25}$</th>
<th>$R_h$ (300 K) (Å)</th>
<th>$E_h$ (300 K) (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MZ1</td>
<td>1 T</td>
<td>150.4</td>
<td>38.59</td>
<td>13.13</td>
<td>26.21</td>
<td>100.46</td>
</tr>
<tr>
<td></td>
<td>2 T</td>
<td>147.6</td>
<td>133.2</td>
<td>15.21</td>
<td>25.26</td>
<td>96.83</td>
</tr>
<tr>
<td></td>
<td>5 T</td>
<td>135.2</td>
<td>41800</td>
<td>32.37</td>
<td>20.91</td>
<td>80.17</td>
</tr>
<tr>
<td>MZ2</td>
<td>1 T</td>
<td>18519</td>
<td>34.2</td>
<td>3.04</td>
<td>37.78</td>
<td>144.81</td>
</tr>
<tr>
<td></td>
<td>2 T</td>
<td>18439</td>
<td>76.7</td>
<td>3.23</td>
<td>37.19</td>
<td>142.59</td>
</tr>
<tr>
<td></td>
<td>5 T</td>
<td>18070</td>
<td>6.47</td>
<td>3.84</td>
<td>35.64</td>
<td>136.60</td>
</tr>
</tbody>
</table>

It is quite clear from Table 5.1 that the density of states at the Fermi level, $N(E_F)$, decreases which corresponds to decrease in conductivity, while the hopping distance ($R_h$) and hopping energy ($E_h$) increase as the Zn concentration goes from 10% to 20%. However, for the samples MZ1 and MZ2, as the magnetic field increases, $N(E_F)$ increases (Table 5.1) and such a high value of $N(E_F)$ was also estimated by other researchers, [29–31] which is due to higher conductivity of these oxides than those of the usual transition-metal–oxide semiconductors [30,32] whereas $R_h$ and $E_h$ goes on decreasing. This suggests that with increasing the magnetic field, the conductivity of both the samples increases because of the increase in $N(E_F)$. The variation in the values of $\rho_0$ estimated from Eq. (5.1) is also shown in Table 5.1, depending on Zn concentration and different fields. These observations suggested that the samples MZ1 and MZ2 obey the VRH model over a limited range of temperature (from 235.5 to 300 K for 10% Zn doped and from 133 to 300 K for 20% Zn doped samples). This indicates that the electronic properties of a system are driven by the induced distortion effects due to the presence of two different valent transition-metal elements (Mn and Zn).
Another attempt was also made to confirm the nature of hopping conduction and to observe the strength of electron–phonon interaction. We have fitted the temperature dependent resistivity data using the small polaron hopping (SPH) model proposed by Mott and Davis [33]. It has been found that the high temperature transport properties of rare-earth transition metal oxide (RETMO) systems are dominated by the thermally activated hopping of small polarons [34,35]. According to the SPH model, the expression for the electrical resistivity is given by

\[
\frac{\rho}{T} = \rho_a \exp \left( \frac{E_p}{k_B T} \right)
\]

(5.4)

where \( \rho_a = \frac{k_B}{v_{ph}N} \left( 2C(1-C) \right) \exp(2\alpha R) \), \( k_B \) is the Boltzmann constant, \( E_p \) is the activation energy and \( T \) is the absolute temperature. \( N \) is the number of ion sites per unit volume, \( R \) is the average intersite spacing obtained from the relation \( R = \frac{1}{N}^{1/2} \), \( C \) is the fraction of sites occupied by the polaron, \( \alpha \) is the electron wave function decay constant obtained from fitting the experimental resistivity data and \( v_{ph} \) is the optical phonon frequency (\( v_{ph} = \frac{k_B}{\hbar} \)). The activation energy, \( E_p \), given by [36]

\[
E_p = W_{1+} W_D/2 \quad \text{(for } T < \theta_D/2 \text{)}
= W_D \quad \text{or } T < \theta_D/4
\]

(5.5)

where \( W_{1+} \) is the polaron hopping energy, \( W_D \) is the disorder energy and \( \theta_D \) is the Debye temperature.

In order to calculate the hopping energy, we re-plotted the resistivity curves as \( \ln(\rho/T) \) versus \( 1/T \) (Figs. 5.2 (a) and (b)) and from the slope of the straight line curve above \( \theta_D/2 \), we have calculated the activation energy \( E_p \) for samples MZ1 and MZ2 (given in Table 5.2). Figs. 5.2 (a) and (b) show the temperature dependence of activation energy above the respective values of \( \theta_D/2 \) (high temperature linear part). The values of \( \theta_D/2 \) are estimated (\( \theta_D \) given in Table 2 for MZ1 and MZ2 samples) from the temperature where deviation from linearity occurs in the high temperature region, as shown in Fig. 5.2 (a) and (b). It is clear from Table 5.2 that \( \theta_D \) decreases and the activation energy \( E_p \) increases with the increase in Zn doping. It is obvious that with the increase of Zn concentration, \( Mn^{3+}/Mn^{4+} \) ratio decreases (as \( Zn^{2+} \) takes the place of \( Mn^{3+} \) ions) and hence the effective ferromagnetic double-exchange (FMDE) interaction between \( Mn^{3+}–Mn^{4+} \) becomes weaker and because of this, the
number of e\textsubscript{g} electrons of Mn\textsuperscript{3+} become more localized which increases the activation energy [25]. We have calculated the corresponding field dependent activation energy shown in Table 5.2. It is observed that for each concentration (x), \( \theta_D \) increases while \( E_P \) decreases gradually as the magnetic field increases which can be explained on the basis of delocalization of e\textsubscript{g} electrons due to the application of magnetic field.

![Graph](image)

**Fig. 5.2:** (a) Plots of ln(\( \rho/T \)) versus 1/T for sample MZ1 under different fields. (b) Plots of ln(\( \rho/T \)) versus 1/T for sample MZ2 under different fields.

Table 5.2: Some important estimated parameters at different fields. \( \theta_D \) is the Debye temperature, \( \nu_{ph} \) is the optical phonon frequency, \( E_P \) is the activation energy, \( W_D \) is the disorder energy, \( W_H \) is the hopping energy and \( \gamma_P \) is the electron-phonon interaction constant.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Field</th>
<th>( \theta_D ) (K)</th>
<th>( \nu_{ph} \times 10^{11} ) (Hz)</th>
<th>( E_P ) (meV)</th>
<th>( W_D ) (meV/( \theta_D/2 ))</th>
<th>( W_H ) (meV)</th>
<th>( \gamma_P )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MZ1</td>
<td>1 T</td>
<td>500.00</td>
<td>104.55</td>
<td>120.71</td>
<td>2.53</td>
<td>119.45</td>
<td>5.53</td>
</tr>
<tr>
<td></td>
<td>2 T</td>
<td>512.82</td>
<td>107.23</td>
<td>117.59</td>
<td>2.59</td>
<td>116.29</td>
<td>5.25</td>
</tr>
<tr>
<td></td>
<td>5 T</td>
<td>512.82</td>
<td>107.23</td>
<td>99.63</td>
<td>2.69</td>
<td>98.29</td>
<td>4.44</td>
</tr>
<tr>
<td>MZ2</td>
<td>1 T</td>
<td>344.82</td>
<td>72.09</td>
<td>135.27</td>
<td>19.41</td>
<td>125.56</td>
<td>8.43</td>
</tr>
<tr>
<td></td>
<td>2 T</td>
<td>350.88</td>
<td>73.37</td>
<td>133.21</td>
<td>16.99</td>
<td>124.72</td>
<td>8.23</td>
</tr>
<tr>
<td></td>
<td>5 T</td>
<td>357.14</td>
<td>74.67</td>
<td>130.61</td>
<td>11.16</td>
<td>125.03</td>
<td>8.12</td>
</tr>
</tbody>
</table>

...109...
To confirm whether the hopping is adiabatic or non-adiabatic, we make use of the Holstein's condition [37]. According to this criterion the polaron band width $J$ should satisfy the following conditions

$$J > \Phi \text{ (for adiabatic condition)}$$

and

$$J < \Phi \text{ (for non-adiabatic condition)}$$  \hspace{1cm} (5.6)

where

$$\Phi = (2k_B T W_H/\pi)^{1/4} (\hbar \nu_{ph}/\pi)^{1/2}$$  \hspace{1cm} (5.7)

Using the values of $W_H$ and $\nu_{ph}$ from Table 5.2, we have estimated the values of $\Phi$ for MZ1 and MZ2 respectively for different temperature ranges at different fields (given in Tables 5.3). The $J$ values were calculated independently applying the relation [37]

$$J(T) = 0.67 \nu_{ph} (T/ \theta_D)^{1/4}$$  \hspace{1cm} (5.8)

Using the values of $\nu_{ph}$ and $\theta_D$ from Table 5.2, the calculated values of $J(T)$ for MZ1 and MZ2 are given in Tables 5.3.

