Studies of structures, transport and magnetic properties of doped novel three-dimensional perovskite compounds

Mohammad Mehdi Farhoudi
University of Wollongong
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Studies of Structures, Transport and Magnetic Properties of Doped Novel Three-Dimensional Perovskite Compounds

A Thesis Submitted
In Partial Fulfillment of the Requirements For
The Award of the Degree of

Doctor Of Philosophy

From the
University Of Wollongong

By:

Mohammad Mehdi Farhoudi

Institute for Superconducting and Electronic Materials
University Of Wollongong

2009
DECLARATION

I, Mohammad Mehdi Farhoudi, declare that this thesis, submitted in partial fulfillment of the requirements for the award of Doctor of Philosophy, in the Institute for Superconducting & Electronic Materials (ISEM), Faculty of Engineering, University of Wollongong, Australia, is wholly my own work unless otherwise referenced or acknowledged. This document has not been submitted for a qualification at any other academic institution.

Mohammad Mehdi Farhoudi

Date:
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## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AC</td>
<td>Alternating Current</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>AFMI</td>
<td>Antiferromagnetic insulator</td>
</tr>
<tr>
<td>ANSTO</td>
<td>Australian Nuclear Science and Technology Organisation</td>
</tr>
<tr>
<td>CMR</td>
<td>Colossal Magnetoresistance</td>
</tr>
<tr>
<td>CW</td>
<td>Curie-Weiss</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>DTGS</td>
<td>Deuterated Tri-Glycine Sulfate</td>
</tr>
<tr>
<td>FC</td>
<td>Field cooled</td>
</tr>
<tr>
<td>FIR</td>
<td>Far-infrared</td>
</tr>
<tr>
<td>FMM</td>
<td>Ferromagnetic metal</td>
</tr>
<tr>
<td>GMR</td>
<td>Giant Magnetoresistance</td>
</tr>
<tr>
<td>ICDD</td>
<td>International Centre for Diffraction Data</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>M</td>
<td>Magnetization</td>
</tr>
<tr>
<td>ME</td>
<td>Magneto-electric</td>
</tr>
<tr>
<td>MPMS</td>
<td>Magnetic Properties Measurement System</td>
</tr>
<tr>
<td>MR</td>
<td>Magnetoresistance</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>PMI</td>
<td>Paramagnetic insulator</td>
</tr>
<tr>
<td>PPMS</td>
<td>Physical Properties Measurement System</td>
</tr>
<tr>
<td>PVR</td>
<td>Polyhedral volume ratio</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>SRRC</td>
<td>Synchrotron Radiation Research Centre (Taiwan)</td>
</tr>
<tr>
<td>TRM</td>
<td>Thermal Remnant Magnetization</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>XANES</td>
<td>X-ray absorption near-edge structure spectroscopy</td>
</tr>
<tr>
<td>ZFC</td>
<td>Zero-field cooled</td>
</tr>
</tbody>
</table>
### Notations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Cross-sectional area</td>
</tr>
<tr>
<td>$B_a$</td>
<td>Applied field</td>
</tr>
<tr>
<td>$B_E$</td>
<td>Finite exchanger field</td>
</tr>
<tr>
<td>C</td>
<td>Curie constant</td>
</tr>
<tr>
<td>E</td>
<td>Potential energy</td>
</tr>
<tr>
<td>$E_c$</td>
<td>Magneto-crystalline energy</td>
</tr>
<tr>
<td>$E_d$</td>
<td>Neighboring dipoles effect</td>
</tr>
<tr>
<td>$E_z$</td>
<td>Zeeman energy</td>
</tr>
<tr>
<td>$G_{ij}$</td>
<td>$\frac{1}{r_{ij}}(3r_{ij}r_{ij} - I)$ Two index tensors depend on the geometry of the dipole system</td>
</tr>
<tr>
<td>H</td>
<td>Magnetic field</td>
</tr>
<tr>
<td>I</td>
<td>Current /unit tensor</td>
</tr>
<tr>
<td>$I(\omega)$</td>
<td>Transmitted intensity through the pellet containing the holmium manganese oxide</td>
</tr>
<tr>
<td>$I_0(\omega)$</td>
<td>Transmitted intensity through pure CsI pellet</td>
</tr>
<tr>
<td>K</td>
<td>Anisotropy constant</td>
</tr>
<tr>
<td>$K_1,K_2$</td>
<td>Experimental constants</td>
</tr>
<tr>
<td>L</td>
<td>Distance between inner contacts (poles)</td>
</tr>
<tr>
<td>$O_d(\omega)$</td>
<td>Optical density</td>
</tr>
<tr>
<td>R</td>
<td>Measured resistance / Various rare earth elements</td>
</tr>
<tr>
<td>$R^2$</td>
<td>Coefficient for best fit</td>
</tr>
<tr>
<td>$S_j$</td>
<td>Oscillator strength of $j$th oscillator</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>$T_B$</td>
<td>Blocking Temperature</td>
</tr>
<tr>
<td>$T_c$</td>
<td>Curie temperature</td>
</tr>
<tr>
<td>$T_N$</td>
<td>Neel temperature</td>
</tr>
<tr>
<td>$T_0$</td>
<td>Spin freezing temperature for spin glass state</td>
</tr>
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<td>Notations</td>
<td>Description</td>
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<td>------------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>( V )</td>
<td>Particle volume</td>
</tr>
<tr>
<td>( v )</td>
<td>Voltage</td>
</tr>
<tr>
<td>( a, b, c )</td>
<td>Lattice parameters</td>
</tr>
<tr>
<td>( a^3 )</td>
<td>Average volume of particle</td>
</tr>
<tr>
<td>( e_g )</td>
<td>Delocalized electrons</td>
</tr>
<tr>
<td>( f )</td>
<td>Frequency</td>
</tr>
<tr>
<td>( f_0 )</td>
<td>Larmor frequency ( \tau_0 = \frac{1}{2\pi f_0} )</td>
</tr>
<tr>
<td>( f_o )</td>
<td>Functional parameter dependent on doping level</td>
</tr>
<tr>
<td>( f_c )</td>
<td>Characteristic frequency</td>
</tr>
<tr>
<td>( k_B )</td>
<td>Boltzmann's constant</td>
</tr>
<tr>
<td>( \bar{m} )</td>
<td>Net magnetization</td>
</tr>
<tr>
<td>( m )</td>
<td>Moment</td>
</tr>
<tr>
<td>( r )</td>
<td>Atomic radius</td>
</tr>
<tr>
<td>( \vec{r}_j )</td>
<td>Position vector</td>
</tr>
<tr>
<td>( \hat{s}_j )</td>
<td>Unit spin vector of a dipole</td>
</tr>
<tr>
<td>( t_{2g} )</td>
<td>Localized spins</td>
</tr>
<tr>
<td>( t_{ij} )</td>
<td>Transfer integral</td>
</tr>
<tr>
<td>( \Delta_c )</td>
<td>The crystal field splitting</td>
</tr>
<tr>
<td>( \Omega )</td>
<td>Sample resistance</td>
</tr>
<tr>
<td>( \chi )</td>
<td>Susceptibility</td>
</tr>
<tr>
<td>( \chi )</td>
<td>magnetic susceptibility</td>
</tr>
<tr>
<td>( \chi' )</td>
<td>Real part of ac susceptibility</td>
</tr>
<tr>
<td>( \chi'' )</td>
<td>imaginary part of ac susceptibility</td>
</tr>
<tr>
<td>( \chi'_0 )</td>
<td>Functional parameter dependent on doping level</td>
</tr>
<tr>
<td>( \beta )</td>
<td>Functional parameter dependent on doping level</td>
</tr>
<tr>
<td>( \delta )</td>
<td>Doping level</td>
</tr>
<tr>
<td>( \delta E )</td>
<td>Energy from the ground state</td>
</tr>
<tr>
<td>( \phi )</td>
<td>Angle between the magnetization direction and the normal to the dense-packed plane dipole</td>
</tr>
<tr>
<td>Notations</td>
<td>Description</td>
</tr>
<tr>
<td>-----------</td>
<td>-------------</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Constant</td>
</tr>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>Effective magnetic moment</td>
</tr>
<tr>
<td>$\mu_B$</td>
<td>Bohr magnetron</td>
</tr>
<tr>
<td>$\omega_f$</td>
<td>Frequency</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Resistivity</td>
</tr>
<tr>
<td>$\rho_o$</td>
<td>Resistivity of the sample at zero magnetic field</td>
</tr>
<tr>
<td>$\rho_H$</td>
<td>Resistivity of the sample under magnetic field</td>
</tr>
<tr>
<td>$\sigma(\omega)$</td>
<td>Optical conductivity</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Angle</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Decay rate</td>
</tr>
<tr>
<td>$\tau_o$</td>
<td>Constant that is related to $f_o$</td>
</tr>
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Abstract

Perovskite oxide compounds have generated a great amount of interest over the past twenty years, as they exhibit exotic magnetic, electric, and magnetolectric properties, which, apart from their intrinsic interest, would have a wide range of applications in industry, with special utilization in the engineering of data storage devices.

Starting with a general definition of the perovskite structure of ABO$_3$ materials, the magnetic and transport properties of cobalt and manganese based compounds are reviewed. The objective of this thesis is focused on the investigation of the structures, and the magnetic and transport properties of some typical cobalt or manganese based three-dimensional perovskite compounds doped with various elements.

Polycrystalline samples of RE$_{1-x}$Sr$_x$CoO$_3$ (RE = Gd, Nd, Ho, Y, and Dy), REM$_x$Co$_{1-x}$O$_3$ (RE = Gd and Ho), and La$_{0.33}$Sr$_{0.66}$Fe$_{1-x}$Cr$_x$O$_3$ were fabricated and characterized in detail using X-ray diffraction, Rietveld structural refinement, magnetic and transport measurements, X-ray absorption near-edge (XANES) spectroscopy, and far-infrared (FIR) spectroscopy.

Perovskite GdCo$_{1-x}$Mn$_x$O$_3$ ($x = 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8$) compounds were prepared by solid-state reaction. Structures were characterized using X-ray
diffraction and the Rietveld refinement method. The compounds crystallized in the orthorhombic structure with $P_{\text{tn}}m$ space group. Crystal lattice parameters constants decreased with increasing Mn doping level. DC magnetization and ac susceptibility were studied over a wide temperature range and different frequencies. A typical spin glass state was observed in all samples around the same temperature of 122 K, where the compounds changed from the paramagnetic to the ferromagnetic state. For $x = 0.5$, secondary transitions were observed both in dc and in ac measurements, which were independent of the frequency, but depended on the doping level. The valences of Co and Mn were estimated with possible spin states.

The structures, magnetism, giant magnetoresistance, and spin and valence states of Co ions were investigated in perovskite $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_3$ ($x = 0-0.5$) compounds synthesized by a solid state reaction method. Results showed that all the samples are ferromagnetic around 150 K, and the magnetization and coercive field increase with the Sr doping level. A spin glass state was observed. Furthermore, the resistivity drops systematically with $x$. Giant magnetoresistance of over 60% was observed for the $\text{Gd}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ sample. Spin state assessment indicates that the $\text{Co}^{3+}$ and $\text{Co}^{4+}$ ions are present in intermediate and high spin states.

Polycrystalline perovskites compounds $\text{HoMn}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0-0.8$) were prepared by conventional solid-state reaction. Rietveld refinement indicated that, instead of a hexagonal structure with $P6_3\text{cm}$ symmetry for $\text{HoMnO}_3$, the compounds doped
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with Co crystallized in the GdFeO$_3$-type orthorhombic structure containing distorted (Co/Mn)O$_6$ octahedral. The dc magnetization was measured in fields up to 5 T over a wide temperature range from 350 K down to 5 K. It was found that the system gradually changed from paramagnetic for $x = 0$ to ferromagnetic with a Curie temperature, $T_C$, of 90 K for $x = 0.5$, then to paramagnetic again for $x = 0.8$. X-ray absorption near-edge spectra (XANES) were collected to determine the valences of both Co and Mn ions. The results showed that Co and Mn were present mainly as mixed valences of Co$^{2+}$ + Co$^{3+}$, Mn$^{4+}$ + Mn$^{3+}$, Co$^{3+}$ + Co$^{4+}$, and Mn$^{4+}$, depending on the value of $x$. When the XANES results were combined with Curie-Weiss fitting, it was found that both Mn$^{4+}$ and Co$^{3+}$ were present as high spin states for $x > 0.2$, whereas, Co$^{4+}$ appeared in either intermediate or high spin states, closely corresponding to the lattice variations along the (010) direction.

HoMn$_{1-x}$Co$_x$O$_3$ ($x = 0$-0.8) compounds were also studied by far-infrared (FIR) spectroscopy in order to gain information on the infrared active phonon modes. The data indicated that phonon modes significantly changed with increasing cobalt doping level. Four main bands were assigned as external, torsional, bending, and stretching bands. The external vibration energy remained the same at 1190 cm$^{-1}$ for Co doping with $x < 0.5$ and shifted to higher energy for $x > 0.5$. The torsional and bending bands exhibited splitting. The stretching band is at 600 cm$^{-1}$ for all samples, but the bandwidth is reduced as Co doping is increased. The transmission spectrum of HoMn$_{4/5}$Co$_{1/5}$O$_3$ was analyzed to obtain the spectrum of
Abstract

the optical density. The minimum number of oscillators to obtain a reliable fit is 5, using a sum of non-interacting harmonic oscillators.

Cr doping effects on the crystal structures and magnetic properties for La$_{1/3}$Sr$_{2/3}$Fe$_{1-x}$Cr$_x$O$_3$ were studied in this work. It was observed that single phase samples with the cubic crystal structure can only form within a narrow solubility range. Magnetic measurements showed that the resulting compounds are magnetic insulators.
Chapter 1: Motivation and the structure of this thesis

One of the very promising approaches to the design of novel materials that has been under very active investigation in recent years is to combine different physical properties in one innovative compound. Perovskites are capable of accommodating different combinations of cations, so long as the crystal charge is neutral. Perovskite compounds are a family of naturally existing minerals with the general formula of ABX₃, which was discovered by Count Perovsky in the 19th century. In its idealized cubic structure, the big A cations are surrounded by 12 oxygen and small B ions. Perovskite has received intensive attention starting from 2001. Usually, when the A cation is of small size, an alteration occurs as a result of tilting in the B octahedral axis with respect to its neighbors. Generally, perovskite ceramics can exhibit magnetic, electric, magneto-electric, and sometimes magneto-elastic properties, which would have a wide range of applications in industry, such as in data storage devices.

Despite the interesting feature of the coexistence of both magnetic and electric properties in one perovskite material, the search for such materials is not so simple, and there is still a need to develop some new techniques and conduct more investigations. Designing and understanding a material that has both magnetic and electric properties are challenging achievements. Furthermore, controlling the coupling between different degrees of freedom in those properties is an even greater
problem, which necessitates acquiring knowledge of the relevant techniques through careful study of the phenomena.

Among materials with the perovskite type structure, the transition metal oxides and their layered structure families, with the formula $A_{n+1}B_nO_{1+3n}$ ($n = 1, 2, 3, \ldots$ and $B$ = an ion from the manganite group), demonstrate a wide range of interesting properties, such as high temperature superconductivity, metal-insulator transitions, and magnetic phase transitions. In recent decades, the manganites have received particular attention from scientists and researchers. This is because of the discovery of negative magnetoresistance behavior in the $La_{1-x}Sr_xMnO_3$ and $La_{1-x}Ba_{1-x}MnO_3$ crystal systems. Their unexpected changes with doping, temperature dependent transitions, and magnetic features were the main reasons for this extensive interest in recent years. In these materials, the degree of freedom of electrons in the Mn type ions plays a crucial role.

The exploration of these manganites with perovskite structure has revealed a very important role for their crystal chemistry, due to their colossal magnetoresistance (CMR). The distinguishable types of perovskite magnetites could be classified as type I, with ferromagnetic metallic (FMM) and paramagnetic insulating (PMI) materials, and type II, consisting of two transition antiferromagnetic insulating (AFMI), ferromagnetic metallic (FMM), and paramagnetic insulating (PMI) materials.
Co-based perovskite-type $\text{ABO}_3$ compounds have always been the focus of research interest due to their fascinating physical properties. Both the magnetic and the electric properties of the cobalt-based perovskite compounds depend on several factors: firstly, whether the spin states of $\text{Co}^{2+}$, $\text{Co}^{3+}$, and $\text{Co}^{4+}$ take high, intermediate, or low spin; and secondly, the existence of an indirect exchange interaction$^{1,2}$. The cobalt ions interact through intermediate oxygen, where the $\text{Co}^{3+} - \text{O}^2- - \text{Co}^{4+}$ and $\text{Co}^{3+} - \text{O}^2- - \text{Co}^{3+}$ systems have ferromagnetic and antiferromagnetic properties, respectively$^{3,4,5}$. In order to force the Co to have multivalences, such as 2+, 3+ and 4+, the most effective way is to introduce alkaline elements to replace rare earth (RE) elements on A sites. At the same time, the charge carrier concentration is increased due to the hole doping. Introducing dopant elements into the Co- and Mn-based parent perovskite will vary its existing properties in the resultant compounds. Replacing Mn with Co could result in different magnetic features, such as a transition from paramagnetic (PM) to ferromagnetic (FM), or ferromagnetic (FM) to antiferromagnetic (AFM), or in cluster-spin-glass-like and inhomogeneous ferromagnets with a specific Curie temperature. In some materials the presence of cobalt will result in highly saturated magnetization, whereas in some others it can lead to an anisotropic magnetic state. The injection of cobalt could also create double-exchange ferromagnets, in which the conductive electrons are more mobile than those in manganese. In order to induce the above mentioned magnetic states, I introduced Mn to replace Co. At the same time, the charge carrier density can remain unchanged compared to the parent Co-based $\text{ABO}_3$ compounds.

Bearing the foregoing discussion in mind, the objective of this thesis will focus on
Chapter 1

the investigation of the magnetic and transport properties of cobalt and manganese in some deliberately designed compounds of novel perovskite materials, which are investigated with various dopants and doping levels. The main structure of the research project was designed to achieve the following:

1- Starting from a literature review of the relevant papers, the properties of pervoskite composites are considered, along with the behavior of certain perovskite-structured materials. The results of this revision are highlighted in the second chapter, which also covers the governing laws and theories to be used in the analysis of the results.

2- The experimental techniques and methodologies that were then designed are explained fully in Chapter Three. Fundamentally, the aim was the observation of magnetic and electric behavior as a function of temperature. All the samples were prepared by solid state reaction. The prepared samples were subjected to X-ray diffraction (XRD) measurements prior to other experiments being carried out. A physical properties measurement system (PPMS) was used to examine the magnetic, magnetoresistance, and other properties of the following perovskite materials:

- \( \text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3, \text{Ho}_{1-x}\text{Sr}_x\text{CoO}_3, \text{Y}_{1-x}\text{Sr}_x\text{CoO}_3, \text{Dy}_{1-x}\text{Sr}_x\text{CoO}_3 \) \( (x = 0.55, 0.66) \);
- \( \text{GdMn}_x\text{Co}_{1-x}\text{O}_3 \) \( (x = 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1) \);
- \( \text{HoMn}_x\text{Co}_{1-x}\text{O}_3 \) \( (x = 0, 0.1, 0.2, 0.3, 0.33, 0.66, 0.9, 1) \);
• Gd$_{1-x}$Sr$_x$CoO$_3$ (x = 0, 0.1, 0.3, 0.4, 0.5, 0.66);
• La$_{0.33}$Sr$_{0.66}$Fe$_{1-x}$Cr$_x$O$_3$ (x = 0, 0.05, 0.1, 0.2, 0.3, 0.5, 0.75, 1).

Far-infrared (FIR) spectroscopy was also conducted to study infrared-active phonon modes and to do a comparative analysis of the infrared transmission spectra of some prepared samples.

3- The results of measurements, observations, and analysis on the prepared perovskite materials are presented in the remaining chapters of the thesis. These chapters provide detailed information on AMn$_x$Co$_{1-x}$O$_3$ (A = Gd and Ho), the characteristics of A$_{1-x}$Sr$_x$CoO$_3$ (A = Nd, Ho, Gd, Dy, and Y), and on La$_{0.33}$Sr$_{0.66}$Fe$_{1-x}$Cr$_x$O$_3$ materials.
Chapter 2: Literature Review

The exploration of materials with the perovskite structure has revealed a very important role for their crystal chemistry, as indicated by the colossal magnetoresistance in some of them. The distinguishable types of perovskite magnetites could be classified as type I, with ferromagnetic metallic (FMM) and paramagnetic insulating (PMI) materials, and type II, consisting of two-transition antiferromagnetic insulating (AFMI), ferromagnetic metallic (FMM), and paramagnetic insulating (PMI) materials.

2.1 Structure of ABO₃ Perovskites and General Remarks

The perovskite materials have a wide range of variation in their structures and properties. Perovskite denotes a general group of crystals which have a structure in accordance with the basic chemical formula of ABO₃, where A and B are cations of different sizes, as schematically shown in Figure 2.1.

The perovskite structure is capable of being adapted to useful applications in new technologies, such as ferroelectrics, superconductors, sensors, and catalysts. Generally, the structure has a simple cubic layout with the A cation in the middle of the cube, the B cations at its corners, and the anion elements, commonly oxygen, in the centre of the cube face edges. The structure consists of six fold
coordinated B cations (octahedral). The packing of the A and O ions would follow a packed cubic array, whereas the B ions occupy the volume of the octahedra. The A cations are usually chosen from the rare earth elements of the periodic table, and the B cations are transition metals. The average size of the cations, from the left side of the periodic table to the right side, has a direct correlation with the degree of tilting/distortion of the octahedra. The elements that were used in this investigation are: A = Nd, Gd, Dy, Ho, Yb, or Sr, and B = Co, Mn, Fe, or Cr.

