Magnetotransport and Multiferroic Properties of Perovskite Rare-earth Manganites

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This work details the studies of several perovskite rare earth manganite (RMnO$_3$) systems, focusing on the effects of both A-site and B-site doping of TbMnO$_3$ and the magnetotransport behavior of La$_{1-x}$Sr$_x$MnO$_3$:insulator composites.

In pure TbMnO$_3$ synthesized by solution route, it was revealed that the magnetic properties could be modulated by structural modifications resulting from different synthesis methods. In bulk Tb$_{0.67}$Ho$_{0.33}$MnO$_3$, signatures of a weak ferromagnetic moment were detected in the magnetization measurements, and an anomaly due to Ho$^{3+}$-Mn$^{3+}$ exchange striction was observed in the polarization measurement. These results signify that both the ionic radius and the magnetic properties of the dopant affect the multiferroic properties in this system. Signatures of both long-range magnetic ordering as well as spin-glass-like behavior were observed in the DC and AC susceptibility data of Tb$_{1-x}$M$_x$MnO$_3$ ($M =$ Ca, Sr). This suggests the importance of the A-site ionic-size mismatch in determining the magnetic interactions. In bulk TbMn$_{1-x}$Cr$_x$O$_3$, the DC and AC susceptibility measurements and neutron diffraction revealed competition between several different spin configurations. A magnetic phase diagram for TbMn$_{1-x}$Cr$_x$O$_3$ is proposed.
Composite thin films of La$_{0.67}$Sr$_{0.33}$MnO$_3$:ZnO and La$_{0.67}$Sr$_{0.33}$MnO$_3$:MgO were grown using solution routes. A shift in the ferromagnetic transition to lower temperatures in the composite films indicates strain effects or doping at the interfaces. Disorder at the interfaces is presumed to result in spin-polarized tunneling at the grain boundaries. A significant enhancement of magnetoresistance, particularly at low applied magnetic fields ($\leq 0.5$ T), was observed in all composite films, making these promising for magnetic field sensing applications.
Magnetotransport and Multiferroic Properties of Perovskite

Rare-earth Manganites

Margo Lauren Staruch

B.S., Boston College, 2006

M.S., University of Connecticut, 2009

A Dissertation

Submitted in Partial Fulfillment of the

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Doctor of Philosophy

at the

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2013
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Chapter 1

Introduction

Functional materials are defined as those that display unique physical properties inherent to the material and not the structure.\textsuperscript{9–11} These properties can be controlled by an external parameter such as temperature, pressure, or an applied field. Functional materials have been utilized in applications such as solar cells, fuel cells, drug delivery, sensors, actuators, magnetic resonance imaging (MRI), light-emitting diodes (LEDs), random access memory (RAM), and many other devices.\textsuperscript{9} Although there are a wide variety of inorganic functional materials, much of the focus in recent years has been on oxides, which are generally chemically and thermally stable and exhibit an array of phenomena such as superconductivity, thermoelectricity, piezoelectricity, metal-insulator transitions, and magnetism.\textsuperscript{12} The work presented in this dissertation focuses on the perovskite rare-earth manganites (RMnO\textsubscript{3}). In RMnO\textsubscript{3}, several emergent phenomena, including multiferroicity and colossal magnetoresistance, arise due to competition between the spin, charge, and orbital degrees of freedom.

1.0.1. Rare-earth manganites (RMnO\textsubscript{3})

Multiferroic behavior has been observed in RMnO\textsubscript{3} for rare-earth ions (R) with smaller ionic radii (R = Gd, \ldots, Lu).\textsuperscript{7,13} In a ferroic material, a switchable electric polarization ($P$), the magnetization ($M$), or strain ($\epsilon$) spontaneously develop with decreasing temperature resulting in (anti)ferroelectricity, (anti)ferromagnetism, or ferroelasticity, respectively. Multiferroics (MFs) are defined as materials exhibiting a coexistence of any two of the ferroic orders, where this may lead to additional interactions.\textsuperscript{14} For example, magnetoelectric (ME) MFs, that have ferroelectric
(FE) and some magnetic order, show magnetoelectric coupling effect due to which an applied magnetic field can tune the polarization or an applied electric field can tune the magnetization of the material. Multiferroics with strong ME coupling between electric and magnetic order parameters are attractive due to a number of potential applications. In particular, TbMnO₃ has been identified as a prototypical ME multiferroic material exhibiting a large ME effect with significant change in the polarization and dielectric constant with applied magnetic fields.³

Colossal magnetoresistance behavior has been observed in doped RMnO₃. Magnetoresistance (MR), defined as the relative change in electrical resistivity with the application of an externally applied magnetic field, has been observed in many systems such as ferromagnetic metals and superlattices of magnetic and non-magnetic layers.¹⁵ However, the largest MR effect that is observed in the doped rare-earth manganites, R₁₋ₓAxMnO₃ (A = Ca²⁺, Sr²⁺). A thousand-fold change in resistivity, labeled ‘colossal’ magnetoresistance (CMR), was observed in a single-crystalline thin film of La₀.₆₇Ca₀.₃₃MnO₃ near the ferromagnetic transition temperature.¹⁶ In addition, a sharp increase in MR at low applied fields was observed in polycrystalline La₀.₆₇Sr₀.₃₃MnO₃.⁵