**Table 5.3: Estimated values of $\Phi$ and $J(T)$ at different temperatures and fields.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Field (T)</th>
<th>Parameters of MZ1 &amp; MZ2 at different temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>At 5K</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MZ1</td>
</tr>
<tr>
<td>$\Phi$ (meV)</td>
<td>1 T</td>
<td>6.67</td>
</tr>
<tr>
<td></td>
<td>2 T</td>
<td>8.93</td>
</tr>
<tr>
<td></td>
<td>5 T</td>
<td>8.57</td>
</tr>
<tr>
<td>$J$ (T) (meV)</td>
<td>1 T</td>
<td>9.26</td>
</tr>
<tr>
<td></td>
<td>2 T</td>
<td>9.32</td>
</tr>
<tr>
<td></td>
<td>5 T</td>
<td>9.32</td>
</tr>
</tbody>
</table>
On comparing the values of $\Delta$ and $\Phi$ (Table 5.3), it can be seen that the condition $J > \Phi$ is well satisfied for the sample MZ1 in the temperature range 5–300 K which suggests that an adiabatic type of conduction is valid for 10% doped sample while for sample MZ2 (Table 5.3), the condition $J < \Phi$ is well satisfied in the same temperature range, corresponding to a non-adiabatic type of conduction for 20% doped sample. This type of change in conduction mechanism is due to the substantial effect on the electronic transport properties in the system leading to the fact that there is a change in the bond angle and bond length of the network $\text{Mn}^{3+}-\text{O}-\text{Mn}^{3+}$ and $\text{Zn}^{2+}-\text{O}-\text{Mn}^{3+}$.

Finally, the electron–phonon (e–ph) coupling constant ($c$) of the samples was calculated using the relation \[ \gamma = \frac{2W_{\text{ph}}}{\hbar v_{\text{ph}}}. \] The theoretical calculations of $\gamma$ given by Millis et al. [38] suggest that if $\gamma$ is greater than 4, there are strong electron–phonon interactions present in the system, otherwise the interactions are weak. Thus, electron–phonon coupling constant, $\gamma$, is the crucial parameter in controlling the various properties of the sample. From the Table 5.2, for the samples MZ1 and MZ2 respectively, the values of $\gamma$ are found to be more than 4 which confirm the strong electron–phonon interactions in the samples. Moreover, for MZ1 (Table 5.2), the values of $\gamma$ alters from 5.53 (at 1 Tesla) to 4.44 (at 5 Tesla) and for MZ2 (Table 5.2), the same alters from 8.43 (at 1 Tesla) to 8.12 (at 5 Tesla). This suggests that the values of $\gamma$ decrease with the increase in magnetic field. However, it is quite clear from the Table 5.2 that as the Zn concentration increases, the strength of e–ph coupling constant also increases very systematically, which results in localization of charge carriers or overall hopping potential. The transport properties of these perovskites are governed by the interplay of the double exchange coupling between $\text{Mn}^{3+}$ and $\text{Zn}^{2+}$ ions as well as the Jahn–Teller coupling. It has been shown that the electrical transport properties are closely related to the structural distortion and in particular to the arrangement of $\text{MnO}_6$ or $(\text{Mn,Zn})\text{O}_6$ octahedra. This distortion modifies the superexchange angle $\text{Mn}–\text{O}–\text{Zn}$ or $\text{Zn}–\text{O}–\text{Zn}$ and bond length which drive the O (2p) and (Mn, Zn) (3d) bands to overlap and control the closing and opening of the charge transfer gap. Moreover, in the case of the orthorhombic lattice, the bond angle varies continuously with tolerance factor, as the ionic radii of Mn and Zn are different and by the doping of Zn, it modifies the octahedra of $\text{MnO}_6$. Thus we believe that it creates significant change in bond length/bond angle. The relation
between the bond angle distortion and the tolerance factor shows little B-site
dependence, and hence is likely to be applicable to doped manganites [39].

5.4. Conclusions

A detailed study of structural and electrical transport properties of
La$_{0.67}$Sr$_{0.33}$Mn$_{1-x}$Zn$_x$O$_3$ ($x = 0.1$ and $0.2$) bulk samples prepared by solid-state
reaction-route have been reported systematically. Both samples show orthorhombic
crystal symmetry with space group Pnma for the Zn-doping level $x \leq 0.2$. The
variable range hopping model is found to be valid for limited range of temperature
(from 235.5 to 300 K for 10% doped sample and from 133 to 300 K for 20% doped
sample). The density of states at Fermi level $N(E_F)$ decreases whereas hopping
distance $R_h$ and hopping energy $E_h$ increase with increase in Zn concentration. But
with the effect of enhancing the magnetic field, $N(E_F)$, increases, while $R_h$ and $E_h$
go on decreasing for each sample. These results are consistent with the behavior in
many semiconducting oxide systems. The adiabatic small polaron hopping conduction
is observed for 10% Zn doped samples whereas the non-adiabatic small polaron
hopping conduction prevails for 20% doped samples in the temperature range 5–300
K. The activation energies and the electron–phonon coupling constant enhances due
to enhancement in bandwidth with Zn ion doping for both samples at all fields. Such a
change of conduction mechanism is associated with the change in the bond angle and
the bond length in Mn–O–Zn and Zn–O–Zn networks. Thus there is a strong
correlation between the structural and electrical transport properties in this system.
The observed features have been explained on the basis of charge-carrier doping in
La$_{0.67}$Sr$_{0.33}$MnO$_3$. 

...112...
References:


***************

...114...
Chapter 6

Study of structural, microstructural and magnetic properties of Zn doped \( \text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3 \) manganite synthesized through Sol-Gel Route
This chapter deals with the synthesis of pure, 10% and 20% Zn doping at Mn site in 
\( \text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3 \) manganite samples synthesized by Sol-Gel Route. The 
microstructural and magnetic properties of all the samples were studied. The 
comparative studies of phase formation, crystal structure and particle size have been 
investigated by using x-ray diffraction (XRD), scanning electron microscopy (SEM) 
and transmission electron microscopy (TEM) techniques respectively. Magnetization 
measurements have been done using vibrating sample magnetometer (VSM).

Superparamagnetic behavior is observed in all the samples at room temperature with 
the reduced particle size estimated by TEM. The 0% (pure), 10% and 20% Zn doped 
samples are onwards symbolized as Z0, Z10 and Z20 respectively.

6.1. Introduction

At the nanometer scale, magnetic and electrical transport properties of manganites 
consist of a concern of immense interest these days. An enormous number of studies 
of the effect of grain size on magnetic and electrical properties of manganites 
\( \text{La}_{1-x}\text{A}_x\text{MnO}_3 \) (A=Ca, Sr, Ba, Pb) nanoparticles have been published in recent times 
[1-17]. Especially, spin electronics derived from half-metallic properties of these 
materials, effect of structure disorders and surface spin on the magnetism of 
manganite nanoparticles are subjects of extreme debate. From earlier investigations, 
the magnetic structure of grain boundary of manganite nanoparticles came into view 
in the following manner: since the double exchange mechanism is sensitive to 
Mn–O–Mn bond, any disorder in structure near the grain boundary (such as 
vacancies, stress, oxygen non stoichiometry etc.) transforms this exchange leading to 
a spin disorder. Because of strong Hund’s interaction, spin disorder in the region of 
grain boundaries serves as centers of strong scattering for highly spin-polarized 
conduction electrons and as a result zero-field high electrical resistance is produced 
[18]. The originally disordered Mn spins can be aligned by applying the reasonable 
amount of magnetic field which causes reduction in the spin scattering and leading to 
a giant magnetoresistance (GMR). Yet, the microscopic nature of the surface region is 
a not well understood up to now. This short of understanding is apparent in some 
discrepancy between the models and the experimental results. For example, it was 
observed that there is suppression in grain surface magnetization in compare to the 
bulk magnetization [2,4] whereas the other group showed the enhancement in Curie 
temperature in the vicinity of grain boundary [7]. Some researchers found that
between the external region and the inner part of the grain, the chemical potential is shifted [6,10] while other observed a tunneling with high probability through paramagnetic impurity states in the intergranular barrier [4,5,9]. However, some significant features observed for manganite nanoparticles as usually known from earlier studies, are (a) a decrease in the magnetization in comparison with bulk polycrystalline samples, (b) a decrease and broadening of the ferromagnetic transition temperature $T_C$, (c) emergence of superparamagnetic (SPM) behavior at very low particle size, etc. In general, these observations were elucidated by assuming the increase in magnetically disordered insulating grain-boundary contribution with the decreasing particle size [19,20–22]. The bonds are broken at the surface due to the formation of grain boundaries which reduces the magnetization value. This is the most general observation in the case of manganite nanoparticles [20,23]. But there are some exceptions to this general rule. Zhang et al. [24] reported that there is a contradiction with the above information on reduced particle size for low doping level in $La_{1-x}Sr_xMnO_3$ nanoparticles. They investigated the effect of annealing temperature on the magnetization for different $x$ values in $La_{1-x}Sr_xMnO_3$ system in detail. They observed that magnetization decreases with an increase in sintering temperature for low doping ($x<0.25$) and the magnetization increases with an increase in sintering temperature for higher doping ($x>0.25$). According to their investigations, the change in magnetization is observed mainly because of the lattice distortions in this system. They found in $La_{1-x}Sr_xMnO_3$ manganite system for the lower doping of Sr ($x<0.15$) that as the sintering temperature increases, the bond angle decreases whereas the bond length increases which in turn explains the observed decrease in the magnetization with increase in sintering temperature. Hence the grain size effect plays a very crucial role if the manganites are expected to be utilized in forthcoming nanoelectronic devices.

Because of their applications such as magnetic sensors, magnetic recording media, permanent magnets, ferro fluids and in biomedicine, magnetic nanoparticles have drawn much attention in recent years [25–27]. The magnetic properties of nanoparticles are strongly influenced by size and shape of the particles, finite-size effect and exchange interaction between the particles. Each particle may have only a single magnetic domain at the nanometer scale and if the particle size is smaller than the size of single domain, the spins are gradually affected by the thermal fluctuations
and basically a ferromagnetic material turns into superparamagnetic. However, the magnetic order still persists within the particles in the superparamagnetic state and each particle behaves like a paramagnetic atom with a superspin. When a superparamagnetic state is attained, the magnetic nanoparticle realizes a superparamagnetic relaxation process, in which there is a rapid fluctuation in the direction of magnetization of nanoparticle instead of being fixed along a certain direction [28].