Despite the primitive cubic structure of perovskite, differences in ionic radii between the A and B cations can distort the structure, causing tilting of the octahedron. The tilted BO$_6$ octahedron twists along one or more axes to

Figure 2.1: Schematic structure of perovskite crystals in ABO$_3$. 
compensate for the difference. Perovskites with more complex structures have two different B-site cations, which results in ordered and disordered alternatives. The perovskite structures can show either ferromagnetic or ferroelectric features, depending on the nature of transition metals, the same as Garnet and Olivine. Most ceramic materials with magnetic and superconducting properties have perovskite-type structures.

The review of such a huge array of different types of materials is beyond the scope of this thesis. However, a selected number of perovskite materials of type ABO$_3$ are summarized in Table 1.1. It should be noted that more information can be found in Goodenough and Longo.$^6$

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Spin Order</th>
<th>Spatial Dimension of Anisotropy</th>
</tr>
</thead>
<tbody>
<tr>
<td>RNiO$_3$</td>
<td>AF*</td>
<td>Perovskite-3</td>
</tr>
<tr>
<td>Ca$_{1-x}$Sr$_x$VO$_3$</td>
<td>------</td>
<td>Perovskite-3</td>
</tr>
<tr>
<td>La$_{1-x}$Sr$_x$TiO$_3$</td>
<td>AF</td>
<td>Perovskite-3</td>
</tr>
<tr>
<td>La$_{1-x}$Sr$_x$VO$_3$</td>
<td>AF</td>
<td>Perovskite-3</td>
</tr>
<tr>
<td>La$_{1-x}$Sr$_x$FeO$_3$</td>
<td>AF</td>
<td>Perovskite-3</td>
</tr>
<tr>
<td>La$_{1-x}$Sr$_x$MnO$_3$</td>
<td>AF</td>
<td>Perovskite-3</td>
</tr>
<tr>
<td>LaCoO$_3$</td>
<td>------</td>
<td>Perovskite-3</td>
</tr>
<tr>
<td>Ca$_{1-x}$Sr$_x$RuO$_3$</td>
<td>------</td>
<td>Perovskite-3</td>
</tr>
</tbody>
</table>

*Antiferromagnetic order

It should be mentioned that in this section only those ABO$_3$ perovskite materials are
considered which are in the scope of this investigation.

Variations in atomic sizes or doping at either A or B sites will change the properties of the system. This is the result of the various types of cations that need to be accommodated within the perovskite structure, which will show its ability to adjust interatomic bond lengths and angles in accordance with the adopted atom. However, this ability relies on the solubility of the compound and determines the maximum possible ratio of introduced adopted atoms that can be accommodated by the perovskite structure.

Despite the doping level or the ratio of adopted atoms, doping will lead to distortion of the ideal structure and result in lower symmetry, which will change the physical properties of the compound. Obviously compounds with different doping levels will show different physical properties.

Ideally, the ABO$_3$ perovskite structure, as shown in Fig. 2.1, has Pm3m symmetry, where the A cation is in the center of the cube and the BO$_6$ octahedral are at the corners. Few of the perovskite materials follow this ideal structure, and the rest are distorted by some degree from this symmetry. This distortion can be described by the tilting of the BO$_6$ octahedra. Changes of temperature and pressure on the ABO$_3$ compound tilt the BO$_6$ octahedral and may lead to phase transformation among orthorhombic, rhombohedral, tetragonal, and cubic systems. The composition of the ABO$_3$ can be another factor affecting the symmetry of the structure.
Distortion is one of the properties of perovskite materials which have been widely considered, and several models have been introduced to explain it. Goldschmidt\(^7\) introduced a phenomenological model based on the tolerance factor of the perovskite structural stability limit. Glazer\(^8,9\) proposed a parameterization approach for the orthorhombic perovskite structures, which later was used by Woodward\(^10\). Later, Howard and Stoles\(^11\) presented a detailed group theory analysis of various perovskite structure interconnections. In the same year Thomas\(^12,13\) developed the Global Parameterization Method (GPM). This method approximates the semi-empirical relationship between the structural parameters, the polyhedral volume ratio, \(V_A/V_B\), and the unit cell volume \(V (v = |a.c×b|)\), where \(V_A\) is the polyhedral volume of the AO\(_{12}\) and \(V_B\) is the polyhedral volume of the BO\(_6\) units. The model can also predict the changes in the structural distortion as consequences of pressure or temperature. The model is based on the degree of structural tilting under pressure or temperature.

Magyari-Köpe\(^14\) used the GPM model to study high pressure crystal structures and presented a revised version of GPM using an \textit{ab initio} study. Relying on an \textit{ab initio} study, which was based on Density Functional Theory, they suggested a linear relationship between the A cation displacement and the polyhedral volume ratio. This approach describes correctly the pressure, temperature, and chemical dependence of the perovskite structure in various compositions.
In the meantime, Avdeev et al. \(^{15}\) used the polyhedral volume ratio (PVR) method rather than GPM to calculate \(V_A/V_B\). PVR is independent of the absolute values of the unit-cell parameters, and therefore, it will allow the comparison of different perovskite space groups. To enhance their method they: a) did not employ any empirical coefficient and presented the exact expressions of the PVR calculations; b) they calculated PVR directly from the atomic coordinates, since their calculations were independent of determining the angles between atoms and the distances of the atoms.

### 2.2 Properties of Perovskites and Related Theories

Materials with the perovskite structure are generally defined by \(A_{1-x}A'_{x}B_{1-y}B'_yO_3\), where \(A\) or \(A'\) is an alkaline or rare earth element, while \(B\) and \(B'\) are transition metals. Any change in \(A\), \(A'\), \(B\), or \(B'\) will result in a change in the structural or physical properties and may also lead to new properties, such as new magnetic, electric, optical, mechanical, electromagnetic, magneto-optic, electro-optic, piezoelectric, pyroelectric, or magneto-elastic properties. Due to the large number of perovskite materials with different types of physical properties, there are several theories that can explain these behaviors. In this section the perovskite properties and relevant theories in relation to this research will be discussed.

#### 2.2.1 Electric properties
Electronic charge transport mechanisms can be best explained in some solid oxides and halides by hopping movement \(^{16}\) (see Figure 2.2) of the localized electrons or holes to adjacent sites rather than by conventional itinerant electrons. A localized electronic carrier next to a spatial displacement can be thermally activated and hop into the displacement, giving rise to a Coulomb interaction \(^{17}\).

Hopping should appear with low carrier mobility (generally \(\leq 0.1-1.0 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}\)). Therefore, it is hopeless to judge materials in such a conduction range by conventional thermoelectric theories\(^{18}\). Study of the thermoelectric properties of materials with hopping conduction has been very limited, but it will provide valuable information. Ohtaki \(^{19}\) has studied the hopping carrier mobility in oxide materials with the perovskite structure. He considered CaMnO\(_3\) with various elements substituted into both A and B sites: \((\text{Ca}_{1-x}\text{A}_x)\text{MnO}_3\) and \((\text{Mn}_{1-x}\text{B}_x)\text{O}_3\).
The results showed that the substituted cation radius, $r_A$, in the A sites has a clear linear relation with the electric conductivity at room temperature. The variation of $r_A$ changes the hopping intersection distance, which governs the conductivity. Substitution into the B site is more complex and could be a great interest for the development of novel thermoelectric materials.

### 2.2.2 Double Exchange and Super-Exchange

When a sufficient proportion of Mn$^{4+}$ is present in perovskite oxides, the oxide becomes ferromagnetic and exhibits metal-like conductivity. This insulator-metallic transition occurs around $T_C$, the Curie temperature. This interaction is formulated as:

$$\text{Mn}^{3+}\text{O}^2\text{Mn}^{4+} \leftrightarrow \text{Mn}^{4+}\text{O}^2\text{Mn}^{3+} \quad \text{Eq. 3.1}$$

and is called Double Exchange, as was explained fully by Zener $^{48}$.

The recent discovery of magnetoresistance in rare-earth perovskite manganites$^{20,21,22}$ with the general formula $\text{Re}_{1-x}\text{A}_x\text{MnO}_3$ (Re: rare earth, A: alkaline earth) has attracted a huge interest in studying their structure, transport, and magnetic properties. Obviously, different types of substitution lead to different crystal structures and thus different magnetic and transport properties. Replacing the trivalent elements by divalent elements results in a mixed manganese valence of
Mn$^{3+}$ and Mn$^{4+}$. This modification can be explained by the double exchange interaction of Mn$^{3+}$ and Mn$^{4+}$ cations. In the meantime, there are other interactions, such as super-exchange, orbital ordering, charge ordering, and the Jahn-Teller interaction, which compete with the double exchange. The double exchange mechanism explains the coupling between the mobile holes and localized $t^3_{2g}$ electrons, which is controlled by the transfer integral $t_{ij}$ between Mn$^{3+}$-O-Mn$^{4+}$ cations and depends on the angle spanned by Mn-O-Mn. The degree of distortion of the lattice determines the Mn-O-Mn bond length and angle, thus indirectly influencing the magnetoresistance. The degree of distortion of the lattice increases in small particles, which leads to an increase in the mean deviation of the Mn-O-Mn angle and the Mn-O length (Fig 2.3).

The double exchange theory is based on the assumption of a strong interatomic exchange between localized $t_{2g}$ spins and delocalized $e_g$ electrons, as shown in Figure 2.3.

![Figure 2.3: Schematic comparison of a non-distorted perovskite (a) with a distorted perovskite structure (b) due to Mn-O-Mn angle and Mn$^{3+}$-O-Mn$^{4+}$ interaction.](image-url)
In this situation the ferromagnetic state appears as a result of kinetic effects, where in many cases, a concentrated transition into the ferromagnetic state coincides with a transition into the metallic state\textsuperscript{26,27}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.4.png}
\caption{(a) Sketch of the double exchange mechanism, which involves two Mn ions and one O ion. (b) The mobility of e\textsubscript{g} electrons improves if the localized spins are polarized. (c) Spin-canted state which appears as an interpolation between the FM and AF states.\textsuperscript{16}}
\end{figure}

In non-metallic compounds, an additional indirect exchange interaction may also appear between magnetic ions which is known as super-exchange and results in the antiferromagnetic state. Goodenough\textsuperscript{44} showed that super-exchange interactions through the oxygen in Mn\textsuperscript{3+}-O-Mn\textsuperscript{3+} are ferromagnetic in the case of a dynamic Jahn-Teller effect. Removal of the cooperative Jahn-Teller distortions in LaMn\textsuperscript{3+}O\textsubscript{3} occurs under doping, due to dilution of the degenerate orbitals of Mn\textsuperscript{3+} ions by a non-Jahn-Teller ion, e.g. Mn\textsuperscript{4+}. From this point of view, the ferromagnetic behavior
is not directly connected with metallic conductivity in the substituted manganates. It is also to be noted that a concentrated transition into the metallic state can not coincide (or can not develop at all) with the transition into the ferromagnetic state.

2.2.3 Magnetic Properties

Magnetic materials are distinguished traditionally by their susceptibility, \( \chi \). In diamagnetic materials, \( \chi \) is small and negative, around \( \chi \approx -10^{-5} \). In a magnetic field, the magnetic dipoles oppose the field direction, and they have no critical temperature. Paramagnetic materials have a similar weak susceptibility, with \( \chi \approx 10^{-3}-10^{-5} \), but it is positive. In a magnetic field, these materials align parallel to the direction of the magnetic field, and there is no critical temperature. Ferromagnetic materials have a positive \( \chi \), around \( \chi \approx 50 \text{ – } 10000 \). In an external field the dipoles align in the direction of the external field, and the Curie temperature is the critical

![Figure 2.5: Magnetic susceptibility, \( \chi \): (a) for antiferromagnetic compound, (b) for ferromagnetic compound.](image-url)
temperature. Antiferromagnetic materials have a positive and small $\chi \approx 10^{-5} - 10^{-3}$. In an external field the dipoles align in the opposite direction to the field. Their critical temperature is the Néel temperature, $T_N$. The magnetic behavior of ferromagnetic and antiferromagnetic materials is plotted schematically in Figure 2.5.

Superparamagnetism, in which paramagnetic behavior is exhibited in ferromagnetic or antiferromagnetic crystallites below the Curie or Néel temperature, is characterized by two experimental features, which are also possessed by ordinary paramagnets: there is no hysteresis in the field dependence of the magnetization (as $M$ versus $H$ is a single-valued curve at a given temperature), and $M$ is a universal function of $H(T)$.

Superparamagnetism can be destroyed by cooling. This follows because the characteristic actuation time for a particle's moment varies exponentially with temperature, so the magnetization appears to switch sharply to a stable state as the temperature is reduced. The temperature at which this occurs is called the blocking temperature, and it depends linearly on the sample's volume and on the magnitude of the crystal field anisotropy.

### 2.2.3.1 Interaction of Dipoles

Ferromagnetic materials are subjected to moments as unpaired electrons are shared in the conduction band under exchange interaction in some transition metals. The exchange is responsible for the spin orbit coupling, which
Chapter 2

establishes the alignment (orientation) as a consequence of the shared electrons in the metal. From the probability density function of electron position proposed by Schrödinger, it is revealed that the exchange interaction has a characteristic length scale of the order of the separation distance between the closest neighboring atoms in the crystal. Therefore, it is expected that the exchange should occur in dense-packed or high atomic density planes and that exchanged electrons will have spin vectors that are normal to the planes.

2.2.3.2 Magneto-crystalline Anisotropy

Due to development of high exchange coupling in the atomic lattice, the net magnetization would have a preferential crystallographic alignment. This characteristic is explained by an energy which varies in accordance with the crystal structure and in a uniaxial system would be expressed as:

$$E_c = V(K_1 \sin^2 \phi + K_2 \sin^4 \phi)$$

Eq. 2.2

where $V$ is the particle volume, $K_1$ and $K_2$ are constants that are usually

Figure 2.5: Dense-packed plane with net magnetization $\vec{m}$ at an angle $\phi$ from the normal $\vec{n}$. 31
determined experimentally, and $\phi$ is the angle between the magnetization direction and the normal to the dense-packed plane.

Figure 2.5 demonstrates a dense-packed (001) plane of a hexagonal close packed (HCP) system with net magnetization $\vec{m}$ at an angle $\phi$ from the normal $\vec{n}$.

If there is no dissipation in the magneto-crystalline energy, the magnetization vector will precess around the normal vector at a fixed angle $\phi$.

### 2.2.3.3 Zeeman Energy

When the material is subjected to an external magnetic field, as shown in Figure 2.6, the moments of the magnetic dipoles interact with the external magnetic field in accordance with the Zeeman equation:

$$ E_z = -\vec{m}.\vec{H} \quad \text{Eq.2.3} $$

Where $E_z$ is Zeeman energy, $\vec{m}$ is the magnetic dipole moment, and $\vec{H}$ is the external field.
When the temperature of the whole system decreases, the Zeeman energy is changed into a gain to the thermal energy. Typically, the net magnetization of spins becomes higher as the temperature decreases, which frequently is observed in field-cooled measurements.

### 2.2.3.4 Dipole-Dipole Interaction

It is understood from any textbook that an isolated magnetic dipole would demonstrate a magnetic field, as depicted in Figure 2.7.

![Dipole-Dipole Interaction](image)

**Figure 2.1:** Interaction of a magnetic dipole $\vec{m}$ with an external field $\vec{H}$.

**Figure 2.2:** Magnetic field lines from a fixed dipole. The test dipole rotates so that it is parallel to the field lines.
To minimize the energy level, the second dipole rotates so that it is tangent to the magnetic lines produced by the first dipole. In Figure 2.8 a minimized energy alignment in a system of five dipoles is sketched. The energy of the system is minimized with respect to the central dipole. It is noteworthy to consider that the energy between the top and right dipoles is not minimized because of their mutually non-parallel orientation to the field lines. Generally, this sort of observation is called a “frustrated condition”, which indicates that some superlattice structure of magnetic nanoparticles would produce a lesser dipole energy system.

The energy of any dipole due to the effect of its neighboring dipoles (E_d) is expressed by:

\[ E_d = -\vec{m}_i \cdot \vec{H}_i \]  
Eq.2.4

where \( \vec{m}_i \) is the moment of the given dipole, and \( \vec{H}_i \) is the magnetic field due to the neighboring dipoles.

This relationship is similar to the Zeeman equation in which the applied field is

![Figure 2.3: A system of five interacting dipoles.](image)
the consequence of neighboring dipoles and defined as:

$$\vec{H}_i = \frac{m}{4\pi a^3} \sum_j G_{ij} \vec{s}_j$$  \hspace{1cm} \text{Eq. 2.5}$$

where $a^3$ is the average volume of a particle, $m$ is the moment of the dipole (assuming the same magnitude for each dipole), $\vec{s}_j$ is the unit spin vector of each dipole, and $G_{ij}$ is a two index tensor depending on the geometry of the dipole system as:

$$G_{ij} = \frac{1}{r_{ij}} (3 \vec{r}_{ij} \vec{s}_{ij} - I)$$  \hspace{1cm} \text{Eq. 2.6}$$

$$\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$$  \hspace{1cm} \text{Eq. 2.7}$$

$$\vec{s}_{ij} = \frac{\vec{s}_i}{r_i}$$  \hspace{1cm} \text{Eq. 2.8}$$

where $\vec{r}_i$ is the vector of position, and the unit tensor is $I^{35}$. If the geometry of the superlattice is known, the interaction energy of the dipole may be computed. It is important to notice that $E_d$ depends on the arrangement of particles in the lattice, whereas the Zeeman energy, $E_z$, and the magneto-crystalline energy, $E_c$, are independent of the lattice geometry, which reflects the influence and controlling effects of certain superlattice configurations on the dynamics of the dipole interaction.

### 2.2.3.5 Self-Assembly Under the Influence of External Magnetic Fields
In a uniform magnetic field, a dipole is subject to a torque, consistent with the Zeeman interaction, as depicted in Figure 2.9. The effective forces on the dipole are equal, but with antiparallel directions, resulting in a torque action.

The energy of the system would be expressed as:

\[ E = -\vec{m} \cdot \vec{H} = -mH \cos \theta \]  

**Eq.2.9**

where \( E \) is the potential energy, \( m \) is the moment of the dipole and \( \theta \) is the dipole angle with the field.

Assuming that there is no way to dissipate the potential energy, the dipole will then tend to form a cone about the field axis. If, however, the dipoles are dissolved in a solution, the potential energy will change to thermal energy in the surrounding fluid and will quickly adjust itself to the direction without significant movement.

Moreover, in a uniform external field, each dipole produces a non-uniform field which affects the behavior of the neighboring dipoles in the fluid. As the effective resultant force acting on the dipole in a non-uniform field can not be zero, it will therefore accelerate the dipole in the direction of the field gradient. Note that the
dipole will be subjected to a drag force as a consequence of the surrounding fluid or the surface tension of the substrate.

If prior to the precipitation of the solution, the dipole is subjected to a uniform field, the dipole will show a tip to tail pattern to minimize the static energy \(^{36}\).

In other words, controlling the self-assembly can demonstrate that the external field influences nanoscale particles, although the magnitude of the dipole moment is small.

### 2.2.3.6 Curie-Weiss Law

The Curie point temperature is one of the main stages where the transition from one magnetic state to another may occur. An appreciation of the Curie-Weiss law is therefore useful for understanding some dipole interactions, such as those which occur under zero-field-cooled (ZFC), field-cooled (FC), and AC susceptibility conditions, which have been briefly formulated below.

The magnetization is expressed as the magnetic moment per unit volume. Using this definition, the magnetic susceptibility per unit volume can be defined as:

\[
\chi = \frac{M}{B}
\]  
Eq. 2.10

Considering the applied field \(B_a\), the paramagnetic susceptibility is given by

\[
M = \chi_p (B_a + B_E)
\]  
Eq. 2.11

where \(B_E\) is the finite exchange field. The Curie law can also give the paramagnetic susceptibility

\[
\chi_p = \frac{C}{T}
\]  
Eq. 2.12
where $C$ is the Curie constant. Therefore:

$$\chi = \frac{M}{B} = \frac{C}{T - C\lambda}$$

Eq. 2.13

where $\lambda$ is the mean field constant. In this relation, there is a singularity at $T = C\lambda$, which is the Curie temperature $T_C$.

From this relation we have the Curie-Weiss law:

$$\chi = \frac{c}{T - T_C}$$

Eq. 2.14

At a temperature close to $T_C$, the mean field constant $\lambda$ can be defined as

$$\lambda = \frac{T_C}{C} = \frac{3k_B T_C}{N g^2 S(S+1) \mu_n^2}$$

Eq. 2.15

Equation 2.15 could be used to determine the spin state.

2.2.3.7 Zero Field Cooled and Field Cooled Magnetization

To investigate the effects of magnetic interaction, Zero Field Cooled (ZFC) and Field Cooled (FC) methods can provide the required information. In ZFC, first the sample is cooled to 4K while no magnetic field is applied. After lowering the sample temperature down to that of liquid helium, a small external field is applied. The sample is then heated up at a constant rate while the net magnetization is measured. While the sample is being cooled in zero applied field, the particles tend to magnetize along a preferential crystal direction in the lattice to minimize the magneto-crystalline energy. The net moment of the system will
be zero, since the orientation of each crystal varies. This will still be the same when a small external field is applied, as is seen in the low temperature portion of the ZFC curve in Figure 2.10. With an increase in temperature, more disturbing energy is introduced into the system, so the magnetic moments will be disordered from the crystal direction and will align in the external field direction to minimize the magnitude of the Zeeman energy. In other words, the thermal energy activates the Zeeman interaction. With further increase in temperature, the net moment reaches its peak, where the greatest population of moments aligns with the external field. The peak temperature is known as the Blocking Temperature, $T_B$. After this point, the thermal vibrations are strong enough to overcome the Zeeman interaction energy and randomize the moments. After reaching room temperature under external field, the sample is cooled down to 4 K. After this stage, while the sample is heated up, the net moment is measured. This is known as the Field
Cooled (FC) method, and the magnetization will diverge from that of ZFC near $T_B$, as shown in Figure 2.10.