Both multiferroic and magnetoresistive rare-earth manganite materials are of technological importance, with potential applications in magnetic field sensors, magnetic read heads, random access memory, and other spintronics devices.¹⁷,¹⁸ However, due to the many complex interactions in the manganites, the mechanisms driving these phenomena are still not well understood. Objectives of this dissertation are:

- To improve the understanding of the multiferroic properties of TbMnO₃ through doping;
- To enhance the low-field magnetoresistance of La₀.₆₇Sr₀.₃₃MnO₃ thin films by fabricating La₀.₆₇Sr₀.₃₃MnO₃ nanocomposites with a secondary insulating phase.
To examine what factors determine the multiferroic and magnetoresistive properties in these materials, it is important to first look at the structure and the magnetic interactions present in the manganites.

1.1. Structure and Physical Properties of RMnO₃

Oxides with the perovskite structure (ABO₃) are attractive for many applications due to significant chemical flexibility, as many different cations can occupy the A and B sites.¹⁹,²⁰ This allows the relationship between the structure, electronic and magnetic properties to be studied.

The B-site ion is surrounded by an oxygen octahedron (Figure 1.1a), and the connectivity of the BO₆ octahedra strongly affects the structural, magnetic, and electric properties. Deviation from the ideal perovskite cubic unit cell can be represented by the Goldschmidt tolerance factor:

\[
t = \frac{r_A + r_O}{\sqrt{2(r_A + r_O)}}
\]

(1.1)

calculated with the ionic radii of the A and B cations (r_A and r_B) and O²⁻ (r_O), where t expresses the mismatch between the A-O and B-O equilibrium bond lengths for a hard-ball model.²¹ A

Figure 1.1. The perovskite structure for (a) cubic ABO₃ and (b) the orthorhombically distorted RMnO₃ (from [1]).

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calculated with the ionic radii of the A and B cations (r_A and r_B) and O²⁻ (r_O), where t expresses the mismatch between the A-O and B-O equilibrium bond lengths for a hard-ball model.²¹ A
tolerance factor of \( t = 1 \) represents an ideal cubic perovskite structure and any bond-length mismatch resulting in \( t < 1 \) is accommodated by cooperative rotations of the BO\(_6\) octahedra. Rare-earth manganites (RMnO\(_3\)) with \( R = \text{La}^{3+}, \ldots, \text{Dy}^{3+} \) are within the range of \( t \) that allows an orthorhombic (\( O \)) distortion of the perovskite structure, while those with smaller rare-earth ions (\( i.e. \ R = \text{Ho}^{3+}, \ldots, \text{Lu}^{3+} \) and \( \text{Y}^{3+} \)) form a hexagonal \( P6_3cm \) structure. However, a metastable orthorhombic (\( m-O \)) form of RMnO\(_3\) for the smaller rare-earth ions can be formed through high-pressure synthesis or by certain chemical methods.\(^{22,23}\) In the perovskite RMnO\(_3\), the rotation of the octahedra forms rhombohedral or orthorhombic (so-called GdFeO\(_3\)-type) distorted perovskite structures with space group \( Pbnm \) (Figure 1.1b).

As can be inferred from equation (1.1), decreasing the ionic radius of the rare-earth ion (Table 1.1) leads to a successive increase of this orthorhombic distortion accompanied by an increase of the buckling/tilting of the MnO\(_6\) octahedra and a decrease of the Mn-O-Mn bond angles.

<table>
<thead>
<tr>
<th>( \text{La}^{3+} )</th>
<th>( \text{Pr}^{3+} )</th>
<th>( \text{Eu}^{3+} )</th>
<th>( \text{Gd}^{3+} )</th>
<th>( \text{Tb}^{3+} )</th>
<th>( \text{Dy}^{3+} )</th>
<th>( \text{Y}^{3+} )</th>
<th>( \text{Ho}^{3+} )</th>
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<td>moment (( \mu_B ))</td>
<td>0</td>
<td>3.58</td>
<td>0</td>
<td>7.94</td>
<td>9.72</td>
<td>10.63</td>
<td>0</td>
</tr>
<tr>
<td>stable structure</td>
<td>( O )</td>
<td>( O )</td>
<td>( O )</td>
<td>( O )</td>
<td>( O )</td>
<td>( O )</td>
<td>( \text{Hex/m-O} )</td>
</tr>
</tbody>
</table>

\( \langle---------------\rangle \) \hspace{1cm} \( \langle-------------------------------\rangle \)

**CMR (with A-site doping)** \hspace{1cm} **Multiferroic site doping**

**Table 1.1.** The ionic radius (in 9-coordination)\(^8\) and the magnetic moment [as calculated from \( g\sqrt{J(J+1)} \)] for selected rare-earth ions. The stable structure is given as orthorhombic (\( O \)) or hexagonal with a meta-stable orthorhombic structure (\( \text{Hex/m-O} \)).
1.1.1. Splitting of valence 3d electrons of Mn\(^{3+}\) in orthorhombic RMnO\(_3\)