Systematic investigations have been carried by various researchers on perovskite manganites in the form of bulk and thin films, due to their variety of unique properties and potential applications [29–31]. They exhibit various unique properties such as surface spin-glass behavior, superparamagnetic behavior and low saturation magnetization as compared to their bulk counterparts when the size of these materials is reduced to nanometer scale [32–36]. For magnetic hyperthermia applications, magnetic nanoparticles of quite identical size, having Curie temperature above room temperature, are required.

Keeping in view the above results, we have doped 10% and 20% Zn at Mn site in La$_{0.67}$Sr$_{0.33}$MnO$_3$. The replacement of manganese by Zn in La$_{0.67}$Sr$_{0.33}$MnO$_3$ seems to be significant because Zn$^{2+}$ ions do not have any magnetic moment and they do not participate in ferromagnetic (FM) interaction and therefore the magnetic sublattice gets diluted.

6.2. Experimental details

We adopted the Sol-Gel method [37] to synthesize the polycrystalline samples of Zn doped La$_{0.67}$Sr$_{0.33}$MnO$_3$ manganites. In this technique, The aqueous solution of high purity La(NO$_3$)$_3$·6H$_2$O, Sr(NO$_3$)$_2$ and Mn(NO$_3$)$_2$·4H$_2$O and Zn(NO$_3$)$_2$·6H$_2$O have been taken in the desired stoichiometric proportions. An equal amount of ethylene glycol has been added to this solution with continuous stirring. After this, the solution is heated on a hot plate at a temperature of ~100–140°C to get a dry thick brown colour sol. At this temperature, ethylene glycol polymerizes into polyethylene glycol due to which the cations disperses homogeneously forming a cation–polymer network. The as obtained sol is further decomposed in an oven at a temperature of ~300°C to get a polymeric precursor in the form of a black resin-like material. To get
phase pure completely crystalline samples, the polymeric precursor thus obtained is sintered at 600°C for 4 hours.

All the synthesized samples have been subjected to structural characterizations using a powder x-ray diffractometer (XRD, Bruker D8 Advance) using Cu-Kα radiation (λ~1.5406Å) in the 2θ range 20–80° at room temperature. The microstructural characterizations have been done by using the scanning electron microscopic (SEM, JEOL: JSM-6510 LV) and transmission electron microscopic techniques (TEM, JEOL: JEM-2100). The magnetization measurements at room temperature are carried out by using a vibrating sample magnetometer (VSM, MicroSense: EV7).

6.3. Results and discussion

6.3.1. Structural characterizations

Fig. 6.1 displays the x-ray diffraction patterns of all studied samples at room temperature. This figure indicates that all the samples Z0, Z10 and Z20 have rhombohedral crystal symmetry with R(-3c) space group analyzed by PowderX software. However some impurity peaks are observed which may be due to some uncontrolled experimental parameters. The highlighted peaks (121) have been magnified to observe any modification by the doping ions and shown in Fig. 6.2.

![XRD patterns of Z0, Z10 and Z20 samples.](image)
The Fig. 6.2 shows the magnified part of the highest intensity peaks (121) with no deviation observed in the position of the peaks for the samples Z0, Z10 and Z20 respectively. This reveals that no lattice strain is produced due to the doped ions.

**Fig. 6.2: Magnified part of the highest intensity peaks (121) for Z0, Z10 and Z20 samples.**

Average crystallite size (CS) is determined using Debye–Scherrer's formula [38,39] from XRD patterns corresponding to the line width of highest intensity peak (121). The unit cell volume is found to increase with increase in Zn content because of larger ionic radius of Zn$^{2+}$ ions (0.088 nm) than that of Mn$^{4+}$ ions (0.067 nm) whereas the crystallite size increases in case of 10% Zn doped sample compared with the parent sample but as Zn concentration increases from 10% to 20%, there is a considerable decrease in crystallite size. This may be due to the enhancement in the force of interaction between Mn$^{4+}$ and Zn$^{2+}$ ions due to the increasing Zn content.

6.3.2. **Microstructural characterizations**

6.3.2.1. **Scanning Electron Microscopy**

Figures 6.3, 6.4 and 6.5 respectively elucidate the scanning electron microscopy (SEM) images of Z0, Z10 and Z20 samples at 10 μm scale and 1000 magnification. It is clear from figures that the particles of all the samples seem to be agglomerated and
a nanofibres type of structure is formed. These results authenticate that the primary particles of all the powder samples in this work are perovskite phase materials of nanometer sizes. All the particles are well connected together with no clear grain boundaries and pores can be seen throughout in all samples [40,41].

The SEM micrographs respectively reveal the following information: (i) In general, the particles are formed by agglomerates of nanosized crystals; (ii) The visible smallest particles correspond to the primary crystallites; (iii) aggregation of crystallites is of primary importance to determine the grain size distribution; and (iv) the increasing Zn content influences the agglomeration process, leads to a bigger particle and also affects growth and nucleation process of the nanosized crystallites [40].

![SEM micrograph of Z0 sample.](image)

**Fig. 6.3: SEM micrograph of Z0 sample.**

It is clear from Fig. 6.3 that grain size (GS) increases in case of Z10 sample compared with the pure sample (Z0) but as the Zn content increases up to 20%, the CS is found to decrease. Due to this, the size of nanoparticles becomes larger in case of Z10 sample causing the reduction in number of grain boundaries. But in case of Z20 sample, the size of nanoparticles decreases which enhances the number of grain boundaries [42].

...120...
Fig. 6.4: SEM micrograph of Z10 sample.

Fig. 6.5: SEM micrograph of Z20 sample.

6.3.2.2. Transmission Electron Microscopy

Figures 6.6 (a-b), 6.7 (a-b) and 6.8 (a-b) show the Transmission Electron Microscopy (TEM) images elucidation of Z0, Z10 and Z20 samples respectively. It is clear from these figures that the surface of nanoparticles is very clean. TEM micrographs show that the particle size distribution is almost uniform in all the samples [42].

TEM is a rather straight way for structural characterization through which the particle size can be estimated exactly. TEM was done on the powders of all the respective samples which are dispersed in a solvent and mounted on a carbon coated...
grid. Figures 6.6 (a), 6.7 (a) and 6.8 (a) show the bright field images of nanocrystalline Z0, Z10 and Z20 samples respectively. An occurrence of nearly spherical particles has been found with particle sizes 11 nm, 14 nm and 13 nm respectively for Z0, Z10 and Z20 samples estimated through Image J software which are in well agreement with the XRD results. The size distribution of all the particles is given by the histograms as shown in figures 6.6 (b), 6.7 (b) and 6.8 (b) respectively for the samples Z0, Z10 and Z20. In these figures, the histograms have been obtained by analyzing several frames of similar bright field images by Image J software for all the samples [43].

Fig. 6.6: (a) TEM micrograph and (b) histogram of Z0 sample.

Fig. 6.7: (a) TEM micrograph and (b) histogram of Z10 sample.
Fig. 6.8: (a) TEM micrograph and (b) histogram of Z20 sample.

6.3.2.3. Analysis of Energy Dispersive Spectra (EDS)

The energy dispersive spectra (EDS) of Z0, Z10 and Z20 samples are displayed in Figures 6.9, 6.10 and 6.11 respectively. The analysis of EDS verified the composition and uniform distribution of all the elements in the respective samples. The average composition for all the respective samples are found from EDS spectra, recorded at different areas and the values are in well agreement in terms of atomic ratio [44].

It is clear from figure 6.9 that for Z0 sample, the peaks corresponding to Lanthanum (La) are observed at 0.5 keV and 4.5 keV, Strontium (Sr) at 2 keV, 14 keV and 16 keV, Manganese (Mn) at 0.5 keV and 6 keV and Oxygen (O) at 0.5 keV.

Fig. 6.9: EDS of Z0 sample.
In figure 6.10 for Z10 sample, the peaks corresponding to Lanthanum (La) are observed at 0.5 keV and 4.5 keV, Strontium (Sr) at 2 keV and 14 keV, Manganese (Mn) at 0.5 keV and 6 keV, Zinc (Zn) at 1 keV, 8.5 keV and 10 keV and Oxygen (O) at 0.5 keV.

![EDS of Z10 sample](image1)

**Fig. 6.10: EDS of Z10 sample.**

In figure 6.11 for Z20 sample, the peaks corresponding to Lanthanum (La) are observed at 0.5 keV and 4.5 keV, Strontium (Sr) at 2 keV, 14 keV and 16 keV, Manganese (Mn) at 0.5 keV and 6 keV, Zinc (Zn) at 1 keV, 8.5 keV and 9.5 keV and Oxygen (O) at 0.5 keV.

![EDS of Z20 sample](image2)

**Fig. 6.11: EDS of Z20 sample.**
The lattice parameters, unit cell volumes, crystallite sizes (CSs), and particle sizes (PSs) estimated for all samples have been provided in Table 6.1.