![Please see print copy for image](image-url)

**Figure 2.5: Variation of net moment with temperature**.  

This behavior occurs as the particle spins try to align with the easy crystal axis in

![Please see print copy for image](image-url)

**Figure 2.11: Variation of net moment with temperature (ZFC, FC and TRM curves).**
the vicinity of the applied field direction and freeze in that direction as the temperature is reduced\textsuperscript{38}.

In a similar way to FC, if the sample is cooled to 4K and the external field is removed, by heating the sample up to room temperature and recording the net moment, the final curve is known as the Thermal Remnant Magnetization (TRM), as is demonstrated in Figure 2.10 and 2.11\textsuperscript{38} for 6nm Co particles.

2.2.3.8 \textit{AC Susceptibility}

When the magnetization dynamics is probed by an oscillator, it will respond to the alternating current with a relaxation time. This time can be modified from the Arrhenius relaxation rate:

\[
\tau = \tau_0 \exp \left( \frac{KV}{k_B T} \right) \tag{Eq. 2.16}
\]

where \(\tau\) is the decay rate, \(K\) is the anisotropy constant, \(V\) is the particle volume, \(k_B\) is Boltzmann's constant, \(T\) is the temperature, and \(\tau_0\) is a constant that is related to the Larmor frequency \(f_0\) according to

\[
\tau_0 = \frac{1}{2\pi f_0} \tag{Eq. 2.17}
\]

Using Arrhenius relaxation expressions, one can calculate the relaxation time. The relaxation time is consistence with the Vogel-Fulcher law\textsuperscript{39}.

\[
\tau = \tau_0 \exp \left( \frac{KV}{k_B (T - T_0)} \right) \tag{Eq. 2.18}
\]
where $T_0$ is the spin freezing temperature for spin glass or the blocking temperature for nanoparticle systems. Because of the relaxation time lag between the applied field and the magnetization response, the susceptibility would have two parts, one real and the second imaginary. As a result the system will show a peak at the characteristic frequency $f_c$.  

2.3 Structures and Physical Properties of Some Typical Perovskite Based Compounds

2.3.1 REMnO$_3$ system (RE = rare earth element)

There are many references or review articles (such in as Tokura’s book) where you can extract the main results concerning this system. Lorenz et al. prepared hexagonal HoMnO$_3$. The sample was multiferroic, i.e., showed simultaneous magnetic and ferroelectric behavior, and its dc magnetization and ac susceptibility were measured at low temperature. During study of the sample below the Néel temperature, $T_N = 76$ K, at a magnetic field of 50 kOe, two new phases were discovered and have been clearly explained. Including the transitions that were discovered, at least five different phases exist below $T_N$ for magnetic field up to 50 kOe. Each phase was well characterized by studying its magnetic properties. The phase boundaries were defined by their different magnetization, ac susceptibility, and specific heat. At 33 K under a magnetic field, an intermediate phase was clearly observed between the $P6_3cm$ and $P6_3cm$ magnetic structures. It
should be noted that this is the same temperature as for the Mn-spin rotation transition.

### 2.3.1.1 LaMO$_3$

LaMO$_3$ (M = Mn, Co) is another perovskite material having potential use in magnetoresistive devices and sensors. With a view to appropriate applications, the magnetic and electrical properties, spin, charge, and orbital ordering were investigated. The orthomanganate LaMnO$_3$ is known as an A-type antiferromagnet, due to anisotropic super-exchange. The $d_{z^2}$-orbital ordering of the Mn$^{3+}$ ions causes a positive sign for the super-exchange interaction in the $ab$-plane and a negative sign between the planes$^{44}$. The compound is converted to the ferromagnetic state by replacing La with divalent alkaline earth$^{45,46}$ (La$_{1-x}$A$_x$Mn$^{3+}_{1-x}$Mn$^{4+}_x$O$_3$) or univalent alkali$^{47}$ (La$_{1-x}$A$^{+}_x$Mn$^{3+}_{1-2x}$Mn$^{4+}_{2x}$O$_3$) ions. The ferromagnetic behavior of the doped manganates is explained by the double exchange mechanism$^{48}$.

### 2.3.1.2 RE(Co$_{1-x}$Mn$_x$)O$_3$ system

In 1969 the first studies on the magnetic properties of perovskite Gd$_2$CoMnO$_6$ were carried out by Troyancuk, Samsonenko, and Shapovalova$^{49}$. They started with the DC susceptibility in fields lower than 1 T and temperatures above 70 K. Then the ferromagnetic behavior of perovskite Gd$_2$CoMnO$_6$ and La$_2$CoMnO$_6$ were
examined, but without investigating the details of the magnetism or the structure.

The sample preparation method for Gd$_2$CoMnO$_6$ and La$_2$CoMnO$_6$ resulted in a single-phase orthorhombic perovskite structure with the Pbnm space group. They also prepared a series of LnMn$_{0.5}$Co$_{0.5}$O$_3$ (Ln = rare earth). The Ln ionic size has a direct relationship with the unit cell volume, which, in turn, has an inverse relationship with the Curie temperature. In the same year they looked carefully at the magnetic properties of the Gd(Mn$_{1-x}$Co$_x$)O$_3$ series. Each group of doping levels exhibited various sorts of metamagnetism.

In 2001, Wang et al. continued the investigation of the magnetic properties of Gd$_2$CoMnO$_6$. They considered DC fields up to 5T and also an AC magnetic field of 1 Oe at the frequencies of 21 Hz, 217 Hz, and 2000 Hz, while the temperatures ranged from 4.2 K to 300 K. At a temperature of 112 K, they observed a sharp reentrant spin glass with a transition width of 1 K. At the same time, they also carried out a complete study of the La$_2$CoMnO$_6$ structure and its magnetic properties. In their study, a range of doped Gd$_2$Co$_x$Mn$_{1-x}$O$_6$ (x = 0.8, 0.7, 0.6, 0.5) compounds were examined to determine their structures and their physical properties in comparison with other previous investigations.

Khalyvin et al. investigated the magnetic and electrical properties of LaMn$_{1-x}$Co$_x$O$_3$ (0 < x < 1). A single disordered crystal perovskite structure was obtained by the electrodeposition technique. The magnetization showed ferromagnetic behavior for LaMn$_{0.82}$Co$_{0.18}$O$_3$ and spin glass-like behavior for LaMn$_{0.46}$Co$_{0.54}$O$_3$. The quasi-
spin glass resulted from the random distribution of cobalt and manganese ions in the B-sites of the crystal lattice under the relatively high temperature which was used to grow the sample.

Beside the very large studies on the magnetic interaction between paramagnetic ions in non-metallic oxides showing antiferromagnetic behavior, there are some reports on ferromagnetic behavior as well. Goodenough 44 and Kanamori 55 have attributed the ferromagnetic contribution to the interaction of the collinear configuration of Me(1)-O-Me(2), where Me = metal element, in the condition where an empty $d$ orbital of Me(1) overlaps a half-filled $d$ orbital of Me(2). Based on this condition, they explained the positive sign of the magnetic 180° interaction between the $d^3$ and $d^4$ octahedral ions. It is worth mentioning that Jonker 56 had earlier found the sign of these interactions and explained it based on the $d$ orbital 180° magnetic interaction. A schematic sketch of the ferromagnetic and antiferromagnetic interactions is shown in Figure 2.13.

Goodenough 57 reported that La(Mn$_{0.5}$Me$_{0.5}$)O$_3$ (Me = Ni, Co) compounds are ferromagnetic with the cubic perovskite structure. The solid solutions La(Mn$_{1-x}$M$_x$)$_3$O$_9$, where M = Co, Ni, for $x > 0.15$, have compositions that are ferromagnetic 58,59 and governed by the positive super-exchange interaction between Co$^{2+}$ and Mn$^{4+}$. Using nuclear magnetic resonance (NMR) measurements 60,61, the three existing ions, Ni$^{2+}$, Co$^{2+}$, and Mn$^{4+}$, make a rock-salt type lattice structure when the sample is prepared at low temperature 51.
Troyanchuk prepared $\text{R(Mn}_{0.5}\text{Co}_{0.5})\text{O}_3$ ($\text{R} = \text{Nd, Sm, Eu, Gd, Tb, Dy, Y, Ho}$) by the conventional ceramic method and found that these compounds are ferromagnetic with a comparatively high Curie temperature and spontaneous magnetization, while $\text{R} = \text{Tb, Y}$ compounds exhibited magnetic behavior around their Curie temperature. He later prepared another series of these compounds, varying the doping levels of Mn and Co as well. $\text{R(Mn}_{1-x}\text{Co}_x)\text{O}_3$ ($\text{R} = \text{Eu, Gd, Tb}$) compounds were made by the same solid state method to study their magnetic properties. Some results for $\text{Eu(Mn}_{0.5}\text{Co}_{0.5})\text{O}_3$ are shown in Figures 2.14 to 2.16.

$\text{EuMnO}_3$ and $\text{GdMnO}_3$ are weak ferromagnets of the Dzialoshinsky-Moriya type, since there are no Mn$^{4+}$ ions interacting ferromagnetically with Mn$^{3+}$. By substitution of Tb ($\text{TbMnO}_3$), the material becomes antiferromagnetic, and thus the magnetization-temperature curve reaches its maximum at 6 K. There is no spontaneous magnetization in the temperature range of 2–40 K. In this sample, the magnetic state changes to cluster-spin-glass-like by substituting Co on the Mn sites.

Figure 2.6 Generation of antiferromagnetic a) or ferromagnetic b) effective interaction between the spins of Mn ions mediated by oxygen, depending on the orientation of the Mn orbital. Error! Reference source not found.
with the doping level in the range of $0.1 \leq x \leq 0.3$. It was found that by substituting more Co ($0.4 \leq x \leq 0.8$), the sample became inhomogeneously ferromagnetic with a well defined Curie temperature. When the doping level is $x = 0.5$, the spontaneous magnetization and Curie temperature reach their highest level. For $x \geq 0.9$ another spin glass state is observed.

Figure 2.7: Magnetization vs. temperature for the Eu(Mn$_{0.5}$Co$_{0.5}$)O$_3$ sample. The inset shows the magnetic susceptibility behavior in the paramagnetic regime $^{63}$.  

Please see print copy for image
Following Troyanchuk's 94 previous studies on the same materials, in R(Mn_{0.5}Co_{0.5})O_3 (R = Gd, Tb, Y), applying an external field induces a magnetic transition. For Tb- and Y-based compounds the transition becomes irreversible at low temperature. The Curie temperature of R(Mn_{0.5}Co_{0.5})O_3 was enhanced by annealing in vacuum. For Eu(Mn_{0.5}Co_{0.5})O_3, the annealing resulted in a metamagnetic transition as well. This magnetic behavior can be interpreted in the

Figure 2.8: Field cooled magnetization of Eu(Mn_{1-x}Co_x)O_3 as a function of temperature, obtained in a field of 14 kOe.63
Co$^{2+}$ sub-lattice by considering the two factors of the Co$^{2+}$ and Mn$^{4+}$ ionic ordering and the possible Co$^{2+}$ 3$d$ orbital ordering.

The field cooled magnetization and H-T magnetic phase results for Y(Mn$_{0.5}$Co$_{0.5}$)O$_3$ obtained by Troyanchuk et. al.$^{63}$ are presented in Figures 2.17 and 2.18.

Figure 2.9: Field cooled magnetization of Eu(Mn$_{1-x}$Co$_x$)O$_3$ as a function of temperature, obtained in a field of 200 Oe.$^{63}$
Figure 2.17: Field cooled magnetization vs. temperature of Y(Mn_{1-x}Co_x)O_3 \textsuperscript{63}. 

Please see print copy for image
2.3.1.3 Double layered $\text{Sr}_2\text{FeMoO}_6$ system

The double-perovskite ferromagnets $\text{Sr}_2\text{FeMoO}_6$ and $\text{Sr}_2\text{FeReO}_6$ have comparatively high Curie temperatures, about 420 K and 400 K, respectively \textsuperscript{64}. Half-metallic states, often with metallic behavior \textsuperscript{65} and sometimes with semiconducting behavior \textsuperscript{64}, are observed. The band-structure calculations had

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Figure 2.18: $H$-$T$ magnetic phase diagrams of $\text{Y(Mn}_{1-x}\text{Co}_x\text{)}\text{O}_3$ \textsuperscript{63}.
indicated the existence of the half-metallic state\textsuperscript{64,66}. Under metallic conditions, the resistivity is sensitive to the preparation conditions, such as annealing and film growth parameters.

The Ru based system SrRuO\textsubscript{3} crystallizes in an orthorhombic structure and is reported to be a strongly correlated \textit{d}-band metal\textsuperscript{67,68,69,70}. It converts to ferromagnetic at 165 K\textsuperscript{71,72} and has an itinerant character.

2.3.1.4 \textit{RE}_{1-x}AE\textsubscript{3}MnO\textsubscript{3} system - Colossal Magnetoresistance Phenomenon

The phenomenon of change in resistance under external magnetic field is known as magnetoresistance, MR. Nearly 20 years ago the colossal magnetoresistance (CMR) phenomenon was discovered\textsuperscript{73,74,75,76,77,78,79,80,81,82} in perovskite \textit{RE}_{1-x}AE\textsubscript{3}MnO\textsubscript{3} (RE = lanthanide elements, AE = alkaline earth elements). Similar behavior occurs in thin films, which is a quantum mechanical effect and very larger much than CMR. It is known as Giant Magnetoresistance (GMR). Although the origin of this phenomenon is not clear yet, the interaction between the electron transport and the ferromagnetic properties of these types of materials has been well studied. Double-exchange can basically explain the coupling exchange from the hopping of Mn \textit{e}_g orbital electrons between neighboring orbitals. However this concept would not be enough. Bearing this in mind, Millis\textsuperscript{83} proposed a new approach to explain the CMR on the basis of strong electron-phonon interaction which distorts the lattice. Despite the ferromagnetic interaction between the magnetic and electrical properties in ternary oxide crystals lightly doped with Co, the CMR was weaker in comparison
to the giant magneto-resistance (GMR) of LaMnO$_{3+\delta}$. 

The observation of CMR in perovskites has attracted enormous attention to REMO$_3$ compounds (RE = rare earth element, M = metal). Colossal magneto-resistance (CMR) is at a maximum near the Curie temperature ($T_C$) when the materials become ferromagnetic (FM). Ferromagnetic and ferroelectric perovskites are thought to be half-metallic oxides and are the most interesting class of materials for the study of extrinsic magneto-transport phenomena. The transport and magnetic behaviors of different types of perovskite materials have been studied to understand the mechanisms for the phenomena.

Ternary ABO$_3$ perovskite is a material comprising A: lanthanide series element (A = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) and B: usually an element from the first series of transition metals (B = Ti, V, Cr, Mn, Fe, Co, Ni, and Cu). Doped A$_{1-x}$A$'$$_x$B$_{1-y}$B$'$$_y$O$_3$ compounds are the composites that have been of the greatest concern in research for more than a decade. The doping level of an element in a compound changes its magnetic and transport behavior. The behavior does not follow a linear trend with systematic changes in the doping level. The following are some of the past studies related to CMR.

In recent years, the manganese oxides with perovskite structure, RE$_{1-x}$AE$_x$MnO$_3$ (RE and AE being rare-earth and alkaline-earth elements, respectively), have been extensively studied, since intriguing and versatile phenomena, such as colossal magneto-resistance (CMR), have been observed, due to the unique coupling among
the spin, charge, and orbital degrees of freedom of the $3d$ electrons.

In $\text{RE}_{1-x}\text{A}_x\text{MnO}_3$ ($\text{RE} = \text{La}, \text{Nd}, \text{Pr}, \text{Gd}, \text{and} \ A = \text{Ca, Sr, Br}$) for $0.15 < x < 0.5$, the compounds are ferromagnetic. The highest Curie temperatures are found in $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ at doping levels of $x \leq 0.1$ with $T_C = 270$ K (for Ca substitution), 360 K (for Sr substitution), and 330 K (for Ba substitution), and the manganates show a metal-insulator transition at the ferromagnetic transition. The ferromagnetic order in the mixed-valence manganates is induced by the double-exchange mechanism proposed by Zener. Doping on the B sites and replacing Mn by Co gives rise to an appreciable magnetoresistance effect.

A series of $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ ($\text{Ln} = \text{La, Nd, Gd, Y}; \ A = \text{Ca, Sr, Ba, Pb}$) compounds were prepared by Mahesh et al.\textsuperscript{84} to study the giant magnetoresistance and its relationship to the doped rare earth manganates. They found that there is a direct relation between the weighted average radius of the A-cation and the ferromagnetic transition temperature, $T_C$, as well as the insulator-metal transition temperature, $T_p$. In Fig. 2.19, the $T_p$ values are depicted as a function of the ionic radius.
Infrared (IR) spectroscopy is a well known tool that provides information on the crystal lattice vibrating modes.

It has been observed by some researchers\(^8\) that IR phonon spectra are sensitive to local lattice distortions\(^{85,87}\) and high frequency shifts of the internal phonon modes.

Millis\(^{85,86}\) and Harley\(^{87}\) showed that in a crystal, the vibration mode of the lattice can be observed using infrared spectra, due to the sensitivity of the beam photons to local lattice distortion. In polycrystalline $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, close to the Curie temperature, $T_C$, there are high frequency shifts of the internal phonon modes\(^{88}\), which indicates the importance of electron-phonon coupling in the dynamics of the manganese oxides.

El-Fadli\(^{89}\) studied the solid solution series $\text{La}_{0.7+y}\text{A}_{0.3-y}\text{Mn}_{1-x}\text{M}_x\text{O}_3$ (with $0.00 \leq x \leq 1$).
0.10; \( A = \text{Sr}^{2+}, M = \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Sc}^{3+}, \text{Cr}^{3+}, \text{Co}^{3+}, \text{Ba}^{2+} \) and \( \text{Ga}^{3+} \) in single phase perovskite samples prepared from acetic acid solutions by a freeze-drying method. This method allowed him to precisely control the stoichiometry. He refined the samples in the R3c space group. From varying the doping level \( x \), the structural parameters, such as the rhombohedral cell volume, rhombohedral cell angle and B-O, A-O bond lengths, were considered as functions of the mean size of cations at the A and B sites. In these series, CMR was present in some manganates. The \( \text{La}_{0.7+y}\text{A}_{0.3-y}\text{Mn}_{1-x}\text{M}_x\text{O}_3 \) critical temperature for the paramagnetic-ferromagnetic transition exhibited three different patterns, which were clearly related to the mean size of the cations at the B sites. Substitution of cations at the B sites was one of the methods used to modify the intrinsic properties of \( \text{La}_{1-x}\text{A}_x\text{MnO}_3 \). This method was used by Obata to improve the room temperature low field sensitivity of those materials for applications in magnetic sensors.  

In the study of Moritomo et al. on \( \text{Ln}_{0.5}\text{Sr}_{0.5}\text{MnO}_3 \) (\( \text{Ln} = \text{La}, \text{Pr}, \text{Nd} \)), a first-order ferromagnetic-antiferromagnetic phase transition was demonstrated around 180 K. The Curie temperature decreased from 320 K to 250 K, as a result of either replacing La with Nd or reducing the lanthanide ionic radius. The antiferromagnetic-ferromagnetic transition for \( \text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3 \) develops simultaneously with charge ordering. When Sr is replaced by Ba, the compound does not show antiferromagnetic-ferromagnetic and charge order-disorder transitions any more. The same properties vanish when in \( \text{Ln}_{0.5}\text{Ba}_{0.5}\text{MnO}_3 \), \( \text{Ln} \) is replaced with Nd. In \( \text{Ln}_{0.5}\text{Ba}_{0.5}\text{MnO}_3 \), where \( \text{Ln} \) is a ferromagnetic element, \( T_C \approx \)

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54
Nd$_{0.5}$Ba$_{0.5}$MnO$_3$ has a Curie point of 120 K\cite{93}, and the spontaneous magnetic moment is lower than the expected value for collinear ferromagnets. Troyanchuk et al.\cite{94} studied magnetization and the magneto-transport properties of both compounds, as well as of reduced Pr$_{0.5}$Ba$_{0.5}$MnO$_{3-\gamma}$. The results were compared with the properties of Ln$_{0.5}$Sr$_{0.5}$MnO$_3$. He showed that Ln$_{0.5}$Sr$_{0.5}$(Mn$_{0.5}^{3+}$Mn$_{0.5}^{4+}$)O$_3$ and reduced Pr$_{0.5}$Ba$_{0.5}$Mn$_{3+}$O$_{2.75}$ demonstrate similar magnetic and magnetoresistance properties. Both samples have similar properties, but the reason is not clear as yet. They had $T_C \approx 320$ K, and they achieved a ferromagnetic-antiferromagnetic transition around 200 K, where a large magnetoresistance developed. The reduced sample has a much larger resistivity than the oxide. Usually the transport and magnetic properties of manganese compounds are explained by double-exchange between Mn$^{3+}$ and Mn$^{4+}$ ions\cite{95}. It could be seen that if the Jahn-Teller distortions are removed, the Mn$^{3+}$-O-Mn$^{4+}$ are in a ferromagnetic orientation\cite{57}. Comparing the obtained data with the results on La$_{0.5}$Ca$_{0.5}$MnO$_{3-\gamma}$\cite{96} indicates that the fascinating properties of manganates can exist without the mixed manganese valences.