Table 6.1: The lattice parameters, unit cell volumes, crystallite sizes (CSs) and particle sizes (PSs) for Z0, Z10 and Z20 samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice Parameters (Å)</th>
<th>Unit Cell Volume (Å³)</th>
<th>Crystallite Size (CS) from XRD (nm)</th>
<th>Particle Size (PS) from TEM (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z0</td>
<td>a: 5.4253, b: 5.4253, c: 13.3211</td>
<td>392.0917</td>
<td>15.74</td>
<td>11</td>
</tr>
<tr>
<td>Z10</td>
<td>a: 5.4556, b: 5.4556, c: 13.3509</td>
<td>397.3705</td>
<td>15.76</td>
<td>14</td>
</tr>
<tr>
<td>Z20</td>
<td>a: 5.4858, b: 5.4858, c: 13.3913</td>
<td>402.9978</td>
<td>13.22</td>
<td>13</td>
</tr>
</tbody>
</table>

6.3.3. Magnetic Properties

Figure 6.12 shows the field dependent isothermal dc magnetization at room temperature for the samples Z0, Z10 and Z20 respectively up to the maximum available field of 1.8 Tesla.

![Graph of M-H curves](image_url)

*Fig. 6.12: Field dependent magnetization (M-H) curves for Z0, Z10 and Z20 samples.*
Moreover, figure 6.12 reveals that all the samples exhibit superparamagnetic behavior. Superparamagnetism is a phenomenon by which magnetic materials may exhibit a behavior similar to paramagnetism even when at temperatures below the Curie or the Néel temperature. This is a small length-scale phenomenon, where the energy required to change the direction of the magnetic moment of a particle is comparable to the ambient thermal energy.

In general, in ferromagnetic materials, coupling forces cause the magnetic moments of neighboring atoms to align, resulting in very large internal magnetic fields. In this way the ferromagnetic materials are distinguished from paramagnetic materials. At temperatures above the Curie temperature (or the Neel temperature for antiferromagnetic materials), the thermal energy is sufficient to overcome the coupling forces, causing the atomic magnetic moments to fluctuate randomly. Due to this fluctuation in magnetic moments, there is no longer any magnetic order, hence the internal magnetic field no longer exists and the material exhibits paramagnetic behavior. If the material is non-homogeneous, one can observe a mixture of ferromagnetic and paramagnetic clusters of atoms at the same temperature, i.e. superparamagnetic stage [45,46].

Superparamagnetism takes place when the material is composed of very small crystallites at nanometer scale. In this case even when the temperature is below the Curie or Neel temperature, the thermal energy is enough to change the direction of magnetization of the entire crystallite. As a result, these fluctuations in the direction of magnetization cause the magnetic field to become zero. Thus the material behaves like paramagnetic material, except that instead of each individual atom being independently influenced by an external magnetic field, the magnetic moment of the entire crystallite tends to align with the magnetic field [45,46].

The energy required to change the direction of magnetization of a crystallite is called the crystalline anisotropy energy and depends both on the material properties and the crystallite size. As the crystallite size decreases, there is a decrease in crystalline anisotropy energy which results in a decrease in the temperature at which the material becomes superparamagnetic [45,46].

It is evident from Figure 6.12 that the hysteresis loops for all the investigated samples measured at room temperature are closed ones and shows almost no coercivity. This may be considered as a typical superparamagnetic behavior. No
complete saturation behavior is detected even at the high values of magnetic field (≈ 1.8 Tesla) for all the inspected samples which can be explained due to the canting of surface spins of nanoparticles [47,48]. The values of the slopes of the M-H curves increase as the Zn doping level increases up to 10% but as the Zn content increases up to 20%, the slopes of M-H curves decrease. These results are in a very good agreement with the XRD and TEM results.

6.4. Conclusions

By concluding our results, the structural, microstructural and magnetic properties of pure, 10% and 20% Zn doped at Mn site in La_{0.67}Sr_{0.33}MnO_{3} samples synthesized through Sol-Gel method have been inspected. The successful partial substitution of Zn ions at Mn site is confirmed by XRD patterns. All samples are found to have rhombohedral crystal symmetry with space group R(-3c).

The scanning electron microscopy (SEM) images of pure, 10% and 20% Zn doped samples at 10 μm scale and 1000 magnification are recorded. It is clear from SEM images that the particles of all the samples seem to be agglomerated, well connected and a nanofibres type of structure is formed. The particles have no clear grain boundaries and pores can be seen throughout in all samples. The agglomeration process is affected by the increasing doping level of Zn, leading to a bigger particle and also influences the growth and nucleation process of the nanosized crystallites.

The transmission electron microscopy (TEM) images of pure, 10% and 20% Zn doped samples are recorded. TEM images reveal the very clear surface of nanoparticles and the particle size distribution is almost uniform in all the samples which is analyzed by the Image J software. An abundance of nearly spherical particles is found with the particle sizes 11 nm, 14 nm and 13 nm respectively for pure, 10% and 20% Zn doped samples estimated through the Image J software. The particle sizes obtained by TEM are in well agreement with the crystallite sizes obtained by XRD. The composition and uniform distribution of all the elements in the respective samples have been confirmed by the energy dispersive spectra.

All the studied samples show the superparamagnetic behavior. No coercivity is shown by the recorded hysteresis loops of all samples. Magnetizations do not saturate up to the available field of 1.8 Tesla. The investigated magnetic properties are consistent with the XRD, SEM and TEM results.
References:


[46] https://groups.yahoo.com/neomorphic/Physics_Made_Easy/conversations/messages/60961


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Chapter 7

Ferromagnetism and adiabatic to non-adiabatic switching process in $\text{La}_{0.33}\text{Sr}_{0.67}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ ($0 \leq x \leq 0.02$) manganite
This chapter deals with the systematic investigations carried out on structural, electrical and magnetic properties of Fe doped $\text{La}_{0.33}\text{Sr}_{0.67}\text{Mn}_1\text{Fe}_x\text{O}_3$ manganites prepared through solid-state reaction-route. The samples are found to have rhombohedral crystal symmetry. The crystallite sizes obtained by XRD data are much smaller than the average grain size obtained by scanning electron microscope (SEM). Temperature dependent resistivity data were fitted using Mott's variable-range hopping (VRH) and small polaron hopping (SPH) models for obtaining different parameters. The adiabatic SPH conduction mechanism is followed almost for both samples in the absence of magnetic field but a switching from adiabatic to non-adiabatic SPH conduction mechanism is found in the presence of magnetic field. Temperature dependent magnetization (M–T) measurements confirm the decrease in Curie-temperature ($T_C$) with Fe doping. The samples exhibited ferromagnetic behavior at 10 K and 300 K with a small hysteresis loop and low coercivity.

7.1. Introduction

In view of the fact that the invention of colossal magnetoresistance (CMR) properties in $\text{RE}_{1-x}\text{AE}_x\text{MnO}_3$ (RE: Rare-earth ion; AE: Alkaline earth ion), many studies have been investigated to make clear many interesting properties of these perovskites [1–3]. It was found that the fluctuation in doping concentration ($0 \leq x \leq 1$) modifies the magnetic and electrical transport properties deeply since the system undergoes several phase transitions with different types of magnetic and structural ordering. The majority of publications are devoted to $\text{RE}_{1-x}\text{AE}_x\text{MnO}_3$ compounds ($0 \leq x \leq 0.5$) with hole type carriers. These compounds exhibit CMR: sample resistivity drops drastically under applied magnetic field near Curie temperature ($T_C$). The application of magnetic field drives the system from a paramagnetic (PM) insulator to a ferromagnetic (FM) metal in these manganites. The simultaneous presence of $\text{Mn}^{3+}$ and $\text{Mn}^{4+}$ ions in these compounds leads to the double Exchange (DE) mechanism for the $\text{Mn}^{3+}$–O$^{2-}$–$\text{Mn}^{4+}$ network which can explain the appearance of the ferromagnetism as well as the phase transition [4]. In addition to DE, a specific role of the Jahn–Teller distortion around the $\text{Mn}^{3+}$ ion is pointed out in several reports [5]. The disorder and doping of the manganese site are the major parameters influencing the CMR properties. They are directly linked to the crystal structure and the chemical bonds. This is all possible because of the high flexibility of the perovskite structure, with large substitution possibilities on the three atomic sites. However, one has to keep in
mind the strong interdependence of these different parameters. They often make understanding and optimizing the properties of these materials highly complex [6]. The simple manganites such as $\text{La}_{1-x}\text{M}_x\text{MnO}_3$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) with $x \approx 1/3$, exhibit a transition from a high temperature PM semi-conducting or insulating phase to a low temperature FM phase. In the PM phase, the electrical resistivity generally exhibits strong temperature dependence. Different $\rho(T)$ laws have been used in fitting experimental data, the most popular ones being: (i) simple thermal activation law; (ii) hopping of adiabatic polarons; and (iii) Mott variable range-hopping (VRH). Each of these laws have some physical origins, which are respectively (i) the existence of a pseudo gap at the Fermi level in the PM phase [7]; (ii) the local lattice distortion accompanying the moving charge carrier (Jahn–Teller polaron); and (iii) the localization of the charge carriers by the magnetic disorder [8]. In a constrained temperature range, it is practically impossible to differentiate between these different $\rho(T)$ laws. At low $T$, the spontaneous alignment of the Mn spins below the $T_C$ allows a delocalization of the $e_g$ electrons, leading to a low resistivity FM phase with $\rho \propto \rho_0 + aT^2$ for $T < T_C$. This alignment of the Mn spins can be induced for $T > T_C$, or reinforced for $T < T_C$, by applying an external magnetic field. The maximum effect is obtained in the vicinity of $T_C$ since the initial magnetic susceptibility diverges as $T \to T_C$. Thus, these manganites have a rather large negative magnetoresistance, the so-called CMR, which peaks at about $T_C$ [9]. A group of researchers reported the role of external and internal perturbations on the FM to PM phase transition in $\text{Sm}_{0.52}\text{Sr}_{0.48}\text{MnO}_3$ single crystal. They showed that $\text{Hcr} \approx 4$ T and $\text{Tcr} \approx 160$K is a critical point below which FM to PM phase transition is first order and above which it becomes second order in nature [10,11]. The magnetic and transport properties of $(\text{La}_{1-x}\text{Dy}_x)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ ($x = 0, 0.114, 0.243$ and $0.347$) samples were investigated by varying the concentration of Dy.

For the particular doping concentration $x = 0.347$ in $(\text{La}_{1-x}\text{Dy}_x)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ manganite, they reported the role of applied external magnetic field to tune quantum critical point (QCP) driven by quenched disorder using the neutron diffraction and small angle neutron scattering (SANS) techniques [12,13]. An extensive study has been presented for the effect of size reduction on the ferromagnetic transition temperature $T_C$ of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ nanoparticles using neutron diffraction along with magnetic measurements whereas the effect of nanometric grain size was
observed on magnetic properties of La_{0.7}Ca_{0.3}MnO_{3} nano particles [14,15]. The crossover from long-range to short-range magnetic ordering in (Nd_{1-x}Tb_{x})_{0.33}Sr_{0.43}MnO_{3} manganite compounds in the doping range 0≤x≤0.6 by using neutron diffraction, neutron depolarization and small angle neutron scattering (SANS) has also been reported [16]. The existence of ferromagnetic domains below 108K was observed in La_{0.67}Ca_{0.33}Mn_{0.9}Fe_{0.1}O_{3} manganite using the neutron depolarization technique. The random substitutions of Mn^{3+} with Fe^{3+} reduces the number of available hopping sites for the Mn e_{g} (up) electron resulting in the reduction of ferromagnetic double-exchange interactions and the competition between the ferromagnetic double-exchange interactions and the co-existing antiferromagnetic superexchange interactions drives the system into a randomly canted ferromagnetic state at low temperatures [17]. The doping by Fe^{3+} also seems to be very appropriate since Fe^{3+} is magnetic, but does not give rise to the Jahn–Teller effect and unlike Cr, does not participate in DE. The influence of Fe doping on magnetic and electrical properties was mainly studied for hole doped La_{1-x}Ca_{x}Mn_{1-y}Fe_{y}O_{3} (x = 0.3 and y = 0.25) systems [18–20]. In view of above extensive and interesting research in this direction, the systematic investigations are carried out on structural, microstructural, electrical transport and magnetic properties of La_{0.33}Sr_{0.69}MnO_{3} (onward said as MF0) and La_{0.33}Sr_{0.67}Mn_{0.98}Fe_{0.02}O_{3} (onward said as MF2) polycrystalline samples.

7.2. Experimental

The samples were prepared by conventional solid-state reaction-route explained in detail in chapter 4 under section 4.2. The as prepared samples were characterized by powder X-ray diffraction (XRD) using a Rigaku Miniflex X-ray diffractometer with a monochromatic Cu-Kα radiation of wavelength ~1.5406Å. The microstructural and electron dispersive spectrum (EDS) characterizations were subjected to the scanning electron microscopic technique (SEM, JEOL JSM-6510LV). The electrical transport measurements were carried out by using four probe technique with the current direction being parallel to the magnetic field direction in a cryostat assembly in the temperature range 5–300K. Magnetotransport studies were performed using a commercial Quantum Design SQUID magnetometer. For temperature dependence of magnetization (M–T), zero-field-cooled (ZFC) runs were performed with temperature ranging from 10 to 310 K. The field dependence of magnetization (M–H) was performed at 10 K and 300K in the field range -3 T to +3 T.
7.3. Results and discussion

7.3.1. Structural characterization

The X-ray diffraction patterns as shown in Fig. 7.1 indicate that both the samples (MF0 and MF2) are found to possess rhombohedral symmetry having space group R(-3c) at room temperature. The Fig. 7.2 displays the magnified part of the highest intensity peaks and shows the deviation in the position of the peaks (110) for MF0 and MF2 samples and reveals that the peak for the doped sample is shifted towards the higher 2θ value due to the strain induced from the doping ions. Rietveld refinement has been done for the XRD data of both the samples as shown in Fig. 7.3 (a) and (b). In Fig. 7.3 (a−b), asterisks (*) show the impurity peaks which may be due to the uncontrolled experimental parameters. The cross points are the actual data and the calculated curve is superposed on them. The vertical lines are the calculated Bragg's positions of the reflections for rhombohedral compounds. The bottom lines, showing the difference between the experimental and calculated XRD patterns, show a good agreement between the observed and calculated intensities. Average crystallite size (CS) is determined using Debye–Scherrer's formula [21,22] from XRD patterns corresponding to the line width of highest intensity peak (110). The unit cell volume and crystallite size increases very slightly with increase in Fe concentration because of the size mismatch of Mn and Fe ions.

![XRD patterns of MF0 and MF2 samples.](image)

*Fig. 7.1: XRD patterns of MF0 and MF2 samples.*
Fig. 7.2: Magnified part of the highest intensity peaks (110) for MF0 and MF2 samples.

Fig. 7.3: Rietveld refinement of (a) MF0 and (b) MF2 sample.

Fig. 7.4 (a–b) shows the representative scanning electron microscope (SEM) images elucidation surface morphology for the samples MF0 and MF2 respectively. The SEM observation reveals that there is a uniform distribution of grains for both samples and the grain size (GS) increases whereas porosity reduces in the case of doped sample. The doped sample (MF2) has well connected grains whereas the undoped sample (MF0) has poor grain connectivity. The average GSs are ~250 nm and 322nm.
respectively, for MF0 and MF2 samples. Obviously, the CSs calculated by XRD are several times smaller than the GSs obtained by SEM. This difference may be because of the fact that the grains are composed of several crystallites, probably due to the internal stress or defects in the structure [23].

Fig. 7.4: SEM micrographs of samples (a) MF0 and (b) MF2 sample.

The energy dispersive spectrum (EDS) for the samples MF0 and MF2 are shown in Fig. 7.5 (a) and (b) respectively. The EDS confirms the presence of all the elements in both samples. The lattice parameters, unit cell volumes, crystallite sizes (CSs) and grain sizes (GSs) estimated for both samples have been provided in Table 7.1.

Fig. 7.5: The energy dispersive spectrum (EDS) of (a) MF0 and (b) MF2 samples.

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Table 7.1: Lattice parameters, unit cell volume, crystallite size and grain size for MF0 and MF2 samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Symmetry</th>
<th>Lattice parameters (Å)</th>
<th>Unit Cell Volume (Å³)</th>
<th>Crystallite Size (CS) from XRD (nm)</th>
<th>Grain Size (GS) from SEM (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MF0</td>
<td>Rhombohedral</td>
<td>a 5.4742, b 5.4742, c 13.3507</td>
<td>346.4759</td>
<td>17.7</td>
<td>250</td>
</tr>
<tr>
<td>MF2</td>
<td>Rhombohedral</td>
<td>a 5.4764, b 5.4764, c 13.3568</td>
<td>346.9085</td>
<td>18.3</td>
<td>322</td>
</tr>
</tbody>
</table>

7.3.2. Transport properties

The plots of temperature dependence of resistivity data at fixed magnetic field are shown in Fig. 7.6 (a) and (b) respectively. From Fig. 7.6, it can be observed that no metal-semiconducting (M–S) transition is present for both undoped and doped samples at 0 and 8T magnetic fields. This may be due to the large amount of divalent cation (Sr²⁺) doping in the LaMnO₃. Other phenomenon for the absence of M–S transition temperature in the doped sample clearly reveals that there should be no charge transfer between the Fe and Mn ions via the O 2p state. The ferromagnetic interaction in the Fe–O–Mn bonds is superexchange rather than double exchange as reported in the Ni–O–Co bonds when the spin glass behavior and giant magnetoresistance effect in the perovskites RECo₀.₃Ni₀.₃O₃ (RE = La, Nd, Sm) were investigated [24]. The samples remain essentially semiconducting in the entire temperature range which has been supported by the decrease in resistivity by increasing the temperature for both samples. Additionally, the resistivity becomes very small and constant above 100K. This is because more charge carriers are induced/delocalized in the sample by getting more energy due to the increasing temperature. However, there is a drastic increase in resistivity in Fe doped sample (MF2) because Fe³⁺ replaces Mn³⁺ which lowers the Mn³⁺/Mn⁴⁺ ratio and so the hopping of electron between Mn³⁺ and Mn⁴⁺ becomes more difficult which makes the DE suppressed. Although, there may also be the electron-hopping between Fe³⁺ and Mn³⁺/Mn⁴⁺ which can cause conduction in the sample but most likely in these type of systems, there are more chances of hopping between Mn³⁺ and Mn⁴⁺. Moreover, we
can also observe that the resistivity decreases very drastically with the application of magnetic field at 8T for both MF0 and MF2. This is because of the fact that the alignment of the core spins of Mn ions under the applied magnetic field can cause the reduction in the spin scattering of the itinerant electrons. As a result the resistivity should decrease with increasing the magnitude of the applied magnetic field [25].

Fig. 7.6: Temperature dependence of resistivity for (a) MF0 and (b) MF2 samples at 0 and 8T.

The electrical resistivity data in the semiconducting region were fitted by Mott’s variable-range hopping (VRH) and Mott and Davis’s small polaron hopping (SPH) models [26,27]. According to the Mott’s VRH model, the expression for electrical resistivity in three dimensional hopping can be written as [28]

\[ \rho = \rho_0 \exp \left( \frac{T_0}{T} \right)^{1/4} \]  

(7.1)

where \( T_0 \) is the Mott's characteristic temperature, which can be expressed in terms of the density of states in the vicinity of Fermi energy, \( N(E_F) \) and localization length, \( a \), as follows:

\[ T_0 = \frac{18}{k_B N(E_F) a^3} \]  

(7.2)

where \( k_B \) is the Boltzmann's constant.