**2.3.1.5 Bi$_{1-x}$Sr$_x$MnO$_3$**

Bi$_{1-x}$Sr$_x$MnO$_3$ is an ABO$_3$ perovskite which was extensively studied by Hervieu et al.\cite{97} Their results showed that there could be a large number of bismuth-based perovskite manganites with a very great sensitivity of the structure to the doping levels of anions and cations.
They investigated the charge ordering (CO) in Bi_{1-x}Sr_xMnO_3 at room temperature and suggested a strip model of the Mn^{3+} and Mn^{4+} charge ordering, using an electron microscope for the first time to observe the charge structure. Using this method, they observed a new charge ordering which was exceptionally stable at a charge ordering temperature, T_{CO} \approx 500K.

Several researchers \cite{98,99,100} have studied Bi_{1-x}Ca_xMnO_3. Since bismuth is stable in the trivalent state, it was expected that a similar behavior to lanthanum based systems might have prevailed. Interestingly, there was no evidence for metallic features in the samples with 0.3 < x < 0.9 for H = 0 \cite{99,100}, which could be attributed to the high polarization of the Bi^{3+} ions. A ferromagnetic state for x > 0.8 was reported by Chiba et al. \cite{100}. They also found that for x = 0.875, the value of \rho was decreased by a factor of up to two in a field of 7 T. Chiba et al. also found that for x = 0.875, the ordered moment is only \sim 50\% of the theoretical Hund’s rule moment. For x = 0.82, an antiferromagnetic state and a charge ordering state were also reported \cite{101}.

Some researchers \cite{102,103,104} know Bi^{3+} as one of the long pair cations. They believe that it can produce a structure with a unique metallic topology with reduced connectivity if it is combined with halides.

It has been discovered that three parameters govern the magneto-transport properties of CMR materials with the perovskite structure: a) the average size of the interpolated cation \cite{105,106,107,108,109,110,111}, b) the size mismatch with the interpolated cation \cite{105,106,107,108,109}, and c) the hole carrier density with respect to the manganese mixed valence \cite{112}. However, in the past few years, the role of the interpolated
cation has been well established, and it has a large influence on CMR, while the mixed valence of manganese is the source of the CMR phenomenon, with the double exchange between Mn$^{3+}$ and Mn$^{4+}$ playing the most important role as long as the Jahn Teller distortion also exists. All these features are specified for manganese, and therefore at the stage of doping CMR material at the Mn sites, a modification of the features should be considered. Raveau doped CMR $\text{ABO}_3$ perovskite on the B sites, replacing manganese with various elements (Al, Ga, In, Ti, Sn, Fe, Cr, Co, Ni, and Mg). The doping results showed some spectacular effects.

Regardless of the particular doping element, the magnetic phase diagram would be considerably modified, which is an important property for optimizing CMR materials. Generally, as the $T_C$ decreases, the CMR effect increases by several orders of magnitude.

When the Mn-site is subjected to doping, interesting CMR effects can be induced in an insulating perovskite. Doping $\text{Ln}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ can generate a metal-insulator (MI) transition and suppress the charge ordering by changing the Mn$^{3+}$/Mn$^{4+}$ ratio. Doping with $M_1 = \text{Mg}, \text{Al}, \text{Fe}, \text{Ga}, \text{Ti}, \text{Sh}$ gave rise to different behavior from doping with $M_2 = \text{Co}, \text{Ni}, \text{Cr}$. The insulating properties were maintained by the $M_1$ elements, while a metal-insulator transition was induced by $M_2$ elements. It was revealed that there is not enough charge ordering suppression in zero magnetic field to generate a ferromagnetic metallic state. This suggests that doping with $M_2$
elements either induces a significant variation in the crystal field for manganese or it can only create a narrow band too close to the manganese conduction band. The reason for this behavior of the M₂ series elements might be attributed to their ability to exhibit high valence states as a source of itinerant carriers in oxides. In a similar way to other researchers’ results, the magnetic phase diagram was modified by doping into the Mn sites.

2.3.1.6 RECoO₃ system

The perovskite oxides RECoO₃ (RE = various rare earth elements) are materials with Co³⁺ cations. The cobalt ion’s electronic configuration is t₂g⁶, which is in a non-magnetic ground state, and the d orbital of Co can be reconfigured, based on Jahn-Teller distortion, as shown in Fig. 2.20.

The low spin state of Co³⁺ can be changed to the intermediate spin (IS; s = 1; t₂g⁵e₉¹) or high spin (HS; s = 2; t₂g⁴e₉²) state, if the Co³⁺ is excited by an energy of δE from the ground state, where δE depends on the crystal field splitting, Δₑ. For example, temperature can excite and change the spin state.

115,116,117,118,119,120,121,122,123,124,125
Meanwhile the octahedral volume (in this sample, CoO₆) and Δₐ have an inverse relationship with each other. Therefore, δE could be controlled by the crystal volume. For this type of sample, changing the ionic radius of R³⁺ would also be one of the possibilities that may introduce other effects. The increasing tendency of the temperature of the spin state to change with decreasing R-ion size¹²⁶ indicates that the idea is essentially correct.

2.3.1.7  RE₁₋ₓAₓCoO₃₋δ system (RE is a rare earth, A is an alkaline element)

Masuda et al.¹²⁷ have studied the magnetic and transport properties of R₁₋ₓAₓCoO₃ (R = La, Pr, Nd; A = Ba, Sr, Ca) for the range of 0 ≤ x ≤ 0.5, except for Nd₁₋ₓBaₓCoO₃. They found that as the Sr or Ba doping level increases, the samples become metallic and ferromagnetic with a large magnetic moment. They reported
that when \( R = \text{Pr} \) or \( \text{Nd} \) and \( A = \text{Ca} \), the samples came close to the metal-insulator phase boundary, but with no transfer to the metallic phase. In samples doped with \( \text{Ca} \), the magnetic moment in \( H = 0.1 \) T was much smaller than in samples doped with \( \text{Ba} \) and \( \text{Sr} \). In these three classes of samples, the thermoelectric power for those doped with \( \text{Ca} \) was positive. However, an increase in \( \text{Ba} \) and \( \text{Sr} \) in the composites decreases the thermoelectric power from high positive values to negative.

Hiroyasu et al. \(^{128}\) prepared and studied samples of \( \text{R}_{1-x}\text{A}_x\text{CoO}_{3-\delta} \) (\( \text{R} = \text{La}, \text{Pr}, \) and \( \text{Nd} \); and \( A = \text{Ba}, \text{Sr}, \) and \( \text{Ca} \)). In his work he considered two effects: the hole-doping effect on the transport in conjunction with the magnetic properties, and the effect of the \( \delta E \) induced by change in the octahedral (\( \text{CoO}_6 \)) volume, where \( \delta E \) induces a change in the spin state distribution. This will change the distribution of the hole-carriers in the \( t_{2g} \) and \( e_g \) orbitals. Change in \( \delta E \) can also affect the double exchange interaction, and the transport and magnetic properties. By changing the \( \text{R} \) and \( \text{A} \) atoms, and varying their concentration \( x \), different types of physical properties can be observed and studied. Up to now, \( \text{Sr} \) and \( \text{Ba} \) have been considered for \( A \) \(^{129,130,131,132,133,134,135}\). It has been found that the sample becomes ferromagnetic with a small \( \delta E \) and becomes metallic with an increase in doping level \( x \). Hiroyasu’s results \(^{136}\) showed that by doping with \( \text{Ba} \) and \( \text{Sr} \), the system becomes ferromagnetic with large moments. On the other hands, the system becomes nearly metallic if \( A = \text{Ca} \). The existence of ferromagnetic moments in this type of sample is much less than for \( \text{Ba-} \) and \( \text{Sr-doped samples}. \)
K.H. Ryu \textsuperscript{137} prepared a series of the perovskite $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_3-y$ (x = 0, 0.25, 0.5, 0.75, 1) system at 1200 °C under atmospheric pressure with and without oxygen flow. X-ray examination showed that materials with x = 0, 0.25, 1 are orthorhombic, x = 0.5 is cubic, and x = 0.75 is tetragonal. By increasing x, the

Figure 2.21: Plot of reduced lattice volume vs. composition (x) for $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_3-y$ system\textsuperscript{137}.

Figure 2.22: Effective magnetic moment ($\mu_{\text{eff}}$) (Co-ions only) vs. composition (x) for $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_3-y$ \textsuperscript{137}.
reduced lattice volume of the system is increased, as shown in Figure 2.21.

Using the quantitative iodometric titration method, the mixed valence state between Co\(^{3+}\) and Co\(^{4+}\) ions, and the amount of Co\(^{4+}\) ion were analyzed. They calculated the effective magnetic moment of the cobalt, \(\mu_{\text{eff-Co}}\), and plotted the results as a function of material composition, as shown in Figure 2.22.

The electrical conductivity of GdCoO\(_{3.00}\) sharply increased, which indicates that the activation energy is higher than for the other composites, as listed in Table 2.1.

<table>
<thead>
<tr>
<th>x</th>
<th>Temperature range (K)</th>
<th>Activation energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>78(\leq T\leq 360)</td>
<td>0.46(\pm 0.01)</td>
</tr>
<tr>
<td></td>
<td>360(\leq T\leq 540)</td>
<td>0.18(\pm 0.01)</td>
</tr>
<tr>
<td></td>
<td>540(\leq T\leq 800)</td>
<td>0.76(\pm 0.03)</td>
</tr>
<tr>
<td>0.25</td>
<td>78(\leq T\leq 350)</td>
<td>0.03(\pm 0.002)</td>
</tr>
<tr>
<td>0.50</td>
<td>78(\leq T\leq 450)</td>
<td>0.01(\pm 0.001)</td>
</tr>
<tr>
<td>0.75</td>
<td>78(\leq T\leq 700)</td>
<td>0.16(\pm 0.005)</td>
</tr>
<tr>
<td>1.00</td>
<td>78(\leq T\leq 500)</td>
<td>0.05(\pm 0.002)</td>
</tr>
</tbody>
</table>

For x = 0.5, the electrical conductivity shows metallic properties in Figure 2.23. The compounds with x = 0–0.75 show paramagnetic properties.
The magnetic measurements show for $x = 0.5$ that the paramagnetic $T_C$ is positive with the maximum amount of $\text{Co}^{4+}$, as is shown in Figure 2.23.

Goossens et al.\textsuperscript{138} prepared $\text{Y}_{0.33}\text{Sr}_{0.67}\text{CoO}_{2.97}$ by the sol-gel method. Their structural characterization showed that the sample was a perovskite of space group $I4/mmm$. It was found that the dc magnetization, ac susceptibility, and neutron diffraction were related to the determined oxygen stoichiometry. There was no imaginary part of the ac susceptibility, as the independence of the magnetic behavior from time would verify. Unlike other cobaltate perovskites, the lack of a cusp in the imaginary part of the ac susceptibility and the lack of

---

Figure 2.23: Variation of $1/\chi$ vs. temperature for $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_3$ (0 ≤ $x$ ≤ 0.75)\textsuperscript{137}.
frequency dependence in the temperature of the cusp in the real part of the susceptibility suggest that there was no glassiness in the sample, as is shown in Figure 2.25 and Figure 2.26.
Figure 2.26: ac susceptibility of a polycrystalline sample of $Y_{0.33}Sr_{0.67}CO_{2.79}$, with $H_{ac} = 6.25$ Oe, $H_{dc} = 0$, and $f = 125$ Hz. \cite{138}.

Figure 2.25: $M-H$ loops for a polycrystalline sample of $Y_{0.33}Sr_{0.67}CO_{2.79}$ at 5 K and 295 K. \cite{138}.
The hysteresis loop indicated a ferromagnetic state that was explained by the presence of independent ferromagnetic regions in an antiferromagnetic matrix. Changing the sample composition increased the distribution of the ferromagnetic transition temperature, as demonstrated in Figure 2.25. According to their report, in the Co lattice, a spin state transition may appear which is due to either Co$^{4+}$ or Co$^{3+}$.

### 2.4 Spin Glass Phenomenon

Spin glass is a magnetic system in which the spins are “frozen” in a random alignment. Spin glass has been observed in the study of REMO$_3$ compounds that exhibit the highest values of CMR ($\sim 10^8$) $^{140, 141}$. Spin glass is also observed in spinels $^{142}$, amorphous materials $^{143, 144, 145}$, and mostly in dilute magnetic alloys $^{146, 147, 148, 149, 150, 151}$. In disordered ferromagnetic materials, spin glass occurs after the material changes from the paramagnetic to the ferromagnetic state at the Curie temperature, and this type is known as a reentrant spin glass coexisting with ferromagnetism $^{152, 153}$. The freezing temperature, $T_f$, is usually below 50 K, with the exception of spinel cobalt, in which $T_f$ occurs at room temperature $^{154, 155}$. In most dilute magnetic alloys, spins freeze directly from the paramagnetic state $^{156}$. Spin glass can also be defined in a different way. The frozen structural disorder may cause a conflict in the interaction between the magnetic moments, which manifests itself as a spin glass $^{157}$. In this state, no conventional long-range order, either ferromagnetic or antiferromagnetic, has been observed, with no freezing transition to a state of random alignment of spins. The nature of this kind of spin order, its
theories, and the characteristics of the freezing transition are still under investigation to answer the two main questions: Is the phenomenon a manifestation of uncertainty in measurements due to the incomplete thermal equilibrium, or is it a new type of transition? In any case, the spin glass is due to the structural disorder and can not be observed in conventional regular crystal systems. Spin glass can be identified by two main characteristic behaviors. The first and universal characteristic of the spin glass phenomenon, “cusp”, is a sharp joining point of two curves in the frequency dependence of the susceptibility in low field, which was first observed by Cannella and Mydosh. The second characteristic of a spin glass is a little cusp at the joining point of the Zero Field Cooled and the Field Cooled curves at \( T_f \) in DC moment measurements.

In some compounds, such as \( \text{SrCr}_{0.9}\text{Ga}_{12-0.9}\text{O}_{19} \) (\( p = 0.92 \)), when two spins are aligned antiparallel, the third spin can not be aligned antiparallel with the two others, and this will produce a frustrated spin. Finding the ground state for a small frustrated spin cluster is easy, but expanding it to the lattice and predicting the results are difficult. Through his experimental studies, Lee tried to overcome this difficulty using quantum mechanics. He found that the phenomenon is unique and neither a spin glass nor a conventional magnet.

2.5 Infrared (IR) properties in the Study of Perovskite Materials

In manganite base perovskites, considering the average particle size of a sample, two extra internal phonon modes would be observed, namely: the stretching and the
bending modes of the MnO₆ octahedra. It is assumed that these observations are related to the surface modes of bending and stretching. The absorption strength of these modes increases while the bulk modes of the sample are reduced. These results would suggest that the electronic and magnetic properties of granular perovskite are responsible for the existing surface modes.

F. Gao has studied the phonon energies in cobaltite/manganite A(Co₁/₂Mn₁/₂)O₃ (A = La, Nd, Dy, Ho, Yb), using far infrared spectroscopy, as is shown in Fig. 2.26. The spectra showed similar features, but on increasing the lanthanide ion mass, the phonon energy systematically shifted and split, while new modes appeared.
Her results suggested a strong correlation between the phonon modes and the magnetic properties, most likely through the electron-phonon interaction, as is demonstrated in Figure 2.27.

\[ A(Co_{1/2}Mn_{1/2})O_3 \] in Figure 2.27 shows ferromagnetic behavior arising from the Co\(^{2+}\) and Mn\(^{4+}\) super-exchange interaction. The Co\(^{2+}\)-O-Mn\(^{4+}\) super-exchange is at a maximum when the Co-O-Mn angle is 180\(^{\circ}\), which obviously appears in the ideal cubic perovskite structure.

**Figure 2.27: Variation in energy of principal phonon bands in \(A(Co_{1/2}Mn_{1/2})O_3\) with the atomic number of the ion on the \(A\) site.**

\( A(Co_{1/2}Mn_{1/2})O_3 \) in Figure 2.27 shows ferromagnetic behavior arising from the Co\(^{2+}\) and Mn\(^{4+}\) super-exchange interaction. The Co\(^{2+}\)-O-Mn\(^{4+}\) super-exchange is at a maximum when the Co-O-Mn angle is 180\(^{\circ}\), which obviously appears in the ideal cubic perovskite structure.
Figure 2.28: Far-infrared spectra of $A(Co_{1/2}Mn_{1/2})O_3$ for $A = \text{La (bottom), Nd, Dy, Ho, Yb (top)}$. Successive spectra have been offset for clarity.\textsuperscript{168}
Chapter 3: Experimental Procedures

3.1 Introduction
To study the compounds in this thesis, a number of experimental techniques have been employed. Fundamentally, the aim was the observation and understanding of magnetic and electrical behavior as a function of temperature. All samples were prepared by solid state reaction through two sintering steps. After determining the ratio of elements and calculating the correct amount of each compound, the compounds were well mixed, pelletized, and sintered. The prepared samples were subjected to X-ray diffraction (XRD) measurements prior to other experiments being carried out. The details will be explained in the individual sections.

The experiments that were conducted include DC and AC magnetization, hysteresis loop, and magneto-transport measurements, as well as Scanning Electron Microscopy (SEM). The overall experimental stages and procedures are shown in Figure 3.1.

3.2 Sample Fabrication
The compounds used in this investigation had a parent $A_xA_{1-x}B_yB_{1-y}O_3$ perovskite structure, where $A$ is a rare earth element, $B$ is a metal, and other elements can also be doped into either $A$ or $B$ sites. The chemicals used for making these samples are shown in Table 3.1.
Table 3.1. The chemicals employed for preparation of the samples.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Formula</th>
<th>Purity</th>
<th>Molecular Weight (mgr)</th>
<th>supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dysprosium(III) oxide</td>
<td>Dy$_2$O$_3$</td>
<td>99.9%</td>
<td>372.997</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Strontium carbonate</td>
<td>SrCO$_3$</td>
<td>99.9%</td>
<td>147.628</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Cobalt(II,III) oxide</td>
<td>Co$_2$O$_4$</td>
<td>99.8%</td>
<td>240.795</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Gadolinium(III) oxide</td>
<td>Gd$_2$O$_3$</td>
<td>99.9%</td>
<td>362.497</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Manganese(II) carbonate</td>
<td>MnCO$_3$</td>
<td>99.9%</td>
<td>114.946</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Holmium(III) oxide</td>
<td>Ho$_2$O$_3$</td>
<td>99.9%</td>
<td>377.797</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Manganese(III) oxide</td>
<td>Mn$_2$O$_3$</td>
<td>99.9%</td>
<td>157.873</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Neodymium(III) oxide</td>
<td>Nd$_2$O$_3$</td>
<td>99.9%</td>
<td>336.477</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Yttrium(III) oxide</td>
<td>Y$_2$O$_3$</td>
<td>99.9%</td>
<td>209.82</td>
<td>Aldrich</td>
</tr>
</tbody>
</table>
Chapter 3

The methodology and equipment employed to prepare the samples are schematically shown in Figure 3.2.

![Methodology and Equipment Flowchart]

**Figure 3.2:** Schematic explanation of the methodologies and equipment employed in the fabrication of the samples.
Enough precursors to make approximately 2 grams of sample material were weighed out with a precise 0.001 mg air flow protected balance and well mixed by means of a mortar and pestle.

The well mixed powder was then pelletized in a cylindrical die 8-10 mm in diameter to make a pellet 2-5 mm in height. The pelletizing pressure was generally about 5 kPa. This pressure was varied, depending on the compound strength, and was adjusted to achieve a well shaped sample, while avoiding any collapse or breakage of the sample as a consequence of pressing. All broken or collapsed samples were simply crushed, re-mixed, and pelletized again. In general, high pressure was not applied, since it would limit and slow down the oxygen reaction of the compounds during the sintering.

The pelletized sample was then heat-treated for the first step of sintering either in a muffle furnace in air or in a tube furnace under flowing oxygen, whichever was necessary. The tube furnace was also used to assess the crucial effect of oxygen flow on some samples. The general range of sintering temperatures was varied between 850°C–1100°C, depending on the class of samples. The sintering temperature mainly depends on the melting point of the compounds in the sample mixture. Note that there was a wide range of melting temperatures in the different precursors for the prepared samples, and the sintering temperature was optimized by a trial and error method, with guidance from the literature. The sintered sample was then crushed into powders in order to carry out XRD examination to assess the
purity, in accordance with the International Center for Diffraction Data (ICDD) standard, 2003. The XRD tests were conducted in a Philips PW-1730 diffractometer.

Samples which were determined to contain no expected phases by the XRD test were heat-treated again at higher sintering temperatures. On the other hand, all successful samples were re-pelletized and prepared for a second sintering, as explained above. Further shaping of the samples might take place after the second sintering for experiments to investigate the magnetic and electrical properties. The re-sintered samples were subjected to a second XRD measurement for further determination of the phase formation and purity. The samples with unknown phases were then examined by SEM. The physical properties of all acceptable samples were then studied by mean of a Quantum Design physical properties measurement system (PPMS).

3.3 Equipment and Measurement Procedures

The different types of equipment, measurement systems, and conditions that were used are described in following sections.

3.3.1 Comparison of samples with the ICDD database

After each step of sintering, the resulting phases of the compounds in the samples were examined by X-ray diffraction using a Philips PW-1730 diffractometer. The
sintering temperature was then suitably adjusted if it was required. In the first stage, a quick scan of the sample was carried out to compare it with the ICDD database, to confirm whether the temperature was suitable to proceed with the second step of sintering. The scanning angles were in the range of $20^\circ \leq 2\theta \leq 90^\circ$ with a scanning rate of $1^\circ$/min. The calibration of the goniometer was achieved by running a test scan on a silicon single crystal plate. Prior to each measurement, the samples were ground in a mortar and then spread onto a glass sample holder plate as a thin flat layer. To fix the powder sample on the glass holder, a drop of pure ethanol was injected onto the sample holder surface prior to spreading the powder sample. When the ethanol was fully evaporated from the sample, the sample was put in the measuring chamber for XRD testing. The diffractogram was then analyzed. Using the “Traces v6” software, the sample phases were assessed and identified from the ICDD database.

After the second step sintering, the sample was re-examined by XRD for careful purity testing to see if the reaction of the compounds was acceptable. The lattice parameters of the crystal structures of the sample were then analyzed to determine if the structure had been changed due to any substitution effect taking place in the parent compound. As a result, some samples showed an increase and some a decrease in the lattice parameters, which was interpreted as shrinkage or expansion of the unit cells.
Since this study was conducted on doped new compounds, the purity testing was based on the parent material in the ICDD database. During the experiments, some samples were scanned more precisely for Rietveld refinement purposes. The patterns of x-ray diffraction for Rietveld analysis were collected by using the abovementioned Phillips apparatus. The scanning angles then were in the range of $10^\circ \leq 2\theta \leq 120^\circ$, with a scan rate of 0.5 $^\circ$/sec and sampling width of 0.02$. Rietica software from the Australian Nuclear Science and Technology Organisation (ANSTO), Australia was used to refine the crystal structure based on the x-ray diffraction patterns.

In some cases, to assess the sample morphology and microstructure, SEM (JEOL JSM-6460A) was employed. Samples were analyzed in either powder form or as pellets. To study the sample compositions, SEM energy dispersive spectroscopy (EDS) was applied using the same equipment.

The phase purity for each sample was examined to determine suitability of the sample for further studies on magnetic and electric properties. It was observed that not all the samples in a certain class were pure enough for physical property characterization.

### 3.3.2 Characterization of Electrical and Magneto-transport Behavior
Electrical transport was one of the significant indices used to characterize the prepared samples of transition metal oxides. On the other hand, the magnetoresistance of a sample could furnish useful information on spin dependent electrical transport, which is considered as one of the key features that describe the intrinsic magnetic properties of compounds.

To measure the transport, bar shaped samples were prepared. A wide temperature range, $4 \text{ K} < T < 360 \text{ K}$, was used to assess the temperature dependency of the electrical resistivity of the samples. To measure the electrical resistivity and magnetoresistance of samples, the “Four Probe” capability on the PPMS was utilized. The technique requires four collinear probes made from copper wires to form contacts with the sample. To achieve a favorable contact, the contact points were painted with silver paste, and while there was a current ($I$) flow between the outer probes, voltage ($V$) was measured between the two inner probes. The collected signals from the voltage wires were measured, and the sample resistance ($\Omega$) was recorded using a computer via an IEEE488 bus interface. The resistivity of the sample ($\rho$) was then calculated by:

$$\rho = \frac{R A}{L}$$  \hspace{1cm} \text{Eq. 3.1}

where $R$ ($\Omega$) is the measured resistance, $A$ ($\text{cm}^2$) is the cross-sectional area, and $L$ (cm) is the distance between the inner contacts (poles).
The samples were tested for magnetoresistance behavior in temperatures ranging from 4 K up to room temperature under a magnetic field of up to 8.7 T. The tests were carried out using the PPMS.

Magnetoresistance (MR) is defined as the change in the resistance of a material under a magnetic field. The MR value was calculated by:

\[
\text{MR} = \frac{\Delta \rho}{\rho_H} = \frac{(\rho_H - \rho_0)}{\rho_H}
\]

where \( \rho_0 \) is the resistivity of the sample at zero magnetic field, and \( \rho_H \) is the resistivity of the sample under magnetic field.

### 3.3.3 Assessing the magnetic properties

The equilibrium magnitude of the magnetization could be found from DC magnetic measurements. On the other hand, the AC moment was measured after the application of an AC field. AC magnetic measurements provide more information on magnetization dynamics than is possible from DC measurements. During the investigation, two types of magnetic measurements were carried out. PPMS equipment was utilized for the measurement of the magnetic properties of samples.

At the first stage, the temperature dependency of the magnetization (M) for the sample was measured under zero-field-cooled (ZFC) and field-cooled (FC) conditions. The applied magnetic field for FC measurements ranged from 50 Oe to 5 T. For ac magnetization measurement, a DC field of 50 Oe was applied, and the measurement was conducted at different frequencies from 117 up to 2 kHz. For some samples, the hysteresis loops were also obtained at different temperatures and
fields up to 8.7 T. From the collected data, the Curie temperature or Néel point and the spin states of magnetic ions could be calculated.

At the second stage, the magnetization (M) of the sample under application of different magnetic fields (H) was collected for the different temperatures. The relative magnetic susceptibility ($\chi_m$) was then calculated by

$$\chi_m = \frac{M}{H}$$

where $M$ is the magnetization, which equals the magnetic moment (emu) divided either by the mass or the volume of the samples measured, and $H$ is the applied magnetic field in either Oe or Tesla. Generally, the magnetic behavior of all the samples was studied in the temperature range from 4 K up to room temperature.

**3.4 Narrowing the range of experimental samples**

The candidate materials were selected mainly from compounds that had the capability of presenting adequate magnetic or electric properties. In designing the samples, the main general aim was the substitution of the rare earth elements and selecting a suitable metal oxide. The degree of substitution that was possible while still maintaining phase purity varied widely. The upper limit on substitution was identified from XRD purity testing. Therefore, the samples that had no phase purity at all were ignored in this research, which resulted in only 8 classes or groups of
samples remaining to be studied. The acceptable samples were experimentally assessed, analyzed, and reported.

In this thesis, various families of transition metal doped oxides were investigated. The parent compounds are: NdCoO$_3$, HoCoO$_3$, YCoO$_3$, DyCoO$_3$, and GdCoO$_3$. The groups of materials which were prepared and studied in this research are listed below. Each sample composition was subjected to some iteration to select the most appropriate compound:

- Nd$_{1-x}$Sr$_x$CoO$_3$
- Ho$_{1-x}$Sr$_x$CoO$_3$
- Y$_{1-x}$Sr$_x$CoO$_3$
- Dy$_{1-x}$Sr$_x$CoO$_3$
- GdMn$_x$Co$_{1-x}$O$_3$
- HoMn$_x$Co$_{1-x}$O$_3$
- Gd$_{1-x}$Sr$_x$CoO$_3$
- La$_{0.33}$Sr$_{0.66}$Fe$_{1-x}$Cr$_x$O$_3$

The collected results were then analyzed and interpreted, and the results will be discussed fully in the following chapters.
Chapter 4: GdCo$_{1-x}$Mn$_x$O$_3$ System

4.1 Introduction

Frozen spins in random alignment define the spin glass state in magnetic systems. The spin glass state has been observed in spinels and amorphous materials, but mostly in dilute magnetic alloys. A spin glass could arise from the paramagnetic state in a disordered system or a transition from the paramagnetic to the ferromagnetic state. In the latter case, the spin glass co-exists with ferromagnetism. Recently, spin glass states have also been widely observed in a number of ReMO$_3$ perovskite (Re = rare earth, M = 3d transition metal) compounds whose structures and magnetic properties are sensitive to doping effects on either Re or M sites. In particular, ReMn$_{0.5}$Co$_{0.5}$O$_3$ perovskites exhibit very interesting paramagnetism, metamagnetism$^{161}$, and ferromagnetism, depending on the size of the particles$^{162,163}$. Very recently, typical spin glass behavior with a very sharp transition width of 1 K at 115 K$^{164}$ was observed in perovskite GdCo$_{0.5}$Mn$_{0.5}$O$_3$ and also observed in YbMn$_{0.5}$Co$_{0.5}$O$_3$ $^{165}$ and LaMn$_{0.5}$Co$_{0.5}$O$_3$ $^{166}$ compounds.

Continuing previous research, a series of polycrystalline samples of GdCo$_{1-x}$Mn$_x$O$_3$ (x = 0.1–0.9) were prepared by conventional solid state reaction as described in the previous chapter. High purity Gd$_2$O$_3$, MnCO$_3$, and CoCO$_3$ were well mixed according to the desired atomic ratios. These powders were then
pressed into pellets 10 mm in diameter and 1 mm in thickness under cold pressure of 5 kPa. The pellets were then sintered in two steps in air in a muffle furnace. They were first sintered at 900°C for 12 hr, and then they were crushed, mixed, re-pelletized, and re-sintered at 1200°C for another 12 hours.

4.2 Structure Characterization

After each sintering the samples were examined for phase purity by XRD. Then, after the second step sintering, the sample phases and crystal structures were determined by powder X-ray diffraction, as shown in Figure 4.1. The XRD results showed that there were no impurities, the samples were single phase, and all the peaks could be indexed. By matching the XRD patterns to the International Centre for Diffraction Data (ICDD) database, it was found that the atoms were crystallized in an orthorhombic structure, and their forms in terms of the $hkl$ indices were obtained for the parent material. The lattice parameters $a$, $b$, and $c$ were calculated for the orthorhombic structure using the formula:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}. \tag{Eq.4.1}$$

In this calculation the higher degree results of the XRD scan were used to test the accuracy of the measurements.
In Figure 4.2 and Table 4.1, the lattice parameters of the prepared samples show that the volume of the sample shrinks with increasing doping level of manganese. The lattice parameter $c$ decreases less (0.0524 Å) compared to $a$ (0.06681 Å) and $b$ (0.08323 Å), or in other words, the sample has less vertical shrinkage than in the $ab$ plane. This is an indication that the CoO$_6$ octahedron is elongated along the $c$-axis by doping with larger amounts of cobalt. The smaller size of the decrease in $c$...
is expected, due to the replacement of the smaller atomic size cobalt ion ($r_{\text{Co}} = 1.35 \, \text{Å}$) by the larger atomic size of manganese ($r_{\text{Mn}} = 1.40 \, \text{Å}$). The structure will tilt to fit the larger atom inside the cell.

Table 4.1: GdCo$_{1-x}$Mn$_x$O$_3$ lattice parameters for various doping levels $x$.

<table>
<thead>
<tr>
<th>Doping</th>
<th>0.2</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>5.31216</td>
<td>5.27284</td>
<td>5.26728</td>
<td>5.24535</td>
</tr>
<tr>
<td>b (Å)</td>
<td>5.57291</td>
<td>5.54508</td>
<td>5.49445</td>
<td>5.48968</td>
</tr>
<tr>
<td>c (Å)</td>
<td>7.5428</td>
<td>7.5164</td>
<td>7.5108</td>
<td>7.4904</td>
</tr>
<tr>
<td>V (Å$^3$)</td>
<td>223.3</td>
<td>219.77</td>
<td>217.37</td>
<td>215.69</td>
</tr>
</tbody>
</table>

Structures were refined using the Rietica Rietveld refinement program, and this required a very slow XRD scan on the samples, which will be further discussed.
below. Rietveld refinement was based on a tetragonal structure with the space group $Pnma$. The crystal structure is schematically shown in Figure 4.3.

Figure 4.3: The crystal structure of GdCoO$_3$.

The results of the observations are shown in Figures 4.4 to 4.10. In these figures, the symbols indicate the experimental results, the red solid line the fit, the vertical blue lines the peak positions of the standard, and the green trace at the bottom the difference between the experimental results and the fit.
Figure 4.4: Rietveld refinement for GdCo$_{0.2}$Mn$_{0.8}$O$_3$.

Figure 4.5: Rietveld refinement for GdMn$_{0.3}$Co$_{0.7}$O$_3$. 
Figure 4.6: Rietveld refinement for GdMn$_{0.4}$Co$_{0.6}$O$_3$.

Figure 4.7: Rietveld refinement for GdMn$_{0.5}$Co$_{0.5}$O$_3$. 
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Figure 4.8: Rietveld refinement for GdMn$_{0.6}$Co$_{0.4}$O$_3$.

Figure 4.9: Rietveld refinement for GdMn$_{0.7}$Co$_{0.3}$O$_3$. 

The Rietveld refinements confirmed the lattice parameters and the angles which are listed in Table 4.2.
### Table 4.2: Lattice parameters for GdMn$_{\delta}$Co$_{1-\delta}$O$_3$, $\delta=0.1-0.8$.

<table>
<thead>
<tr>
<th>$\delta$</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>5.46831</td>
<td>7.49076</td>
<td>5.25102</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>0.7</td>
<td>5.50111</td>
<td>7.51204</td>
<td>5.26603</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>0.6</td>
<td>5.55019</td>
<td>7.54094</td>
<td>5.28948</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>0.5</td>
<td>5.56833</td>
<td>7.54724</td>
<td>5.29692</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>0.4</td>
<td>5.60280</td>
<td>7.55017</td>
<td>5.30305</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>0.3</td>
<td>5.66242</td>
<td>7.53392</td>
<td>5.31037</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
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The atomic positions for each of the elements in the compounds were determined as shown in Table 4.3.

### Table 4.3: Atomic positions for GdMn$_{\delta}$Co$_{1-\delta}$O$_3$, $\delta=0.1-0.8$

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</table>
It can be seen that all the samples are single phase for doping levels from \( x = 0.2 \) up to \( x = 0.9 \), as all the diffraction peaks are from the expected phase. No extra peaks from any impurities are present. Although the intensities of the peaks are not high enough for an accurate determination of the atomic positions, the results allow a reasonably precise determination of the lattice parameters as well as the trend of coordination variations with doping. It can be seen that the coordination in \( x \) and \( z \) changes gradually with increasing Mn. The in-plane and out-of-plane Co-O bond lengths as a function of doping are presented in the following graph.

<table>
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<th>( \delta )</th>
<th>Co-O1 In-plane</th>
<th>Co-O2 In-plane</th>
<th>Co-O Out-of-plane</th>
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<td>0.8</td>
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</table>

It can be seen from the table that the bond lengths of Co-O1 (in-plane), Co-O2 (in-plane), and Co-O (out-of-plane) are very sensitive to the doping levels. Generally speaking, the Co-O1 bond length decreases with increasing Mn for \( \delta < 0.7 \) and then increases for \( \delta > 0.7 \). However, the bond lengths for Co-O2 and Co-O fluctuate with Mn doping, indicating distorted CoO\(_6\) or MnO\(_6\) octahedra for all the doped samples. The complexity of the valences of Co, Mn, and oxygen vacancies are believed to contribute to the distortions.
4.3 Magnetic Properties

4.3.1 DC Magnetization

After confirmation of the purity of the samples, the next step was examining the temperature dependence of the magnetic susceptibility to determine the magnetic states and behaviors of the samples in terms of paramagnetism, ferromagnetism, or antiferromagnetism. Samples with doping levels of $x = 0.2–0.5$ were studied under

![Graph showing FC and ZFC measurements of GdCo$_{1-x}$Mn$_x$O$_3$.](image)

Figure 4.12: FC measurements of GdCo$_{1-x}$Mn$_x$O$_3$, $x = 0.2, 0.3, 0.4$, and $0.5$ and ZFC measurements of GdCo$_{0.5}$Mn$_{0.5}$O$_3$. 
DC fields of 50 Oe and 2000 Oe for a temperature range of 4–340 K were used for the measurements, and the results are presented in Figure 4.12. It is clearly seen from Figure 4.12 that a mixture of magnetic behaviors was observed in different parts of the temperature range. All the samples showed a ferromagnetic transition starting below 120 K. GdCo$_{0.8}$Mn$_{0.2}$O$_3$ has another antiferromagnetic transition at 80 K and GdCo$_{0.7}$Mn$_{0.3}$O$_3$ around 100 K. In GdCo$_{0.8}$Mn$_{0.2}$O$_3$, the magnetization increases rapidly with falling temperature compared to the other samples and reaches a maximum at a very low temperature. In the other two samples, GdCo$_{0.6}$Mn$_{0.4}$O$_3$ and GdCo$_{0.5}$Mn$_{0.5}$O$_3$, the samples first showed a reduction in magnetization in the low temperature region (T < 50 K) with falling temperature and ferromagnetic behavior at higher temperature (50 K < T < 120 K). However, for GdCo$_{0.6}$Mn$_{0.4}$O$_3$, there was a reduction in magnetization at 45 K, which is expected, as the magnetization was measured in zero applied field mode. It was expected that the magnetic dipoles would be aligned in the preferred crystal direction in the lattice and reduce the magneto-crystalline energy. In these two samples, as expected, in ZFC, the magnetic dipoles largely align themselves in the preferred crystal direction, and a large magnetization is observed to arise from reduction of the temperature, but there is no blocking temperature. As the temperature is raised in the ZFC measurement, the thermal distortion completely overcomes the magnetic field, and the dipoles can not align in the direction of the external field to reduce the Zeeman energy, so that the thermal distortion produces randomized moments or magnetic clusters. From 125 K up to room temperature, all the samples are insensitive to DC magnetic field, as they are all paramagnetic.
4.3.2 AC Susceptibility and the Spin Glass State

Study of the magnetic moment in an alternating magnetic field (AC) and measuring the susceptibility of the samples will provide more detailed information on the atomic moments of the compounds in the samples. The magnetic susceptibility of GdCo$_{1-x}$MnxO$_3$ samples was measured in the three different frequencies of 21 Hz, 217 Hz, and 2000 Hz, and results are shown in Figures 4.13, 4.14, and 4.15, respectively.
These frequencies were kept fixed for the other samples as well for comparison purposes. All the samples showed a peak in the real part of the ac susceptibility, which indicates a transition from a paramagnetic state to a ferromagnetic, antiferromagnetic, or spin glass state.

Figure 4.14: AC susceptibility of GdMn$_{0.5}$Co$_{0.5}$O$_3$. 
Regardless of the doping level, all the samples have a transition point at 122 K, which is the same as the transition point for all the samples in the DC magnetization moments. In GdCo_{1-x}MnxO_3 for x < 0.4, the samples showed a secondary peak, and by decreasing the doping level from x = 0.4 down to x = 0.2, the peak was downshifted to lower temperatures. In all the samples with x \leq 0.5, on changing the frequency, the first peak was fixed at 122 K, which is an indication of spin glass. The spin glass is the result of frozen spins in random alignment. However, for x < 0.4, the samples have two peaks, and the secondary peaks are shifted by the change in frequency.
A typical magnetic hysteresis loop for the sample with $x = 0.5$ is shown in Fig. 4.15. It can be seen that hysteresis is present, indicating that the ferromagnetic state exists in the samples at 5 K, in agreement with what is seen from the temperature dependence of the magnetization. However, the magnetic moment does not tend to saturate. This implies that an antiferromagnetic or ferromagnetic state is present at the low temperature. The spin glass state that is observed could be due to co-existence or competition between antiferromagnetic and ferromagnetic interactions.

Figure 4.17: Hysteresis loop of GdMn$_{0.5}$Co$_{0.5}$O$_3$ at 5 K showing a weak ferromagnetic state.
A spin glass state present at 122 K has been reported in GdCo$_{1-x}$Mn$_x$O$_3$ ($x = 0.5$)\textsuperscript{165}. From the M-H loops and M-T curves of the compounds with different x values, these compounds are ferromagnetic. The spin glass state appears when the compounds change from paramagnetic to ferromagnetic. It should be noted that the spin glass state co-exists with the FM state in this compound.

### 4.4 Spin States

All the samples are doped with Mn ions at various levels, which can change the magnetic states of both Co and Mn ions. Determination of the spin contribution of each atom to the total magnetic moment is one of the interests in this study, and this can be calculated from the Curie-Weiss law, using the magnetization measurement results. Considering the paramagnetic susceptibility as $\chi = M/H$, there is an inverse relationship with the temperature, according to the Curie-Weiss law. Drawing the $\chi^{-1}$ graph vs. temperature can lead to the estimation of $T_C$ and the Curie constant, which can be converted to $\mu_{\text{eff}}$. The spin contribution of each atom can then be estimated for each sample.
Figure 4.18: The FC GdCo$_{1-x}$Mn$_x$O$_3$ inverse susceptibility results for 2 kOe at different doping levels.

The field cooled magnetization was also measured at the high field of 2 kOe to obtain the inverse molar susceptibility, $\chi^{-1}$, as plotted against temperature in Figure 4.18. The $\chi^{-1}$ data above 100 K can be well fitted to the Curie-Weiss law, as in the above figure. The obtained $\mu_{\text{eff}}$ from the Curie-Weiss law fitting indicates that $\mu_{\text{eff}}$ per magnetic ion (Co, Mn, Gd) decreased from 7.11 to 5.70 $\mu_B$ when Mn decreased from 0.5 to 0.4. Then, $\mu_{\text{eff}}$ increased up to 6.72 $\mu_B$ as Mn further decreased down to 0.2. As the Gd$^{3+}$ ion contributes half of the 7.94 $\mu_B$, both the Co and the Mn ions could only contribute about 1.7-3.1 $\mu_B$ /magnetic ion (Co, Mn, Gd). As the valences of Co and Mn are very complicated in this system, we can only roughly estimate the possible combination of spin states of Co and Mn which could give rise to a value of $\mu_{\text{eff}}/(\text{Co, Mn, Gd})$ that is close to the observed
\( \mu_{\text{eff}} \) from fitting. For the \( x = 0.5 \) sample, a combination of high spin (\( s = 2 \)) only for both Co\(^{3+}\) and Mn\(^{3+}\) plus \( 1/2 \) Gd\(^{3+}\) \( \mu_{\text{eff}} (\text{Gd}^{3+})^2 + 0.25 \mu_{\text{eff}} (\text{Co}^{3+}(\text{HS}))^2 + 0.25 \mu_{\text{eff}} (\text{Mn}^{3+}(\text{HS}))^2(0.5) \) gives 6.60 \( \mu_B \), close to the \( \mu_{\text{eff}} \) determined for the \( x = 0.5 \) samples (7.11 \( \mu_B \)). For \( x = 0.4 \), a combination of low spin for both Co\(^{2+}\) and Mn\(^{4+}\) \( \mu_{\text{eff}} (\text{Gd}^{3+})^2 + 0.2 \mu_{\text{eff}} (\text{Co}^{2+}(\text{LS}))^2 + 0.3 \mu_{\text{eff}} (\text{Mn}^{4+}(\text{LS}))^2(0.5) \) results in an excellent agreement with the observed 5.70 \( \mu_B \). However, we can not make a convincing estimate of the spin states of the Co and Mn, as both of them might take various valences as \( x \) changes. However, it is possible that as \( x \) increases, the Co valence may change from 2\(^+\) to 3\(^+\), while that of Mn may change from 4\(^+\) to 3\(^+\), and the presence of multi-valences for both Co and Mn is also highly possible, making the system very complicated. A possible combination of high spin states of Co\(^{2+}\) and Mn\(^{4+}\) \( \sim 6.24 \mu_B \) and high spin states of both Co\(^{3+}\) and Mn\(^{3+}\) (6.53 \( \mu_B \)) led to the best fitting to the observed \( \mu_{\text{eff}} \) of 6.22 or 6.72 \( \mu_B \) for the \( x = 0.3 \) and 0.2 samples.