The mean hopping distance, \( R_h(T) \), and hopping energy, \( E_h(T) \), can be written at a given temperature \( T \), as [29]

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The effect of disorder-induced localization on the electrical transport behavior can be understood by fitting the resistivity data using the Mott's VRH model [30]. The fitted plots for MF0 and MF2 are shown in Fig. 7.7 (a) and (b) respectively, revealing that the data fit very well with the VRH model for the limited range of temperature as shown in Table 7.2 suggesting that the conduction is accompanied by the disorder-induced localization of charge carriers.

Using the fitted values of $T_0$ obtained from the above equations, we have calculated the values of $N(E_F)$, $R_h$ and $E_h$ at room temperature (300K) by taking the localization length, $a \approx 4.5 \, \text{Å}$, as reported by Viret et al. [8] for such type of materials. The calculated values of $N(E_F)$, $R_h$ and $E_h$ for MF0 and MF2 samples at 0 T and 8 T magnetic fields are tabulated in Table 7.2. It is quite clear from Table 7.2 that the density of states at the Fermi level, $N(E_F)$, decreases which corresponds to decrease in conductivity, while the hopping distance ($R_h$) and hopping energy ($E_h$) increase as the Fe concentration goes from 0% to 2% at all temperatures.

Fig. 7.7: (a) Plots of Inp versus $T^{1/4}$ for samples MF0 and MF2 at 0T (b) Plots of Inp versus $T^{1/4}$ for samples MF0 and MF2 at 8T.
However, for the samples MF0 and MF2, as the magnetic field increases, $N(E_F)$ increases (Table 7.2) and such a high value of $N(E_F)$ was also estimated by other researchers [8,31,32] which is due to higher conductivity of these oxides than those of the usual transition-metal-oxide semiconductors [31,33] whereas $R_h$ and $E_h$ decrease at all temperatures, which also suggests increase in conductivity of both samples. Moreover, we can also observe from Table 7.2 that $R_h$ decreases with increasing temperature at both fields for MF0 and MF2 whereas $E_h$ increases with increasing temperature at both fields for MF0 and MF2. The variation in the values of $\rho_0$ estimated from Eq. (7.1) is also shown in Table 7.2, depending on Fe concentration and different fields. These observations suggested that the samples MF0 and MF2 obey the VRH model over a limited range of temperature as shown in Table 7.2. This indicates that the electronic properties of a system are driven by the induced distortion effects due to the presence of two different valent transition-metal elements (Mn and Fe).

Table 7.2: The estimated values of resistivity at room temperature, density of states at the Fermi level, $N(E_F)$, the hopping distance, $R_h$, and the hopping energy, $E_h$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Field (T)</th>
<th>$\rho$(300K)$\times10^{-4}$ (m$\Omega$-cm)</th>
<th>$\rho_0$ (m$\Omega$-cm$\times10^{16}$)</th>
<th>$N(E_F)$ (eV$^{-1}$m$^{-3}$$\times10^{25}$)</th>
<th>$R_h$ (Å)</th>
<th>$E_h$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100 K</td>
<td>150 K</td>
</tr>
<tr>
<td>MF0</td>
<td>0</td>
<td>29.84</td>
<td>3458</td>
<td>5.99</td>
<td>41.97</td>
<td>37.92</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>28.61</td>
<td>2870000</td>
<td>11.23</td>
<td>35.86</td>
<td>32.4</td>
</tr>
<tr>
<td>MF2</td>
<td>0</td>
<td>22.65</td>
<td>20.97</td>
<td>4.07</td>
<td>46.22</td>
<td>41.78</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>22.01</td>
<td>563.4</td>
<td>5.43</td>
<td>43.01</td>
<td>38.86</td>
</tr>
</tbody>
</table>

Another attempt was also made to confirm the nature of hopping conduction and observe the strength of electron-phonon interaction. We have fitted the temperature dependent resistivity data using the small polaron hopping (SPH) model proposed by Mott and Davis [34]. It has been found that the high temperature transport properties of rare-earth transition metal oxide (RETMO) systems are...

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dominated by the thermally activated hopping of small polarons [35,36]. According to the SPH model, the expression for the electrical resistivity is given by

$$\rho = \rho_{a} \exp \left( \frac{E_{p}}{k_{b}T} \right)$$

(7.4)

where $\rho_{a} = \left[ k_{B}v_{ph}N_{e}R^{2}C(1-C) \right] \exp(2\alpha R)$, $k_{B}$ is the Boltzman constant, $E_{p}$ is the activation energy, and $T$ is the absolute temperature. $N$ is the number of ion sites per unit volume, $R$ is the average intersite spacing obtained from the relation $R = (1/N)^{1/3}$, $C$ is the fraction of sites occupied by the polaron, $\alpha$ is the electron wave function decay constant obtained from fitting the experimental resistivity data and $v_{ph}$ is the optical phonon frequency ($v_{ph} = k_{B}\theta_{D}/\hbar$). The activation energy, $E_{p}$, given by [37]

$$E_{p} = W_{H}^{+} W_{D}/2 \text{ (for } T < \theta_{D}/2)$$

$$= W_{D} \quad \text{ (for } T < \theta_{D}/4)$$

(7.5)

where $W_{H}$ is the polaron hopping energy, $W_{D}$ is the disorder energy and $\theta_{D}$ is the Debye temperature.

In order to calculate the hopping energy we re-plotted the resistivity curves as $\ln (\rho/T)$ versus $1/T$ shown in Fig. 7.8 (a) and (b). From the slope of the straight line curve above $\theta_{D}/2$, we have calculated the activation energy $E_{p}$ for samples MF0 and MF2 (given in Table 7.3). Fig. 7.8 (a) and (b) show the temperature dependence of activation energy above the respective values of $\theta_{D}/2$ (high temperature linear part). The values of $\theta_{D}/2$ are estimated ($\theta_{D}$ given in Table 7.3 for MF0 and MF2 samples) from the temperature where deviation from linearity occurs in the high temperature region, as shown in Figs. 7.8 (a) and (b). It is clear from Table 7.3 that $\theta_{D}$ decreases and the activation energy $E_{p}$ increases with the increase in Fe doping. It is obvious that with the increase of Fe concentration, Mn$^{3+}$/Mn$^{4+}$ ratio decreases (as Fe$^{3+}$ takes the place of Mn$^{3+}$ ions) and hence the effective ferromagnetic double-exchange (FMDE) interaction between Mn$^{3+}$ and Mn$^{4+}$ becomes weaker and because of this, the number of $e_{g}$ electrons of Mn$^{3+}$ ions become more localized which increase the activation energy [27]. We have calculated the corresponding field dependent activation energy shown in Table 7.3. It is observed that for each concentration ($x$), $\theta_{D}$ increases while $E_{p}$ decreases gradually as the magnetic field increases which can be...
explained on the basis of delocalization of $e_g$ electrons due to the application of magnetic field.

![Graphs showing plots of $\ln(p/T)$ versus $1/T$ for samples MF0 and MF2 at 0T and 8T.](image)

Fig. 7.8: (a) Plots of $\ln(p/T)$ versus $1/T$ for samples MF0 and MF2 at 0T. (b) Plots of $\ln(p/T)$ versus $1/T$ for samples MF0 and MF2 at 8T.

Table 7.3: Some important estimated parameters at different fields. $\theta_D$ is the Debye temperature, $v_{ph}$ is the optical phonon frequency, $E_P$ is the activation energy, $W_D$ is the disorder energy, $W_H$ is the hopping energy and $\gamma_p$ is the electron-phonon interaction constant.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Field (T)</th>
<th>$\theta_D$ (K)</th>
<th>$v_{ph} \times 10^{11}$ (Hz)</th>
<th>$E_P$ (meV) ($T&gt;\theta_D/2$)</th>
<th>$W_D$ (meV) ($T&lt;\theta_D/4$)</th>
<th>$W_H$ (meV)</th>
<th>$\gamma_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MF0</td>
<td>0</td>
<td>414.08</td>
<td>86.58</td>
<td>132.44</td>
<td>131.48</td>
<td>66.7</td>
<td>3.73</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>431.42</td>
<td>90.21</td>
<td>125.25</td>
<td>42.59</td>
<td>103.96</td>
<td>5.58</td>
</tr>
<tr>
<td>MF2</td>
<td>0</td>
<td>374.54</td>
<td>78.31</td>
<td>134.48</td>
<td>98.02</td>
<td>85.47</td>
<td>5.29</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>383.36</td>
<td>80.16</td>
<td>126.66</td>
<td>33.94</td>
<td>109.69</td>
<td>6.63</td>
</tr>
</tbody>
</table>

...142...
To confirm whether the hopping is adiabatic or non-adiabatic, we make use of the Holstein's condition [38]. According to this criterion the polaron band width $J$ should satisfy the following conditions:

$$J > \Phi \text{ (for adiabatic condition)}$$

and

$$J < \Phi \text{ (for non-adiabatic condition)}$$  \hspace{1cm} (7.6)

where

$$\Phi = (2 k_B T W_H/\pi)^{1/4}(\nu_{\text{ph}}/\pi)^{1/2}$$  \hspace{1cm} (7.7)

Using the values of $W_H$ and $\nu_{\text{ph}}$ from Table 7.3, we have estimated the values of $\Phi$ for MF0 and MF2 respectively for different temperature ranges at different fields (given in Table 7.4). The $J$ values were calculated independently applying the relation [38]

$$J(T) = 0.67 \nu_{\text{ph}} (T/\theta_D)^{1/4}$$  \hspace{1cm} (7.8)

Using the values of $\nu_{\text{ph}}$ and $\theta_D$ from Table 7.3, the calculated values of $J(T)$ for MF0 and MF2 samples are given in Table 7.4.