### 4.5 Valence Studies

It is expected that when Co substitutes for Mn, the valence of Mn may not remain as 3\(^+\), as in the parent compound, because the Co ions may vary between 2\(^+\) and 4\(^+\) depending on the charge balance. Determination of the valences of both Mn and Co ions would be useful in precise estimations of the possible spin states of both ions in the present compounds. X-ray absorption near edge spectroscopy (XANES) was used to achieve this purpose on GdCo\(_{1-x}\)Mn\(_x\)O\(_3\) samples.
4.5.1 Mn Valences

A series of spectra of the Mn L-edge X-ray absorption structure for some typical samples, including reference samples, of MnO, Mn$_3$O$_4$, and MnO$_2$, having Mn$^{2+}$, Mn$^{3+}$, and Mn$^{4+}$ valences, are shown in Figure 4.19. The results showed that the presence of the different Mn valences is complex and sensitive to the level of Co. Mn is present in mixed valence states of 2+, 3+, and 4+ for $x = 0.1$ and 0.2, then changes to both 3+ and 4+ for $x = 0.67$, and remains mainly as 4+ for $x > 0.67$. 

![Figure 4.19: Mn L-edge X-ray spectra for GdMn$_{x}$Co$_{1-x}$O$_3$.](image-url)
The peaks indicated by the dashed lines in Figure 4.19 are believed to come from Mn\(^{2+}\). This trend is also in agreement with the decrease in the volume of the unit cell when the amount of cobalt increases, due to the fact that the radius of the Mn\(^{4+}\) ion (0.67 Å) is smaller than that of the Co\(^{3+}\) ion (0.75 Å).

**4.5.2 Co Valences**

To examine the valence states of Co, some spectra of Co L-edge X-ray absorption with varying concentrations of Co in GdMn\(_{1-x}\)Co\(_{x}\)O\(_3\) are shown in Figure 4.20.
structures for some typical samples were collected. The observations, including those on reference samples of $\text{Co}_2\text{O}_3$ and $\text{Co}_3\text{O}_4$, having $\text{Co}^{2+}$ and $\text{Co}^{3+}$ valences, respectively, are shown in Figure 4.20. The results showed that the presence of the different Co valences is complex and sensitive to the level of Mn. Co presents as a mixed valence, and the valences decreased from a mixture of $4^+$ and $3^+$ for $x \leq 0.5$ to $3^+$ for $x > 0.5$. The peaks indicated by arrows in Figure 4.20 in fact come from $\text{Co}^{4+}$. In general, an increase in Co content induces an increase in the Mn valence and results in a decrease in the Co valence in the GdMn$_{1-x}$Co$_x$O$_3$ perovskite. This trend also agrees with the decrease in the volume of the unit cell when the amount of cobalt increases, due to the fact that the Mn$^{4+}$ is smaller than Co$^{3+}$, as was mentioned in previous sections.
Chapter 5: Gd$_{1-x}$Sr$_x$CoO$_3$ System

5.1 Introduction

Referring to the foregoing chapters, the magnetic properties of the cobalt-based perovskite compounds depend on several factors: the first is whether the spin states of Co$^{2+}$, Co$^{3+}$, and Co$^{4+}$ take high, intermediate, or low spin. The second is the exchange interaction. The cobalt ions interact through an intermediate oxygen, where the Co$^{3+}$-O$^{2-}$-Co$^{4+}$ and Co$^{3+}$-O$^{2-}$-Co$^{3+}$ systems have ferromagnetic and antiferromagnetic states, respectively. Thornton et al. studied the electrical properties of LnCoO$_3$ (Ln = La, Nd, Gd, Ho, Y) and suggested that these compounds should show a broad and high-order semiconductor-to-metal transition over a range of temperatures from 490 to 770 K for Ln = Gd. They also suggested that the transition involves $t_{2g}^6e_g^0 \rightarrow t_{2g}^4e_g^2$ excitation and delocalization of $e_g$ electrons. A decade later, Ryu et al. studied a series of compounds in the Gd$_{1-x}$Sr$_x$Co$^{3+}_{1-y}$Co$^{4+}_y$O$_{3-d}$ (x = 0, 0.25, 0.5, 0.75, 1) system with perovskite structures. The structural characterizations by XRD indicated that the structure for x = 0, 0.25, and 1 is orthorhombic, cubic for x = 0.5, and tetragonal for x = 0.75. They found that the volume shrinks as the amount of strontium is reduced. The conductivity measurements indicated that GdCoO$_3$ is a semiconductor and metallic for x = 0.5. In this chapter, studies of the structures, large magnetoresistance, magnetism, and spin states of Co ions in perovskite Gd$_{1-x}$Sr$_x$O$_3$ compounds are presented.
5.2 Sample preparation

Polycrystalline samples of Gd\textsubscript{1-x}Sr\textsubscript{x}CoO\textsubscript{3} (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5) were prepared by conventional solid-state reaction. High purity powders of Gd\textsubscript{2}O\textsubscript{3}, SrCO\textsubscript{3}, and Co\textsubscript{3}O\textsubscript{4} were well mixed according to the desired atomic ratios for each sample. As explained in previous chapters, these powders were then pelletized to a size 10mm in diameter and about 5mm in thickness. The pellets were then heat treated in two steps: first, sintering at 950°C for 12 hr, then crushing, mixing, and pelletization again for the second step, and finally, sintering at 1100°C for 24 hr. The sample phases were determined using powder X-ray diffraction. Magnetic and transport properties were studied using a commercial Physical Properties Measurement System (PPMS). Zero-field cooled (ZFC) and field cooled (FC) magnetizations were recorded in a field of 0.2 T over a wide range of temperatures from 5 K to 340 K. AC susceptibility was measured at the different frequencies of 21 Hz, 117 Hz, 217 Hz, and 2 kHz. Magnetic hysteresis loops were measured in fields between ±7 T at 5 K.

5.3 Structure Characterization

XRD patterns for Gd\textsubscript{1-x}Sr\textsubscript{x}O\textsubscript{3} are shown in Figure 5.1, where it can be seen that all the compounds are crystallized in the orthorhombic structure with Pnma symmetry for x < 0.5, as schematically shown in Fig. 5.2(a). The crystal structure changes to cubic for x > 0.5, as shown in Fig. 5.2(b).
Figure 5.2: Powder X-ray diffraction patterns for Gd$_{1-x}$Sr$_x$CoO$_3$. 

![Powder X-ray diffraction patterns for Gd$_{1-x}$Sr$_x$CoO$_3$.](image-url)
Fig 5.2: The crystal structure of Gd$_{1-x}$Sr$_x$CoO$_3$ with $x < 0.5$ (a), and $x > 0.5$ (b).

The lattice parameters calculated from XRD are plotted in Figure 5.3. It can be seen that the lattice parameters $a$, $b$, and $c$ gradually decrease with increasing Sr content, resulting in a decrease in the volume of the unit cell.
Figure 5.3: Variation of the lattice parameters with the doping level for Gd$_{1-x}$Sr$_x$CoO$_3$, $x \leq 0.5$. 
Figure 5.4: Variation of cell volume with the doping level for Gd$_{1-x}$Sr$_x$CoO$_3$, $x \leq 0.5$.

The Rietveld refinement method was used to analyze the XRD patterns and to determine the lattice parameters and the atomic positions of the Gd$_{0.5}$Sr$_{0.5}$CoO$_3$ elements in the crystal. The results are shown in Table 5.1.
Chapter 5

Figure 5.5: Rietveld refinement for Gd_{0.5}Sr_{0.5}CoO_3. The symbols indicate the experimental results, the red solid line the fit, and the green line the difference. The short blue lines indicate the peak positions in the standard, and the vertical blue zone indicates a range that was not included in the fit.

Table 5.1: Gd_{0.5}Sr_{0.5}CoO_3 Lattice parameters and Atomic positions

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</table>

5.4 Magnetic Properties

5.4.1 DC-magnetization

The temperature dependence of the field cooled dc magnetization was collected in a field of 2000 Oe, and the results are shown in Fig. 5.4. It can be seen that all the
samples exhibited a ferromagnetic transition at a temperature around 150 K, where the magnetization increases as the value of x increases. It should be noted that the magnetization increases sharply when the temperature drops below 50 K.

Figure 5.6: Temperature dependence of the magnetization for Gd$_{1-x}$Sr$_x$CoO$_3$. 
In order to investigate the field effect on magnetic interactions of Gd$_{0.5}$Sr$_{0.5}$CoO$_3$, the FC and ZFC magnetizations were measured in fields of 20 Oe, 2 kOe, 3T, and 5T, as depicted in Figure 5.5. It can be seen that the ZFC moment is gradually eliminated with increasing magnetic field. At this point, the ZFC and FC moments overlap, and the typical features of a ferromagnetic transition are no longer clearly seen. This indicates that the ferromagnetic state dominates at low field, and both ferromagnetic and paramagnetic interactions coexist at high magnetic field, which can be further proved from M-H loop measurements.

5.4.2 Hysteresis loops

Magnetic hysteresis loops were measured at the temperature of 5 K in fields from –8 T to +8 T, and the results are plotted in Fig. 5.6. It can be seen that samples
changed from a weak to a strong ferromagnetic phase when the value of $x$ changed from 0.1 to 0.4, as a consequence of increases in the moment values with $x$. In addition, the coercive fields are also enhanced with $x$. No saturation of magnetization was present for any of the samples, indicating the presence of an antiferromagnetic or paramagnetic interaction coexisting with the ferromagnetic interaction. Further work needs to be carried out to determine the magnetic structures using neutron diffraction.

![Hysteresis loops for Gd$_{1-x}$Sr$_x$CoO$_3$, measured at 5 K. The inset shows an enlargement of part of the field range.](image)

Hysteresis loops for the Gd$_{0.5}$Sr$_{0.5}$CoO$_3$ sample at the different temperatures of 2 K, 5 K, 30 K, and 100 K were collected, and the results are presented in Figure 5.8. It can be seen that at 2 K and 5 K, the sample demonstrates two transitions between 1 T and 3 T, becoming magnetically saturated after 3 T. The reason for
the transition is the contribution of both Gd and Co ions. In other words, the effect of Co is dominant for the total magnetic moment at low field, whereas the influence of Gd becomes greater as the field shifts to higher values. The effect of the Sr doping level on the hysteresis loops of Gd$_{1-x}$Sr$_x$CoO$_3$ is also illustrated for $x = 1/2$ and $x = 2/3$ in Fig. 5.9 and Fig. 5.10. It can be seen that the ferromagnetic state in low field that is seen in the $x = 0.5$ sample is absent in the $x = 2/3$ sample. The $x = 2/3$ sample only shows typical paramagnetic behavior.

Judging from the magnetic moments in high magnetic field, the estimated moment from Co is about 0.08 $\mu_B$/Co, which means that the Co is present in the low spin state ($S = 0$) in the $x = 2/3$ sample. However, the moment of Co is about 0.7 $\mu_B$/Co, which is close to that of its low spin state ($S = 1/2$). These results indicate that the spin state of Co changes with the crystal field as well as with the magnetic field. This is more clearly seen in the inverse susceptibility vs. temperature for the $x = 0.5$ sample, as seen in Fig. 5.11.

$$\text{Gd }\frac{1}{2}(3.5\mu_B)\rightarrow(4.2-3.5) = 0.7\mu_B/\text{Co}$$

![Hysteresis loop for $x = 0.5$ at 5 K.](image)

**Figure 5.9: Hysteresis loop for $x = 0.5$ at 5 K.**
A similar regime was also observed in the measurement of the ac susceptibility. A plot of the inverse susceptibility against temperature for the x = 0.5 sample is presented in Figure 5.11. It can be seen that for the low field of 2 kOe, a short range ferromagnetic state starts at about 150 K, and long range ferromagnetic ordering occurs between 100 and 125 K. However, for fields greater than 3 T, \(1/\chi\) tends to deviate upward from the dashed line, which is completely opposite to what is seen for the low field range. A second linear range can be seen below 100 K for both 3 and 5 T. This is a strong indication that the low field magnetic state is contributed from the Co, while the high field state comes from the Gd moment, in agreement with what is seen from the M-H loops.
5.4.3 AC Susceptibility

The temperature dependence of the ac susceptibility was measured at various frequencies for the Gd$_{0.5}$Sr$_{0.5}$CoO$_3$ sample, the results of which are shown in Figure 5.12. There is a peak in the real part of the ac susceptibility, and the peak position shifts towards high temperatures as a result of increased frequency, which is indicative of a spin glass state at a temperature around 122 K. It can also be seen that the maximum ac susceptibility decreases with increasing frequency.

Close examination of Figure 5.12 reveals that the variation in the peak susceptibility ($\chi'_{\text{peak}}$) values with frequency ($f$) falls in an exponential manner, with the best fit occurring with $R^2 = 0.997$, which is shown in Figure 5.13 and mathematically expressed as:

$$\chi'_{\text{peak}} = \chi'_0 + f_0 \exp\left(-\frac{f}{\beta}\right)$$

Eq. 5.1
where \( \chi'_o = 4.172, \ f_o = 1.935, \ \beta = 1.032 \times 10^3 \).


Figure 5.13: Variation of the peak in the real part of the susceptibility of Gd$_{0.5}$Sr$_{0.5}$CoO$_3$ as a function of frequency.

5.5 Transport Properties

The results on the measured temperature dependence of the resistance at both zero field and 8 T are shown in Figure 5.14 and Figure 5.15, respectively. It can be seen that doping with Sr monotonically reduces the resistance of the compounds. It can also be observed that the temperature dependence of the resistance follows a thermal activation law (Eq. 5.2) over a wide temperature range, as indicated in the inset of Figure 5.14.
\[
\frac{R}{R_n} = \exp^{\frac{U}{k_B T}}
\]  
Eq. 5.2

Figure 5.14: The temperature dependence of the resistivity of \( \text{Gd}_{1-x}\text{Sr}_x\text{CoO}_3 \) for various \( x \).
The resistance of all the samples dropped below 15 K under the application of a magnetic field of 8 T, which is similar to what happens with colossal magnetoresistance manganites. The variation of the magnetoresistance with field was measured at 5 K, and the results are shown in Figure 5.15. It was discovered that all the samples exhibited large magnetoresistance, with field values from > 20% in 4.5 T for $x = 0.1$, to 45% in 8 T for $x = 0.3$, and about 60% in 8 T for both $x = 0.3$ and 0.4 samples. To the best of our knowledge, the magnetoresistance value of 60% is the highest among all the cobalt-based perovskite compounds reported so far.

The trend in the resistivity vs. temperature of Gd$_{1-x}$Sr$_x$CoO$_3$, $x < 0$, and the magnetoresistance of Gd$_{0.5}$Sr$_{0.5}$CoO$_3$ at 7 T are illustrated in Figures 5.16 and 5.17,
Figure 5.16: Resistivity vs. magnetic field for Gd$_{1-x}$Sr$_x$CoO$_3$, $x < 0.5$.

respectively. Figure 5.17 shows that the trend in the resistivity of Gd$_{1/2}$Sr$_{1/2}$CoO$_3$ does not change. The MR values for this sample increase with decreasing temperature. This is due to possible enhancement of the spin polarization at low temperatures.
**Figure 5.17:** Magnetoresistance dependency of Gd$_{0.5}$Sr$_{0.5}$CoO$_3$ on temperature at a field of 7 T.

**Figure 5.18:** Temperature dependence of the resistivity of Gd$_{0.5}$Sr$_{0.5}$CoO$_3$. 

\[ H_{dc} = 7 \text{ T} \]
Chapter 5

5.6 Spin States

The temperature dependence of the inverse susceptibility is plotted in Figure 5.19. It can be seen that all observations fall into a linear relationship between 200 and 330 K and can be well fitted by a linear Curie-Weiss law, where the values of the observed $\mu_{\text{eff}}$ from the fittings range from 6.6 to 7.6 $\mu_B$/Mol.

![Figure 5.19: Temperature dependence of the inverse susceptibility. The straight lines are fittings to the Curie Weiss law.](image)

In order to estimate the possible spin state of the Co ions, several combinations of spin states, such as low, intermediate, and high spin for both Co$^{3+}$ and Co$^{4+}$ were considered, and the resulting values of $\mu_B$ are illustrated and compared to the results of the Curie-Weiss law fitting in Figure 5.20. The results indicate that a
combination of Co$^{4+}$(LS) and Co$^{3+}$(LS) resulted in the best fit to the observed values of $\mu_{\text{eff}}$.

![Figure 5.20: Observed and calculated effective moments with various combinations of spin states.](image)

**Summary**

The explanations in the foregoing sections can be summarized by the statement that Gd$_{1-x}$Sr$_x$CoO$_3$ ($x = 0.1$-$0.4$) compounds are ferromagnetic around 150 K and that the magnetization and the coercive fields increase with Sr doping level. A spin glass state was observed for the $x = 0.5$ sample. Furthermore, the resistivities drop systematically with $x$. Giant magnetoresistance over 60% was observed for
the $\text{Gd}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ sample. Spin state assessment indicates that the $\text{Co}^{3+}$ and $\text{Co}^{4+}$ are present as intermediate and high spin states.
CHAPTER 6: HoMn$_{1-x}$Co$_x$O$_3$

6.1 Introduction

Materials having coupled ferroelectric and magnetic parameters that result in simultaneous ferroelectricity and ferromagnetism (recently referred to as the so-called multiferroic or magnetoelectric (ME) materials) have attracted a considerable revival of interest in recent years. From a technical point of view, the mutual control of electric and magnetic properties is an attractive possibility, for it adds one more degree of freedom to manipulate the properties of both magnetic and electric materials. HoMnO$_3$ is one of the typical ME materials whose magnetic phases can be controlled by electric fields. HoMnO$_3$ crystallizes in a hexagonal structure with P6$_3$cm symmetry, displays ferroelectric ordering around 875 K, antiferromagnetic Mn$^{3+}$ ordering at the Néel temperature ($T_N$) of 75 K, and magnetic Ho$^{3+}$ ordering at 4.6 K. Recently, novel field-induced magnetic phases were observed below the $T_N$, making HoMnO$_3$ more complex and interesting in terms of magnetic properties than other rare earth based manganates of the REMnO$_3$ type (where RE = rare earth). Co ions having different valences, 2+, 3+, and 4+, with various spin states are interesting dopant species that could induce changes in structures and magnetic phases. This chapter contains studies of the cobalt doping effects on the structures, magnetic properties, valences, and spin states of both Mn and Co ions in the multiferroic parent compound HoMnO$_3$. 
6.2 Sample preparation

Eight polycrystalline samples of HoMn$_{1-x}$Co$_x$O$_3$ compounds with different doping levels (x = 0–0.9) were prepared and synthesized by solid state reaction. High purity powders of Ho$_2$O$_3$, MnCO$_3$, and Co$_3$O$_4$ were well mixed according to the desired atomic ratios for each sample. The masses of the precursor materials were weighed using an electronic balance up to point two digits (±0.01 mgr), and then well mixed and combined in a mortar. The mixed powder was then pelletized using a cylindrical die 10 mm in diameter to a size with a minimum 5 mm of height under 5 kPa pressure. Immediately after pelletizing, all the samples were heat-treated together in two steps. After the first step of heat-treatment, the purity of the samples was examined by a quick x-ray diffraction (XRD) scan. After the second heat-treatment, the samples’ structure was examined again by XRD. The single phase samples were then considered for further physical property assessment. The successful samples of Ho$_{1-x}$Mn$_x$CoO$_3$ were examined for their physical properties related to magnetism.

Rietveld refinement from powder X-ray diffraction data indicated that, instead of the hexagonal structure with P6$_3$cm symmetry that is characteristic of HoMnO$_3$, the compounds doped with Co crystallized in the GdFeO$_3$-type orthorhombic structure containing distorted (Co/Mn)O$_6$ octahedra. The dc magnetization was measured in fields up to 5 T over a wide temperature range from 350 K down to 5 K. It was found that the system gradually changed from paramagnetic for x = 0 to
ferromagnetic with a Curie temperature \(T_C\) of 90 K for \(x = 0.5\), and then to paramagnetic again for \(x = 0.8\). X-ray absorption near-edge spectra (XANES) were collected to determine the valences of both the Co and the Mn ions. The results showed that Co and Mn presented mainly as mixed valences of \(\text{Co}^{2+} + \text{Co}^{3+}\), \(\text{Mn}^{4+} + \text{Mn}^{3+}\), \(\text{Co}^{3+} + \text{Co}^{4+}\), and \(\text{Mn}^{4+}\), depending on the value of \(x\). When the XANES results were combined with Curie-Weiss fitting, it was found that both \(\text{Mn}^{4+}\) and \(\text{Co}^{3+}\) were present as high spin states for \(x > 0.2\), whereas, \(\text{Co}^{4+}\) appeared in either intermediate or high spin states, closely corresponding to the lattice variations along the (010) direction.