**Table 7.4: Estimated values of $\Phi$ and $J(T)$ at different temperatures and fields.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Field (T)</th>
<th>Parameters of MF0 &amp; MF2 at different temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>At 5K</td>
</tr>
<tr>
<td>$\Phi$ (meV)</td>
<td>0</td>
<td>MF0</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>6.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$J &gt; \Phi$</td>
</tr>
<tr>
<td>$J$ (T) (meV)</td>
<td>0</td>
<td>7.94</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>8.19</td>
</tr>
</tbody>
</table>
On comparing the values of $J$ and $\Phi$ at 0 T (Table 7.4), it can be seen that the condition $J > \Phi$ is well satisfied for the samples MF0 and MF2 in the temperature range 5–300 K, suggesting an adiabatic type of conduction. But for the doped sample MF2 at 300K (Table 7.4), the condition $J < \Phi$ is satisfied corresponding to a non-adiabatic type of conduction. At 8 T magnetic field, the condition $J > \Phi$ is satisfied in the entire temperature range for MF0 which corresponds to an adiabatic conduction while for the sample MF2, the condition $J < \Phi$ is satisfied in the entire temperature range, corresponding to a non-adiabatic type of conduction. Therefore, in the presence of magnetic field, the hopping conduction process is switching from adiabatic type to non-adiabatic type as we go from undoped sample to doped one. This type of change in conduction process is due to the substantial effect of magnetic field on spin alignment and anisotropic energy in Fe content sample.

Finally, the electron-phonon (e'-ph) coupling constant ($\gamma$) of the samples was calculated using the relation [34,36], $\gamma = W_{hh}/h\gamma_{ph}$. The theoretical calculations of $\gamma$ given by Millis et al. [39] suggest that if $\gamma$ is greater than 4, there are strong electron-phonon interactions present in the system, otherwise the interactions are weak. Thus, electron-phonon coupling constant, $\gamma$, is the crucial parameter in controlling the various properties of the sample. From the Table 7.3, for the samples MF0 and MF2 respectively, the values of $\gamma$ are found to be more than 4 almost for both samples at both fields except for the sample MF0 at 0 T magnetic field. This confirms the strong electron-phonon interactions in the samples. Moreover, for MF0 (Table 7.3), the values of $\gamma$ alters from 3.73 (at 0 T) to 5.58 (at 8T) and for MF2 (Table 7.3), the same alters from 5.29 (at 0 T) to 6.63 (at 8 T). This suggests that the strength of e'-ph interaction increases with the increase in both Fe content and magnetic field which results in localization of charge carriers or overall hopping potential. It has been shown that the electrical transport properties are closely related to the structural distortion and in particular to the arrangement of MnO$_6$ or (Mn,Fe)O$_6$ octahedra. This distortion modifies the superexchange angle Mn–O–Fe or Fe–O–Fe and bond length which drives the O(2p) and (Mn,Fe) (3d) bands to overlap and control the closing and opening of the charge transfer gap. Moreover, in the case of the orthorhombic lattice, the bond angle varies continuously with tolerance factor, as the ionic radii of Mn and Fe are different and by the doping of Fe, it modifies the octahedra of MnO$_6$. Thus we believe that it creates significant change in bond...
length/bond angle. The relation between the bond angle distortion and the tolerance factor shows little B-site dependence, and hence is likely to be applicable to doped manganites [40].

7.3.3. Magnetic Properties

Fig. 7.9 shows the temperature dependence of dc-magnetization (M–T) of the samples MF0 and MF2 measured in a magnetic field of 1T during the warming up process, after being zero field cooled (ZFC) from 310 K to 10 K. The inset of this figure shows the temperature dependent dc-susceptibility (χ–T).

![Graph of M-T plots for samples MF0 and MF2 in ZFC mode. Inset shows the variation in susceptibility as a function of temperature.](image)

The Curie temperature \( T_C \) values, determined from the maximum point in the \( dM/dT \) or \( d\chi/dT \), are 190.90 K and 183.24 K for MF0 and MF2 samples respectively. There is a monotonous decrease in \( T_C \) for both samples as compared to the earlier reported results [41]. For the samples MF0 and MF2, the paramagnetic (PM) state to FM state transition is narrow, corresponding to a wider distribution of exchange interactions in the Mn–O network.

The analysis of high-temperature dc susceptibilities (\( \chi = M/H \)) of the samples studied was performed using the Curie–Weiss (CW) law:

\[
\chi(T) = \frac{C}{T-\theta}
\]

(9)
where the Curie constant \( C = \left( \frac{1}{3k_B} \right) \mu_{\text{eff}}^2 \), \( \mu_{\text{eff}}(S) = \mu_B g \sqrt{S(S+1)} \) is the effective magnetic moment and \( \theta \) is the paramagnetic CW temperature. The fitting of the experimental \( 1/\chi(T) \) dependences on the linear function \( 1/\chi(T) \) from (9) has shown that the temperature dependences of the inverse susceptibility are linear for the paramagnetic phase and obey the CW law as shown in Fig. 7.10 (a) and (b). The CW temperatures, \( \theta \), calculated as a result of the fitting of CW law to the experimental data, were found to have a positive sign that is an indication of dominant ferromagnetic interactions. The \( \theta \) and \( T_C \) values for the samples studied are summarized in Table 7.5.

![Graphs showing 1/\chi versus T for MF0 and MF2 samples.](image)

**Fig. 7.10: The plots of 1/\chi versus T fitted with Curie-Weiss Law for (a) MF0 and (b) MF2 samples.**

**Table 7.5: Evaluated magnetic parameters.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \theta ) (K)</th>
<th>( T_C ) (K)</th>
<th>( M_S ) (emu/gm)</th>
<th>( H_C ) (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MF0</td>
<td>225.19</td>
<td>190.90</td>
<td>10 K</td>
<td>300 K</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>38.64</td>
<td>17.09</td>
</tr>
<tr>
<td>MF2</td>
<td>235.44</td>
<td>183.24</td>
<td>32.17</td>
<td>10.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>228.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>13.85</td>
</tr>
</tbody>
</table>
The field dependence of magnetization (M–H) of both samples at 10 K is shown in Fig. 7.11. As it shows, the samples have a ferromagnetic behavior with a small hysteresis loop (shown as magnified part of hysteresis loop in Fig. 7.12) and low coercivity. For better understanding the magnetic behavior of both samples, we have plotted the well-known Arrott-Belov-Kouvel (ABK) plots (M^2 versus H/M) as shown in Fig. 7.13. ABK plots show a strong convex curvature at 10K for both samples with a finite spontaneous magnetization which is a signature of ferromagnetic phase of the samples [42,43].

Fig. 7.11: M–H plots for the samples MF0 and MF2 at 10 K.

Fig. 7.12: Magnified part of the hysteresis loop for the samples MF0 and MF2 at 10 K.
**Fig. 7.13:** ABK plots for the samples MF0 and MF2 at 10 K.

The field dependence of magnetization (M-H) of both samples at 300 K is shown in Fig. 7.14. Both samples show a ferromagnetic behavior with a small hysteresis loop (shown as magnified part of hysteresis loop in Fig. 7.15) and low coercivity. To understand the magnetic behavior of both samples in a better way, we have plotted the ABK plots ($M^2$ versus $H/M$) as shown in Fig. 7.16. Here in this case, the ABK plots reveal that the strong convex curvature is shown only by the MF0 sample.

**Fig. 7.14:** M-H plots for the samples MF0 and MF2 at 300 K.
Fig. 7.15: Magnified part of the hysteresis loop for the samples MF0 and MF2 at 300 K.

Fig. 7.16: ABK plots for the samples MF0 and MF2 at 300 K.

Moreover, the values of spontaneous magnetization ($M_s$) and coercivity ($H_c$) at 300 K are lower than at 10 K for both the samples (see Table 7.5). The lower value of coercivity ($H_c$) at the higher temperatures (300K) corresponds to the soft magnetic nature of the studied samples.
7.4. Conclusions

The structural, electrical transport and magnetic behavior of undoped \( \text{La}_{0.33}\text{Sr}_{0.67}\text{MnO}_3 \) (MF0) and Fe ion doped \( \text{La}_{0.33}\text{Sr}_{0.67}\text{MnO}_3 \) (MF2) samples prepared by solid-state reaction-route have been investigated. Summarizing the experimental results, the following conclusions can be drawn: (i) in the doped sample, the Mn ion site is successfully substituted by Fe ions, both the samples are found to possess rhombohedral crystal symmetry and space group R-3c confirmed by Rietveld refinement; (ii) the surface morphology of the samples investigated by SEM reveals that the doped sample (MF2) has well connected grains, more grain size and less porosity comparing with the undoped sample (MF0). The presence of all the corresponding elements is confirmed by EDS for both samples; and (iii) both samples show the semiconducting behavior in the entire temperature range favoured by decreasing resistivity with increasing temperature. (iv) The VRH model is found to be valid for limited range of temperature. The density of states at Fermi level \( N(E_F) \) decreases whereas hopping distance \( R_h \) and hopping energy \( E_h \) increase for doped sample in the entire temperature range. But with the effect of magnetic field, \( N(E_F) \), increases, while \( R_h \) and \( E_h \) decrease for each sample in the entire temperature range. (v) The SPH model is valid in the temperature range from 212 K to 300 K for undoped sample at both fields and from 192 K to 300 K for the doped sample at both fields. Except at 300 K for doped sample, there is an adiabatic small polaron hopping conduction for both samples at 5K and 100 K at 0 T while there is a switching from adiabatic to non-adiabatic small polaron hopping conduction from undoped to doped sample in the entire temperature range at 8 T. (vi) From M–T measurements, it is found that \( T_C \) decreases with Fe doping; the CW law is fitted well with M–T data. The CW temperatures, \( \theta \), are found to have a positive value which confirms the dominant ferromagnetic behavior for the studied samples and the M–H measurements at 10 K and 300 K respectively show that both the samples are found to have a ferromagnetic behavior with a small hysteresis loop and low coercivity confirmed by ABK plots.
References:


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Chapter 8

Conclusions and Future Plan
Zn doped $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ and Fe doped $\text{La}_{0.33}\text{Sr}_{0.67}\text{MnO}_3$ compounds were synthesized by Standard Solid-State Reaction-Route and Sol-Gel Route. Effects of doping on structural, microstructural, electrical and magnetic properties have been carried out. Structural and Microstructural analysis were done by utilizing X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) equipped with an energy dispersive X-ray spectrometer (EDS) and Transmission Electron Microscopy (TEM). Electrical and Magneto-resistance properties have been studied by Four-Probe Resistivity set up while the Magnetic properties have been investigated by using Vibrating Sample Magnetometer (VSM) and a SQUID magnetometer. According to the results obtained during the course of this work, the key conclusions for the studied compounds are summarized as follows:

8.1. 10% and 20% Zn doped at Mn site in $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ manganite samples prepared by Solid-State Reaction-Route

1. XRD patterns confirm that the Zn ions are successfully substituted at Mn site having orthorhombic crystal symmetry with $\text{Pnma}$ space group.

2. SEM micrographs illustrate that the particles of the 20% Zn doped sample are in better and clear shape than those of the 10% Zn doped sample, revealing that increase in Zn doping could improve the crystallization of the sample.

3. The resistivity data confirms that both sample show metal to semiconducting (M–S) transition and the M–S transition temperature is shifted towards the higher temperature value with the effect of increasing magnetic field.

4. For the 10% Zn doped sample except at 300 K and 1 T magnetic field, the magnetoresistance is found to be negative in the entire temperature range while for 20% Zn doped sample it can be seen only up to 150 K.

5. Strong decrease of the Curie temperature ($T_c$) is observed because of suppression of ferromagnetism due to the Zn doping at Mn site.

6. The variable range hopping (VRH) model is found to be valid for limited range of temperature for both samples. The density of states at Fermi level $N(E_F)$ decreases whereas hopping distance ($R_h$) and hopping energy ($E_h$) increase with increase in Zn concentration from 10% to 20%.
7. But with the effect of enhancing the magnetic field, N(E_M), increases, while R_b and E_b are found to decrease for each sample.

8. The adiabatic small polaron hopping (SPH) conduction is observed for 10% Zn doped sample whereas the non-adiabatic small polaron hopping conduction is found to be active for 20% Zn doped sample in the temperature range 5–300 K at all fields.

9. The activation energies and the electron–phonon coupling constant enhances due to enhancement in bandwidth with Zn ion doping for both samples at all fields.

8.2. 10% and 20% Zn doped at Mn site in La_{0.67}Sr_{0.33}MnO_3 manganite samples prepared by Sol-Gel Route

1. The successful partial substitution of Zn ions at Mn site is confirmed by XRD patterns.

2. All samples are found to have rhombohedral crystal symmetry with space group R̅(3c).

3. SEM images at 10 μm scale and 1000 magnification reveal that the particles of all the samples seem to be agglomerated, well connected and nanofibres type of structure is formed.

4. The particles have no clear grain boundaries and pores can be seen throughout in all samples.

5. The agglomeration process is affected by the increasing doping level of Zn, leading to a bigger particle and also influences the growth and nucleation process of the nanosized crystallites.

6. TEM images reveal the very clear surface of nanoparticles and the particle size distribution is almost uniform in all the samples which is analyzed by the Image J software.

7. An abundance of nearly spherical particles is found with the particle sizes 11 nm, 14 nm and 13 nm respectively for pure, 10% and 20% Zn doped samples estimated through the Image J software.
8. The particle sizes obtained by TEM are in well agreement with the crystallite sizes obtained by XRD.

9. The composition and uniform distribution of all the elements in the respective samples have been confirmed by the energy dispersive spectra.

10. All the studied samples show the superparamagnetic behavior.

11. No coercivity is shown by the recorded hysteresis loops of all samples.

12. Magnetizations do not saturate up to the available field of 1.8 Tesla.

13. The investigated magnetic properties are consistent with the XRD, SEM and TEM results.

8.3 2% Fe doped at Mn site in La$_{0.33}$Sr$_{0.67}$MnO$_3$ manganite samples prepared by Solid-State Reaction-Route

1. In the Fe doped sample, the Mn ion site is successfully substituted by Fe ions, both the samples are found to possess rhombohedral crystal symmetry and space group R-3c confirmed by Rietveld refinement.

2. The surface morphology of the samples investigated by SEM reveals that the Fe ion doped sample has well connected grains, more grain size and less porosity comparing with the undoped sample. The presence of all the corresponding elements is confirmed by EDS for both samples.

3. Both samples show the semiconducting behavior in the entire temperature range favoured by decreasing resistivity with increasing temperature.

4. The VRH model is found to be valid for limited range of temperature. The density of states at Fermi level $N(E_f)$ decreases whereas hopping distance $R_h$ and hopping energy $E_h$ increase for Fe ion doped sample in the entire temperature range. But with the effect of enhancing the magnetic field, $N(E_f)$ increases, while $R_h$ and $E_h$ decrease for each sample in the entire temperature range.

5. The SPH model is valid in the temperature range from 212 K to 300 K for undoped sample at both fields and from 192 K to 300 K for the Fe ion doped
sample at both fields. Except at 300 K for Fe ion doped sample, there is an adiabatic small polaron hopping conduction for both samples at 5K and 100 K at 0 T while there is a switching from adiabatic to non-adiabatic small polaron hopping conduction from undoped to Fe ion doped sample in the entire temperature range at 8 T.

6. From M–T measurements, it is found that Tc decreases with Fe doping; the Curie-Weiss (CW) law is fitted well with M–T data. The CW temperatures, θ, are found to have a positive value which confirms the dominant ferromagnetic behavior for the studied samples and the M–H measurements at 10 K and 300 K respectively show that both the samples are found to have a ferromagnetic behavior with a small hysteresis loop and low coercivity confirmed by ABK plots.

Planned future work

Nowadays, doped perovskite manganites with ferromagnetic character seem to be promising candidates for magnetic hyperthermia applications in biomedical sciences. So, encouraged by above results of our study, we are planning to continue our research work in this direction with particular focus on hyperthermia. Due to the unique properties, the perovskite type magnetic nanomaterials offer an outstanding biocompatibility and multi-purpose biomedical potential. Magnetic hyperthermia is thought to be a promising approach for the cancer treatment by using magnetic nanoparticles. Hyperthermia based on heat generation of magnetic nanoparticles, is a novel non-invasive approach for the ablation of tumor, such as superparamagnetic iron oxide nanoparticles, when subjected to an alternating magnetic field. The perovskite nanomaterials such as strontium (Sr) doped LaMnO₃ are thought to be a promising candidate for the magnetic hyperthermia due to their various physical properties and technology applications. But these magnetic nanoparticles can not be used directly for the treatment of cancer as they may be toxic and harm the body. So, the toxicity of these nanoparticles before use in this application should be properly investigated.
LIST OF PUBLICATIONS
PAPERS PUBLISHED IN INTERNATIONAL REFEREED JOURNALS:

- “Study of structural, electrical and magnetic properties of Zn doped La$_{0.67}$Sr$_{0.33}$MnO$_3$”; Hilal Ahmed, Shakeel Khan, Wasi Khan, Razia Nongjai and Imran Khan, J. Alloy Compd. 527 (2012) 48-52.


- “Adiabatic to non-adiabatic change in conduction mechanism of Zn doped La$_{0.67}$Sr$_{0.33}$MnO$_3$ perovskite”; Hilal Ahmed, Shakeel Khan, Wasi Khan, Razia Nongjai, Imran Khan, J. Alloy Compd. 563 (2013) 12–17.


- “Ferromagnetism and adiabatic to non-adiabatic switching process in La$_{0.33}$Sr$_{0.67}$Mn$_{1-x}$Fe$_x$O$_3$ (0 ≤ x ≤ 0.02) manganite”; Hilal Ahmed, Shakeel Khan, Wasi Khan, Razia Nongjai, Imran Khan, J. Magn. Magn. Mater. 368 (2014) 273–280.

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➢ “Structural and Magnetic Properties of La_{0.67}Sr_{0.33}Mn_{0.93}Zn_{0.07}O_3 Manganite”; Hilal Ahmed, Shakeel Khan, Wasi Khan, Razia Nongjai and Imran Khan, International Journal of Modern Physics: Conference Series, 22 (2013) 203-206.


➢ “Variation in band gap of lanthanum chromate by transition metals doping LaCr_{0.9}A_{0.1}O_3 (A:Fe/Co/Ni)”; Swaleha Naseem, Wasi Khan, A. A. Saad, M. Shoeb, Hilal Ahmed, Shahid Husain, and A. H. Naqvi, AIP Conference Proceedings, 1591 (2014) 259.