### 6.3 Structure Characterization

The XRD results are plotted in Figure 6.1. The analysis for \(\text{Ho}_{0.5}\text{Mn}_{0.5}\text{CoO}_3\)

![Figure 6.1: XRD spectra of Ho\(_{1-x}\)Mn\(_x\)CoO\(_3\) for different doping levels.](image)
showed that there was nearly 10% Ho$_2$O$_3$ impurity.

In order to increase the reaction of Ho$_2$O$_3$ and reduce any un-reacted amount, the injected oxygen level was increased to activate the reaction of more particles. The rate of oxygen flow inside the sample was also increased by increasing the inter-particle distance to ease O$_2$ flow. This was achieved by reducing the pressure during the pelletizing process. These attempts to increase the reaction rate did not succeed. Increasing the O$_2$ flow rate in the tube furnace was also tried with no success.

![Figure 6.2: Variation with x of lattice parameters and the cell volume (inset) of HoMn$_{1-x}$Co$_x$O$_3$.](image)

As is evident from Figure 6.2, the volume of Ho$_{1-x}$Mn$_x$CoO$_3$ shrinks with the doping level. The shrinkage might be attributed to the tetragonal tilting of the perovskite structure rather than its expansion.
As was mentioned, the results of XRD indicated that the HoMnO$_3$ sample is single phase and crystallizes in a hexagonal structure. However, Rietveld refinement of the XRD data indicated that the compounds doped with Co had crystallized in the GdFeO$_3$-type orthorhombic structure with Pnma symmetry and contained distorted (Co/Mn)O$_6$ octahedra. XRD patterns, collected at 300 K, with Rietveld refinement results for HoMnO$_3$ and x =0.2 - 0.6 samples, based on the Rietica program, are shown in Figures 6.3 to 6.8. The figures show the observed (crosses) and calculated (solid line) patterns, and the difference diffraction profile at the bottom. The vertical blue lines indicate the peak positions for the standard. The results show that a small amount of Ho$_2$O$_3$ secondary phase is present. The lattice parameters $a$ and $c$ obtained from refinement analysis decreased systematically with increasing cobalt content, as shown in Figure 6.2. In contrast, lattice parameter $b$ increased at low doping levels and then dropped for high Co doping levels. Note, however, that the change in lattice parameter $b$ is very small, only about 0.06 Å, compared to 0.1 and 0.2 Å for $a$ and $c$, respectively. However, the volume of the unit cell decreased monotonically with increasing Co content.
Figure 6.3: Rietveld refinement for HoCoO$_3$.

Figure 6.4: Refined pattern for HoMn$_{0.2}$Co$_{0.8}$O$_3$.
Figure 6.5: Refined pattern for HoMn$_{0.33}$Co$_{0.66}$O$_3$.

Figure 6.6: Rietveld refinement for HoMn$_{0.4}$Co$_{0.6}$O$_3$.
From the refinement, the lattice parameters and atomic positions were determined, and the results are shown in Tables 6.1 and 6.2, respectively.
Table 6.1: Lattice parameters obtained from refinement for HoMn$_{0.5}$Co$_{0.5}$O$_3$, $\delta$=0.2-0.6.

<table>
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<tr>
<th>$\delta$</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
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<td>90</td>
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<tr>
<td>0.3</td>
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<td>90</td>
<td>90</td>
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<tr>
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<td>90</td>
<td>90</td>
</tr>
<tr>
<td>0.6</td>
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<td>7.46903</td>
<td>5.23804</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
</tbody>
</table>

Comparing the results in Table 6.1 with those depicted in Figure 6.2 shows a good agreement between the refinements results and the calculated values.

Table 6.2: Atomic positions obtained from refinement for HoMn$_{0.5}$Co$_{0.5}$O$_3$, $\delta$=0.2-0.6.

<table>
<thead>
<tr>
<th>Coordinates</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic Position</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HoMn$<em>{0.5}$Co$</em>{0.5}$O$_3$</td>
<td></td>
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</tr>
</tbody>
</table>

<table>
<thead>
<tr>
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<th>Mn</th>
<th>Co</th>
<th>O-1</th>
<th>O-2</th>
</tr>
</thead>
<tbody>
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<td>0.0000</td>
<td>0.0000</td>
<td>0.4791</td>
</tr>
<tr>
<td>y</td>
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<td>0.2500</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.2500</td>
</tr>
<tr>
<td>z</td>
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<td>-0.0126</td>
<td>0.5000</td>
<td>0.5000</td>
<td>0.0904</td>
</tr>
</tbody>
</table>

Using the atomic position values in Table 6.2, the 3D structure of HoMn$_{0.5}$Co$_{0.5}$O$_3$ crystal from different perspectives was plotted and is presented in Figures 6.9 to 6.12.
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Figure 6.9: Schematic diagram showing the y-axis view of the crystal structure of HoMn$_{0.5}$Co$_{0.5}$O$_3$.

Figure 6.10: Schematic diagram showing the x-axis view of the crystal structure of HoMn$_{0.5}$Co$_{0.5}$O$_3$. 
Figure 6.11: Schematic x direction view of HoMn$_{0.5}$Co$_{0.5}$O$_3$ crystal, semi-rotated around the y axis.

Figure 6.12: Schematic x direction view of HoMn$_{0.5}$Co$_{0.5}$O$_3$ orthogonal crystal, semi-rotated around the y axis.
It can be seen from the table that the bond lengths of Co-O1 (in-plane) Co-O2 (in-plane) and Co-O (out-of-plane) are very sensitive to the doping levels, similar to the case for GdCo$_{1-x}$Mn$_x$O$_3$. General speaking, the Co-O1 deceases with increasing Mn for $\delta < 0.6$ and then increases for $\delta > 0.5$. The Co-O bond length shows the opposite trend, as it increases with Mn doping, then drops as $\delta$ reaches 0.6. However, the bond lengths for Co-O2 fluctuate with Mn doping, indicating a distorted CoO$_6$ or MnO$_6$ octahedron for all the doped samples. The complexity of the valences of Co, Mn, and oxygen vacancies are believed to contribute to the distortions.

### 6.4 Magnetic Properties

Magnetic properties were measured using a Physical Properties Measurement System (PPMS, Quantum Design) and a Magnetic Properties Measurement System (MPMS XL, Quantum Design) over a wide temperature range between 10 and 340 K in fields up to 8.5 Tesla. The valences of both Co and Mn ions in our samples were determined by X-ray absorption near edge structure spectroscopy (XANES) using synchrotron irradiation at the Synchrotron Radiation Research Centre (SRRC, Taiwan).
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The temperature dependence of the field-cooled (FC) magnetization measured at 0.2 T is shown in Fig. 6.15. The substitution of Co for Mn induced a dramatic evolution in the magnetic states. It can be seen that the system gradually changed from paramagnetic for $x = 0$ to typical ferromagnetic with a $T_C$ of around 90 K for $x = 0.5$, and then to paramagnetic for $x = 0.8$. In addition, the $x = 0.5$ sample was characterized by the maximum magnetization among all the samples.

The temperature dependence of the inverse susceptibility $\frac{1}{\chi}$ is plotted in the inset in Fig. 6.15. It can be seen that all the data was well matched to a linear Curie-Weiss (CW) law fitting over a wide temperature range from 110 to 330 K. The $\mu_{\text{eff}}$

![Figure 6.13: Temperature dependence of the field cooled magnetization and the inverse susceptibility (inset) of HoMn$_{1-x}$Co$_x$O$_3$ samples. Straight lines are linear fittings to the Curie-Weiss law.](image-url)
obtained from the fitting gives rise to values of about 12.8 $\mu_B$ for $x = 0.2$ and around 11.3 $\mu_B$ for $x > 0.2$, as shown in Fig. 6.13.

It is expected that when Co substitutes for Mn, the valence of Mn may not remain 3+ as in its parent compound, because the Co ion valences may vary between 2+ and 4+, depending on charge balance. Determination of the valences of both Mn and Co ions would be useful in the precise estimations of possible spin states of both ions in the present compounds.

### 6.5 Valence studies

A series of spectra of the Mn and Co L-edge X-ray absorption structures for some typical samples, including reference samples, of MnO, Mn$_3$O$_4$, and MnO$_2$, having Mn$^{2+}$, Mn$^{3+}$, Mn$^{4+}$, Co$^{2+}$, and Co$^{3+}$ valences, are shown in Figure 6.14. The results showed that the presence of the different Mn valences is complex and sensitive to the level of Co. Mn presents in the mixed valence states of 2+, 3+, and 4+ for $x = 0.1$ and 0.2, changes to both 3+ and 4+ for $x = 0.67$, and remains mainly as 4+ for $x > 0.67$. Meanwhile, the Co valences decreased from a mixture of 4+ and 3+ for $x \leq 0.5$ to 3+ for $x > 0.5$, as shown in Figure 6.15. The peaks indicated by arrows in Figure 6.15 are believed to come from Co$^{4+}$, since these peak positions are the same as what is observed in SrCoO$_3$ containing pure Co$^{4+}$ ions. In general, an increase in Co induces an increase in Mn valence and a decrease in Co valence in the HoMn$_{1-x}$Co$_x$O$_3$ perovskite. This trend is also in agreement with the decreasing volume of the unit cell when the amount of cobalt increases, due to the fact that the radius of the Mn$^{4+}$ ion (0.67 Å) is smaller than that of the Co$^{3+}$ (0.75 Å).
Based on the above values of the valences of both Mn and Co ions, an assessment of the possible spin states of both ions present in the system was carried out by considering several combinations of low spin (LS), intermediate spin (IS), and high spin (HS). Ho$^{3+}$ contributes a constant moment of 10.60 $\mu_B$ for all the samples. For $x = 0.2$, a combination of 50% Mn$^{3+}$ (HS), 30% Mn$^{2+}$ (IS) and 20% Co$^{4+}$ (IS) resulted in 11.38 $\mu_B$/mol (the same as the observed value of 11.37 $\mu_B$/mol). For $x = 0.33$ a combination of 67% Mn$^{4+}$ (HS) + 15% Co$^{4+}$ (HS) + 18% Co$^{3+}$ (HS) yields 11.48 $\mu_B$/mol. 50% Mn$^{4+}$(HS) + 25% Co$^{4+}$(HS) + 25% Co$^{3+}$ (HS), 33% Mn$^{4+}$(HS)
+ 17% Co^{4+} (IS) + 50% Co^{3+} (HS), and 20% Mn^{4+} (HS) + 80% Co^{3+} (HS) for x = 0.5, 0.33, and 0.2, respectively, lead to values of $\mu_{\text{eff}}$ that are close to what was observed from the Curie-Weiss fitting. A comparison of calculated and observed $\mu_{\text{eff}}$ is shown in Figure 6.16. It can be seen that the above combinations of spin states and the ratio of valences (determined from XANES studies) give the best match to the experimental data for the x = 0 to 0.67 samples. For x = 0.8, the difference between observation (12.78 $\mu_B$/mol) and calculation (11.68 $\mu_B$/mol) is slightly larger compared to the other samples, even though the high spin contribution from both Mn^{4+} and Co^{3+} was considered. The compound with the

![Figure 6.14: Mn L-edge X-ray absorption structure spectrum for HoMn$_{1-x}$Co$_x$O$_3$. Dot-dashed lines represent characteristic peaks from Mn$^{2+}$, Mn$^{3+}$, and Mn$^{4+}$.](image-url)
much higher Co content of 0.8 might have more oxygen deficiencies than the other samples, resulting in an inaccurate estimation of the molar mass for $\mu_{\text{eff}}$ calculations.

\begin{center}
\includegraphics[width=0.6\textwidth]{fig615.png}
\end{center}

\textbf{Figure 6.15:} Co L-edge X-ray absorption structure spectrum for HoMn$_{1-x}$Co$_x$O$_3$. The solid line represents characteristic peaks from Co$^{3+}$ or Co$^{2+}$. The peaks indicated by arrows are from Co$^{4+}$, as seen in SrCoO$_3$.

From the results of the spin state assessment, it can be seen that both Mn$^{4+}$ and Co$^{3+}$ take HS states in all the samples with $x \geq 0.67$. Because of the sizes of the HS states of Co$^{3+}$ (0.75 Å) and of Mn$^{4+}$, the volume of the unit cell gradually decreases with increasing (decreasing) cobalt (manganese) doping levels as Co$^{3+}$ becomes the majority valence. However, Co$^{4+}$ changes from IS for $x = 0.2$ to HS
for $x = 0.33$ and $0.5$, and back to IS again for $x = 0.67$. This evolution of the spin states of Co$^{4+}$ coincides with the trend shown by the variations in lattice parameter $b$ at the same corresponding $x$ values.

![Figure 6.16 Observed and calculated effective moments vs. doping levels.](image)

This reveals that the changes in crystal field along the (010) direction play an important role in determining the spin states of Co$^{4+}$. Shrinkage (expansion) of the lattice along the (010) direction enhances (reduces) the crystal field in favor of IS (HS) states of Co ions. Such a spin state evolution of Co$^{4+}$ has been seen in some three-dimensional cobalt based perovskite compounds, such as Ca or Ba doped LaCoO$_3$ $^{179}$, HoCoO$_3$ $^{180}$, and the novel two dimensional Sr$_{2-x}$Y$_x$CoO$_4$ system, where either Co$^{3+}$ or Co$^{4+}$ present as HS and IS states $^{181}$. 

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6.6 Optical Studies

The polycrystalline perovskite compounds of HoMn$_{1-x}$Co$_x$O$_3$ ($x = 0–0.8$) were examined by far-infrared (FIR) spectroscopy to study infrared active phonon modes and facilitate a comparative analysis of infrared transmission spectra of polycrystalline HoMn$_{1-x}$Co$_x$O$_3$ ($x = 0–0.8$). The data indicated that phonon modes were changed significantly with increasing cobalt doping level. Four main bands were assigned as external, torsional, bending, and stretching bands. The external vibration energy remained the same at $\omega \approx 190$ cm$^{-1}$ for Co doping with $x \leq 0.5$ and shifted to higher energy for $x > 0.5$. The torsional and bending bands exhibited splitting. The stretching band is at 600 cm$^{-1}$ for all samples, but the band width is reduced as Co doping is increased. The transmission spectrum of HoMn$_{4/5}$Co$_{1/5}$O$_3$ was analyzed with respect to the spectrum of optical density. The minimum number of oscillators to obtain a reliable fit is 5, when using a sum of non-interacting harmonic oscillators.

Perovskite polycrystalline samples of HoMn$_{1-x}$Co$_x$O$_3$ ($x = 0, \frac{1}{2}, \frac{4}{7}, \frac{1}{7}, \frac{2}{7}, \frac{4}{7}$) were synthesized by the standard solid-state reaction method. Appropriate amounts of Ho$_2$O$_3$, Mn$_2$O$_3$, and CoCO$_3$ were mixed and sintered at 900°C in air with intermediate grinding, then pressed into pellets. A final sintering process step was carried out at 1400°C. The structures of HoMn$_{1-x}$Co$_x$O$_3$ were characterized by XRD using a Philips diffractometer with CuK$\alpha$ radiation. The magnetic properties were investigated at temperatures from 4.2–300 K using a
Quantum Design Physical Properties Measurement System (PPMS). For infrared transmission measurements, polycrystalline samples diluted in CsI were finely milled and pressed into pellets. The transmission experiments were carried out using a Bomem DA3.26 rapid scan interferometer with a Deuterated Tri-Glycine Sulfate (DTGS) detector, which has a range from 10 – 700 cm\(^{-1}\). The experimental resolution and scan speed were 4 cm\(^{-1}\) and 0.2 cm\(^{-1}\)/s, respectively.

We performed measurements on the HoMn\(_{1-x}\)Co\(_x\)O\(_3\) samples at room temperature. The intensity, \(I(\omega)\), is the transmitted intensity through the pellet containing the holmium manganese oxide, and \(I_0(\omega)\) is the transmitted intensity through a pure CsI pellet.

For the samples with \(x = 0\)-0.8 doping levels, x-ray diffraction shows that their structures are orthorhombic, while HoMnO\(_3\) is hexagonal. The lattice parameters increase as the Co doping level decreases for HoMn\(_{1-x}\)Co\(_x\)O\(_3\) \((x = \frac{1}{2}, \frac{1}{3}, \frac{1}{2})\). The ferromagnetism is gradually suppressed, when doping level are greater or less than \(x = 0.5\). The details of structures, and the electronic and magnetic properties of HoMn\(_{1-x}\)Co\(_x\)O\(_3\) will be further discussed in a forthcoming report \(^{182}\).

Figure 6.10 shows the doping-dependent transmission spectra (ratio of \(I(\omega)/I_0(\omega)\)) of HoMn\(_{1-x}\)Co\(_x\)O\(_3\) \((x = 0\)-0.8) at room temperature in the range from 150 –700 cm\(^{-1}\). It should be noted that we were not able to obtain the same range as the detector, because CsI is opaque at lower frequencies \(^{183}\). The optical modes of the ideal cubic structure have the irreducible representation \(\Gamma = 3F_{1u} \, \text{(infrared active)} + F_{2u} \, \text{(infrared inactive)}\). Thus threefold degenerate infrared active modes are expected for \(k = 0\). Last \(^{184}\)
identifies the bands in order of increasing energy as external A-(BO\textsubscript{3})
vibration, O-B-O bending, and B-O stretching. As the crystal symmetry is
reduced, more optical modes are expected. There are 25 infrared active
modes for orthorhombic (\textit{D\textsubscript{2h}}, Pnma) symmetry\textsuperscript{185}. In particular, the
forbidden torsional mode F\textsubscript{2u} (o\textsubscript{t}) is now allowed and has been calculated
to lie between the external and the bending modes\textsuperscript{186}. In view of the big
differences that can be seen in the transmission spectrum of HoMnO\textsubscript{3},
which is hexagonal in Figure 6.17, further discussion will now be
concentrated on the spectra of HoMn\textsubscript{1-x}Co\textsubscript{x}O\textsubscript{3} (x = 0.2–0.8). The phonon modes
of HoMn\textsubscript{0.5}Co\textsubscript{0.5}O\textsubscript{3} were the same as those observed in a previous report\textsuperscript{187}.
Consequently, the four broad bands for HoMn\textsubscript{0.5}Co\textsubscript{0.5}O\textsubscript{3} are assigned as
follows: the external band is at \omega\textsubscript{1} \approx \SI{190}{\text{cm}^{-1}}, and weaker bands are seen to
develop on either side (~\SI{160}{\text{cm}^{-1}}, ~\SI{210}{\text{cm}^{-1}}); the torsional band is at \omega\textsubscript{2} \approx
\SI{280}{\text{cm}^{-1}} and splits into two; the bending band is located at \omega\textsubscript{3} \approx \SI{450}{\text{cm}^{-1}},
and the stretching band is broadened, at \omega\textsubscript{4} \approx \SI{600}{\text{cm}^{-1}}. The behavior of the
four main bands of HoMn\textsubscript{1-x}Co\textsubscript{x}O\textsubscript{3} with changes in Co doping is as follows: The
external vibration energy remain the same at \omega\textsubscript{1} \approx \SI{190}{\text{cm}^{-1}} for Co doping for x
\leq 0.5 and shifts to higher energy for x > 0.5, while the weaker band at \approx \SI{210}{\text{cm}^{-1}}
starts to appear from x = \frac{1}{3} and disappears at x = \frac{4}{5}. The disappearance of the
subsidiary band at lower energy (~\SI{160}{\text{cm}^{-1}}) accounts for the increasing
energy of the main external band as Co doping increases. The stretching
band is at \omega\textsubscript{4} \approx \SI{600}{\text{cm}^{-1}} for all the samples, but the band’s width is reduced
as Co doping increases.
The bending mode shows the most dramatic behavior. The dependence of the bending and stretching modes, related respectively to the B–O distance and the B-O-B angle, on the radius of the ion on the A site, and the effect on the infrared spectrum have been discussed by Arulraj and Rao \cite{arulraj188} in the context of the $\text{Ln}_{1/2}\text{A}_{1/2}\text{MnO}_3$ compounds. As the radius of the ion on the A site decreases, the B-O distance increases, while the angle B-O-B decreases. Increasing the B-O distance should decrease the energy of the stretching mode. Both stretching and bending modes would be sensitive to octahedral...
Chapter 6

distortion and the associated lowering of symmetry arising from charge-ordering or Jahn-Teller effects. This would result in splitting of these bands. The increased splitting in the bending mode is also observed in torsional bands.

![Graph showing optical density spectrum of HoMn$_{4/5}$Co$_{1/5}$O$_3$. The bottom curve was measured at room temperature. The top curve represents the best fit of this data according to Eq. 6.1.](image)

**Figure 6.18:** Optical density of polycrystalline HoMn$_{4/5}$Co$_{1/5}$O$_3$. The bottom curve was measured at room temperature. The top curve represents the best fit of this data according to Eq. 6.1.

The normalized optical density, $O_\omega(\omega)$, spectrum is proportional to the optical conductivity $\sigma(\omega)$\textsuperscript{183, 189}. The energies of phonon modes can be obtained from spectra of optical density. Figure 6.18 shows the optical density spectrum of HoMn$_{4/5}$Co$_{1/5}$O$_3$. The spectrum exhibits peaks associated with the infrared active phonon modes. To extract information on phonons we fit the spectrum of
optical density using a sum of non-interacting harmonic oscillators. It was shown \(^{189, 190}\) that in the first approximation \(O_d(\omega) \propto \sigma(\omega)\). By taking this into account, the equation can be written as

\[
O_d(\sigma) = \sum_j \frac{S_j \sigma_j^2 \gamma_j}{(\sigma_j^2 - \sigma^2) + \gamma_j^2 \sigma^2},
\]

where \(\omega_j\), \(\gamma_j\) and \(S_j\) are the frequency, the linewidth, and the oscillator strength of the \(j\)th oscillator, respectively. The minimum number of oscillators to obtain a fit is 5 for \(\text{HoMn}_{4.5}\text{Co}_{1.5}\text{O}_3\). In Figure 6.18, the top panel is the calculation using equation (1), and the resulting phonon frequencies are shown. In Table 6.3, the best fit values are listed that were extracted from the measured phonon peaks.

<table>
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<th>189</th>
<th>268</th>
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<tr>
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<td>(S_j)</td>
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**Conclusions**

Cobalt doping into \(\text{HoMnO}_3\) converts structures from hexagonal with \(\text{P6}_3\text{cm}\) symmetry to an orthorhombic perovskite structure with \(\text{Pnma}\) symmetry. The \(\text{HoMn}_{1-x}\text{Co}_x\text{O}_3\) system gradually changes from paramagnetic for \(x = 0\) to
ferromagnetic with $T_c$ of 90 K for $x = 0.5$, and back to paramagnetic for $x = 0.8$. Co and Mn are present mainly as mixtures of $\text{Co}^{2+} + \text{Co}^{3+}$, $\text{Mn}^{4+} + \text{Mn}^{3+}$, $\text{Co}^{3+} + \text{Co}^{4+}$, and $\text{Mn}^{4+}$, depending on the exact value of $x$. Both $\text{Mn}^{4+}$ and $\text{Co}^{3+}$ were present in high spin states for $x > 0.2$, while $\text{Co}^{4+}$ appeared in either intermediate or high spin states, depending on the lattice expansion or shrinkage along the (010) direction.

Using the atomic position values the structures of HoMn$_{0.5}$Co$_{0.5}$O$_3$ crystal were plotted, and the bond lengths were calculated. The bond lengths of Co-O1 (in-plane) Co-O2 (in-plane), and Co-O (out-of-plane) are very sensitive to the doping levels, similar to the case for GdCo$_{1-x}$Mn$_x$O$_3$. Generally speaking, the Co-O1 bond length decreases with increasing Mn for $\delta < 0.6$ and then increases for $\delta > 0.5$. The Co-O bond length shows the opposite trend: it increases with Mn doping and then drops as $\delta$ reaches 0.6. However, the bond lengths for Co-O2 fluctuate with Mn doping, indicating a distorted CoO$_6$ or MnO$_6$ octahedron for all the doped samples. The complexity of valences of Co, Mn, and oxygen vacancies are believed to contribute to the distortions.

Infrared transmittance spectra of polycrystalline samples of HoMn$_{1-x}$Co$_x$O$_3$ ($x = 0, \frac{1}{5}, \frac{1}{7}, \frac{1}{9}, \frac{2}{11}, \frac{4}{13}$) were reported. The phonon spectrum of HoMn$_{4/5}$Co$_{1/5}$O$_3$ was measured and analyzed. It was found that the oscillator strength is predominantly carried by two modes at 415 cm$^{-1}$ and 600 cm$^{-1}$.
Chapter 7: \( \text{Y}_{1-x}\text{Sr}_x\text{CoO}_3 \) and \( \text{Dy}_{1-x}\text{Sr}_x\text{CoO}_3 \)

Several polycrystalline samples of \( \text{Y}_{1-x}\text{Sr}_x\text{CoO}_3 \) and \( \text{Dy}_{1-x}\text{Sr}_x\text{CoO}_3 \) were prepared and examined for their structural and physical properties. This chapter is divided into two sections to present the results obtained for \( \text{Y}_{1-x}\text{Sr}_x\text{CoO}_3 \) and \( \text{Dy}_{1-x}\text{Sr}_x\text{CoO}_3 \), respectively.

7.1 \( \text{Y}_{1-x}\text{Sr}_x\text{CoO}_3 \)

In order to study the Y doping effect on the physical properties of \( \text{YCoO}_3 \), two polycrystalline samples of \( \text{Y}_{1-x}\text{Sr}_x\text{CoO}_3 \) (\( x = 0.5, \ 0.66 \)) were prepared by conventional solid state reaction. High purity \( \text{Y}_2\text{O}_3 \), \( \text{SrCO}_3 \), and \( \text{Co}_3\text{O}_4 \) were well-mixed according to the desired atomic ratios. It was revealed from XRD measurements that the impurity phase \( \text{Y}_2\text{O}_3 \) is present in both samples. Additional heat treatment did not increase the reaction among particles of the sample, and as a result, the structure was unchanged.
Using the Rietica software package for Rietveld refinement, the XRD pattern of Y\textsubscript{1/2}Sr\textsubscript{1/2}CoO\textsubscript{3} was refined and is presented in Figure 7.1. The lattice parameters, as well as the atomic positions, were determined and are listed in Table 7.1. The results revealed that the crystal has a cubic structure with lattice parameter $a = 3.81709 \text{ Å}$.

<table>
<thead>
<tr>
<th>Y\textsubscript{1/2}Sr\textsubscript{1/2}CoO\textsubscript{3}</th>
<th>Lattice parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (Å)</td>
<td>b (Å)</td>
</tr>
<tr>
<td>3.81709</td>
<td>3.81709</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Atomic Position</th>
</tr>
</thead>
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<td>Sr</td>
</tr>
<tr>
<td>Co</td>
</tr>
<tr>
<td>O</td>
</tr>
</tbody>
</table>
In Figure 7.2, the results of dc magnetization over a wide range of temperatures in different fields are illustrated. All measurements showed that the Curie temperature, $T_C$, occurs at 300 K. $1/\chi$ is plotted against temperature in Figure 7.3. It can be seen that the Weiss temperature determined by extrapolating the linear range at high temperature to zero is about 20–50 K. This means that the sample has long-range ferromagnetic ordering at low temperature, but a short-range interaction starting from 300 K.
7.1.1 Hysteresis loops

Hysteresis loops were collected at different temperatures, 5 K, 280 K, and 300 K, and the results are shown in Figure 7.4. It is clear that the ferromagnetism at 300 K becomes more pronounced at 280 K. It disappears at 5 K, with a typical feature of the antiferromagnetic state. It is believed that the ferromagnetic and the antiferromagnetic states coexist in this system. A further study on the magnetic structure using neutron diffraction will be carried out in the future.
7.1.2 Transport

The temperature dependence of the resistance of $Y_{1/2}Sr_{1/2}CoO_3$ is shown in Figure 7.5. The data from Gd-based samples are also shown for comparison. It can be seen that the Y-based sample with $x = 0.5$ has much higher resistance than the Gd-based samples. The resistance goes up exponentially with temperature, and the trend with temperature is also different from that of the Gd-based system. Resistance was also measured under a field of 7 T. However, no magnetoresistance was observed for either the $x = 0.5$ or the $x = 2/3$ samples.
Figure 7.5: Logarithmic variation of resistance vs. temperature of Y_{1/2}Sr_{1/2}CoO$_3$ in comparison to Gd_{1/3}Sr_{2/3}CoO$_3$ and Gd_{1/2}Sr_{1/2}CoO$_3$ over a wide range of temperatures.
7.2 \textit{Dy}_{1-x}\textit{Sr}_x\textit{CoO}_3

Polycrystalline samples of \textit{Dy}_{1-x}\textit{Sr}_x\textit{CoO}_3 (x = 0.5, 0.66) were prepared by conventional solid-state reaction. High purity powders of \textit{Dy}_2\textit{O}_3, \textit{SrCO}_3, and \textit{Co}_3\textit{O}_4 were well mixed according to the desired atomic ratio for each sample, as is listed in Table 1.2.

Using the Rietica refinement method, \textit{Dy}_{0.5}\textit{Cr}_{0.5}\textit{CoO}_3 was refined, and the XRD pattern is shown in Figure 7.6. The lattice parameters were determined, as well as the atomic positions, as listed in Table 7.2. The results show that the crystal has a cubic structure with lattice parameter \( a = 3.81359 \, \text{Å} \), which is very similar to that of \textit{Y}_{1/2}\textit{Sr}_{1/2}\textit{CoO}_3.

![XRD pattern of \textit{Dy}_{1-x}\textit{Sr}_x\textit{CoO}_3 for x = 0.5. The observed (crosses), calculated (solid red line), and difference diffraction (bottom line) profiles at 300 K.](image-url)
Table 7.2: Lattice parameters and atomic positions for Dy_{0.5}Cr_{0.5}CoO₃.

<table>
<thead>
<tr>
<th>Element</th>
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<th>z</th>
</tr>
</thead>
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<td>0.0000</td>
</tr>
<tr>
<td>O</td>
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<td>0.5000</td>
</tr>
<tr>
<td>Co</td>
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<td>0.5000</td>
<td>0.0000</td>
</tr>
<tr>
<td>Sr</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

7.2.1 Magnetic properties:

The dc magnetic measurements vs. temperature are shown in Figure 7.7. It can be seen that the ZFC and FC branches separate at T = 300 K, implying that a possible ferromagnetic interaction starts at this temperature. However, the possible ferromagnetic state is absent from the real part of the susceptibility measurement, $\chi'$, vs. temperature, as shown in Figure 7.8.
Figure 7.7: dc magnetization vs. temperature of Dy$_{0.5}$Sr$_{0.5}$CoO$_3$. 

Dy$_{0.5}$Sr$_{0.5}$CoO$_3$  
DC magnetization at 50 Oe
Chapter 7

The susceptibility of Dy$_{0.5}$Sr$_{0.5}$CoO$_3$ was measured in three different frequencies: 117 Hz, 217 Hz, and 2000 Hz, and the results are shown in Figure 7.8. Assessment of these graphs indicates that the samples demonstrate paramagnetic behavior without any Curie temperature ($T_C$). It is also observed that the frequency variations do not affect the susceptibility of the sample and result in a unique curve accommodating all data points, which is clearly shown in Figure 7.8.

Figure 7.8: Real part of ac susceptibility for Dy$_{0.5}$Sr$_{0.5}$CoO$_3$ at different frequencies.
Chapter 7

Figure 7.9: Inverse susceptibility of Dy_{0.5}Sr_{0.5}CoO_3 vs. temperature at 2 kHz.

The $1/\chi'$ results clearly show that this compound is typically paramagnetic over a wide range of temperatures. $C$ is determined from $\chi = C/T$, where mass = 66.80 mg.

Conclusion

The XRD pattern of Y_{1/2}Sr_{1/2}CoO_3 shows that the crystal has a cubic structure with lattice parameter $a = 3.81709 \text{ Å}$. A long-range ferromagnetic ordering at low temperature, as well as a short-range interaction at 300 K, was revealed. Hysteresis loop analysis showed that the ferromagnetic and the antiferromagnetic states coexist in this system. The temperature dependence assessment of
Y$_{1/2}$Sr$_{1/2}$CoO$_3$ showed that the Y-based sample with $x = 0.5$ has much higher resistance than the Gd-based sample.

The lattice parameters, as well as the atomic positions of Dy$_{0.5}$Sr$_{0.5}$CoO$_3$ were determined and showed a cubic structure crystal with a lattice parameter $a = 3.81359$ Å, similar to that of Y$_{1/2}$Sr$_{1/2}$CoO$_3$. A ferromagnetic interaction for Dy$_{0.5}$Sr$_{0.5}$CoO$_3$ would commence at $T = 300$ K. It was observed that the frequency variations do not affect the susceptibility of the sample, and the compound is typically paramagnetic over a wide range of temperatures.
Chapter 8: Structural and magnetic properties of La_{1/3}Sr_{2/3}Fe_{1-x}Cr_xO_3

8.1 Introduction

LaFeO_3 and LaCrO_3 are well known to be anti-ferromagnetic perovskite compounds \cite{192, 193} with Néel temperatures of about $T_N = 740$ K \cite{191} and $T_N = 258$ K, respectively. LaFeO_3 crystallizes in the orthorhombic structure with the lattice parameters $a = 5.552$ Å, $b = 5.563$ Å, $c = 7.843$ Å, and space group $Pbnm$, while LaCrO_3 crystallizes in the orthorhombic structure with $a = 5.803$ Å, $b = 7.7599$ Å, $c = 5.5168$ Å, and space group $Pnma$ \cite{192, 193}. The valences of Fe or Cr are $3^+$ in both compounds, and the spins on Fe$^{3+}$ and Cr$^{3+}$ are arranged so as to be antiferromagnetic in the lattice.

It has been reported that substitution for La by Sr leads to a series of changes in the crystal structure in La_{1-x}Sr_xCrO_3. The crystal structure remains orthorhombic for $x = 0.95$ and $x = 0.85$, but it changes to rhombohedral for $x = 0.55$ and $x = 0.75$ \cite{194}. The structure can also become cubic with $a = 3.874$ Å for $x = 0.1$-0.2 and then rhombohedral for $x = 0.4$ \cite{195}. The fabrication conditions determine the final crystal structure. It was reported that La_{0.85}Sr_{0.15}CrO_3 has a rhombohedral crystal structure at 250 K with space group $R\overline{3}c$, and at 50 K the structure achieves an orthorhombic structure with space group $Pnma$. 


As for La\(_{1-x}\)Sr\(_x\)FeO\(_3\), its structure remains orthorhombic for \(x = 0, 0.1,\) and 0.2, and converts to rhombohedral for \(0.6 \geq x \geq 0.3\) \(^{196}\).

These results indicate that the crystal structure of both LaFeO\(_3\) and LaCrO\(_3\) are very sensitive to the Sr doping. With increasing Sr doping level, the valences of Fe or Cr change from Fe\(^{3+}\) to a mixed state of 3+ and 4+. The conductivity of the compounds can also increase as the Sr doping content increases.

It was reported \(^{194}\) that the magnetic properties of La\(_{2-x}\)Sr\(_x\)CrO\(_3\) (\(x = 0, 0.05, 0.10, 0.15, 0.20,\) and 0.25), including the DC magnetic susceptibilities, were measured over the temperature range of 4.5 K to 320 K, with the results showing that all the samples exhibited antiferromagnetic behaviour at a Néel temperature. By increasing the doping level of Sr the \(T_N\) decreased from 286K for LaCrO\(_3\) as shown in Figure 8.1.

![Figure 8.1: Néel temperature vs. Sr substitution for La\(_{1-x}\)Sr\(_x\)CrO\(_3\)](image-url)
Below the Néel temperature, two other types of magnetic behavior were observed, and except for LaCrO$_3$, all samples showed magnetic hysteresis. In this chapter, the results of Fe doping on the crystal structure and magnetic properties in LaCrO$_3$ are presented.

Solid state reaction was used to prepare the samples for the parent materials of: La$_2$O$_3$, SrCO$_3$, Fe$_2$O$_3$ and Cr$_2$O$_3$; then they were mixed and sintered following the heat-treatment pattern in Figure 8.2.

### 8.2 Structural characterization

After the first step of the heat treatment, the purity of the samples was examined by a quick XRD. After the second heat treatment, the sample structure was again examined by the XRD, the results of which are shown in Figure 8.3.
For these second XRD measurements, the samples were crushed to achieve a very fine powder.

![XRD patterns](image)

**Figure 8.3**: XRD patterns of $\text{La}_{1/3}\text{Sr}_{2/3}\text{Fe}_{1-x}\text{Cr}_x\text{O}_3$ for $x=0$ to $1$

It can be seen that the $x=1$ sample contains $\text{La}_2\text{O}$, $\text{SrCO}_3$, and $\text{Cr}_2\text{O}_3$, indicating a pure phase of $\text{La}_{1/3}\text{Sr}_{2/3}\text{Cr}_0\text{O}_3$ can not be formed under the fabrication condition given in Figure 8.2. When $x$ increases gradually, the cubic phase forms for $x \geq 0.7$.

Using the Rietveld refinement method (Rietica software package), $\text{La}_{1/3}\text{Sr}_{2/3}\text{Fe}_{1-\delta}\text{Cr}_\delta\text{O}_3$ was refined based on a cubic structure (Figure 8.8) with space group $\text{Pm}-3\text{m}$. The XRD patterns containing experimental data and refinement patterns are shown in Figure 8.4 to Figure 8.7. The lattice parameters and the atomic positions were then determined and the results are listed in Table 8.1 and Table 8.2. The
lattice parameters indicate that the La\textsubscript{1/3}Sr\textsubscript{2/3}Fe\textsubscript{1-δ}Cr\textsubscript{δ}O\textsubscript{3} crystal has a cubic structure with approximate dimensions of $a = 3.88 \, \text{Å}$.

Figure 8.4: Rietveld refinement for La\textsubscript{1/3}Sr\textsubscript{2/3}Fe\textsubscript{0.95}Cr\textsubscript{0.05}O\textsubscript{3}. In this and the following figures, the symbols indicate the experimental results, and the solid red line the calculated fit. The green line shows the difference diffraction pattern. The short blue lines mark the peak positions in the standard, and the blue zones areas that were not included in the refinement.

Figure 8.5: Rietveld refinement for La\textsubscript{1/3}Sr\textsubscript{2/3}Fe\textsubscript{0.85}Cr\textsubscript{0.15}O\textsubscript{3}.
Figure 8.5: Rietveld refinement for La$_{1/3}$Sr$_{2/3}$Fe$_{0.9}$Cr$_{0.1}$O$_3$.

Figure 8.6: Rietveld refinement for La$_{1/3}$Sr$_{2/3}$Fe$_{0.8}$Cr$_{0.2}$O$_3$. 
From the atomic position values in Table 8.2, the 3D structure of La$_{1/3}$Sr$_{2/3}$Fe$_{0.5}$Cr$_{0.5}$O$_3$ crystal was plotted, which is demonstrated in Figure 8.8.

![Figure 8.7: Cubic crystal of La$_{1/3}$Sr$_{2/3}$Fe$_{0.5}$Cr$_{0.5}$O$_3$.](image)

**Table 8.1: Lattice parameters for La$_{1/3}$Sr$_{2/3}$Fe$_{1-\delta}$Cr$_{\delta}$O$_3$.**

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<td>90</td>
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</tr>
</tbody>
</table>

Using the obtained values in Table 8.1 the variations in crystal volume and lattice parameters with doping level were determined and are depicted in Figure 8.9.
From Figure 8.9 it can be observed that as the doping level of Cr increases from zero to 0.1 ($0 \leq x \leq 0.1$), the lattice parameters and crystal volume increase to 3.876 Å and 58.261 Å³, respectively. The increase can be attributed to replacement of mixed Fe³⁺ and Fe⁴⁺ ions with the larger atom of Cr. When the doping level changes from 0.1 to 0.2 ($0.1 \leq x \leq 0.2$), the population of Cr³⁺ ions increases as it replaces Cr⁴⁺, while the amount of Fe is reduced as well, which shrinks the crystal size. By increasing the doping level of Cr from 0.2 to 0.3 ($0.2 \leq x \leq 0.3$), obviously the amount of Fe is reduced, leaving more space for Cr atoms to be part of the crystal structure. In the meantime during this replacement, many
Cr ions change from Cr\(^{3+}\) to Cr\(^{4+}\). This also reduces the oxygen deficiency, which will help to expand the crystal size. There is also the possibility of the presence of Cr\(^{6+}\) at \(x \geq 0.2\), which can reduce the amount of oxygen.

**Table 8.1: Atomic positions for La\(_{1/3}\)Sr\(_{2/3}\)Fe\(_{1-x}\)Cr\(_{x}\)O\(_3\).**

<table>
<thead>
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<th>Coordinates</th>
<th>(\delta)</th>
<th>La</th>
<th>Sr</th>
<th>Fe</th>
<th>Cr</th>
<th>O</th>
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**8.3 Magnetic properties:**
Figure 8.10: Variation of real part of magnetic susceptibility vs. temperature for $\text{La}_{1/3}\text{Sr}_{2/3}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_3$.

The temperature dependence of the real part of the magnetic susceptibility $\chi'$ measured at $H_{dc} = 50$ Oe and 1 T and $f = 117$ Hz for the $x = 0.3$ sample is shown in Fig. 8.10, it can be seen that $\chi'$ is far above zero, indicating that the sample seems to be ferromagnetic with the Curie temperature far above 300 K.

The dc magnetization was also measured under a field of 1 T. It can be seen that the moment is far above zero over the entire temperature range. At the low temperature of 70 K, the ZFC and the FC branches start to separate, indicative of a ferromagnetic transition. A more detailed study of this series of samples will be conducted in the future.
Conclusion

Structure refinements and physical property measurements of \( \text{La}_{1/3}\text{Sr}_{2/3}\text{Fe}_{1-x}\text{Cr}_{x}\text{O}_3 \) were conducted, and the following conclusions are outlined.

1- The \( \text{La}_{1/3}\text{Sr}_{2/3}\text{Fe}_{1-x}\text{Cr}_{x}\text{O}_3 \) crystal has a cubic structure regardless of the doping level. It is observed that the lattice parameters and crystal volume change, however, as the doping level varies.

2- The interchange of mixed \( \text{Fe}^{3+} \) and \( \text{Fe}^{4+} \) with \( \text{Cr}^{3+} \), \( \text{Cr}^{4+} \), and \( \text{Cr}^{6+} \) ions will change the spin contributions of Fe and Cr, which results in variation of total magnetic properties or the magnetic state of the sample.
3- \( \text{La}_{1/3}\text{Sr}_{2/3}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_3 \) exhibits a ferromagnetic state at a Curie temperature higher than room temperature.
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