The 3\(d\) orbitals of Mn are subject to the partial lifting of the degeneracy into lower energy t\(_{2g}\) states (\(xy, yz, \text{and} \ zx\)) and higher energy e\(_g\) states (3\(z^2-r^2\) and \(x^2-y^2\)) due to the crystal field splitting (Figure 1.2). The e\(_g\) orbitals are directed towards the adjacent oxygen ions and therefore hybridize strongly with the O\(^{2-}\) 2\(p\) orbitals, whereas the t\(_{2g}\) orbitals are considered to be localized by strong correlation effects. In Mn\(^{3+}\), manganese strongly couples to Hund’s rules as the electron pairing energy is larger than the crystal field energy, and therefore the high spin t\(_{2g}^3 e_g^1\) state is observed. When one of the e\(_g\) orbitals are occupied, the Jahn-Teller effect results in an elongation of the oxygen octahedron along the z-axis (crystallographic c-axis) and this additional distortion lifts the degeneracy of the two e\(_g\) orbitals.

Figure 1.2. Splitting of the Mn 3\(d\) orbitals from the crystal field and the Jahn-Teller distortion (from [1]).
1.1.2. Superexchange

In the perovskite manganites, the Mn\(^{3+}\) cations interact with each other via a virtual electron transfer known as superexchange. In a 180° Mn–O–Mn bridge, covalent bonding of the 3\(d\) orbitals with the O\(^{2-}\) 2\(p\) orbital extends the Mn wavefunction to give an orbital overlap between two Mn ions allowing for the superexchange electron transfer. The bonding energy gained from the virtual electron transfer was calculated by Anderson to be:

\[
\Delta E = \text{const.} + \sum \frac{2b_{ij}^2}{U} S_i \cdot S_j
\]  

where \(U\) is the mutual repulsion of electrons on the same ion, \(b_{ij}\) is the transfer integral, and \(S_i \cdot S_j\) is the scalar product between Mn spin vectors.\(^{24}\) The magnetic interactions for a 180° cation–anion–cation bridge can also be empirically described by the Goodenough-Kanamori-Anderson rules.\(^{24-26}\) A virtual transfer between two partially-filled orbitals is restricted by the Pauli exclusion principle and is therefore antiferromagnetic (AFM), while a transfer from a partially-filled to an empty orbital has no restrictions although the ferromagnetic (FM) intra-atomic potential exchange on the receiving cation favors FM interactions. There is an additional superexchange interaction along 90° Mn–O–Mn bonds. However, as there is less overlap between 3\(z^2-r^2\) and 2\(p\) orbitals along the \(a\)-axis and \(b\)-axis and therefore less hybridization, the 90° FM superexchange is weaker than the 180° AFM interactions.

This indicates that for a Mn\(^{3+}\)–O–Mn\(^{3+}\) bond, with one electron in the 3\(z^2-r^2\) \(e_g\) orbital, the superexchange interaction is strongly AFM along the \(c\)-axis but FM in the \(ab\) plane resulting in A-type AFM ordering below Néel temperature \((T_N)\) in LaMnO\(_3\). However, with decreasing
Mn–O–Mn bond angle away from 180°, the competition between the AFM and FM superexchange interactions is modulated. This results in a decrease in $T_N$ with decreasing bond angle and increased magnetic frustration, eventually leading to an incommensurate sinusoidal ordering below $T_N$ for smaller rare-earth ions (R = Gd, Tb, …, Lu) as seen in Figure 1.3.

**Figure 1.3.** The magnetic properties of RMnO$_3$ versus Mn-O-Mn bond angle (from [2]). $A$-AF denotes A-type antiferromagnetic ordering, $IC$-AF denotes incommensurate sinusoidal ordering, and $E$-AF denotes E-type antiferromagnetic ordering.

### 1.2. Single Phase Multiferroics

In conventional ferroelectrics, the non-centrosymmetric lattice distortion arises from atomic displacement of the B-site ion resulting from chemical bond formation that favors empty $d$ orbitals. However, in conventional ferromagnets, the magnetic moment is primarily due to the spin contribution of $d$ electrons at the B-site. In addition, another requirement of ferroelectrics is that they must be insulating to allow an applied voltage to change polarization direction but in magnetic insulators, the off-centering of the transition metal ion is not energetically favorable. The conflicting requirements suggest that an alternative mechanism for
magnetism or for ferroelectricity is necessary for these orders to coexist in a single phase. Although there has been some work on the former, for example with the magnetism at the A-site in EuTiO$_3$, most multiferroics combine conventional $d$-electron magnetism with improper ferroelectricity. Four primary routes to ferroelectricity have been identified in single phase multiferroics:

- Lone pair stereochemical activity at the A-site, like the spontaneous electric polarization due to the displacement $6s^2$ lone pairs in BiFeO$_3$ (AFM below 643 K) and BiMnO$_3$ (FM below 110 K) below ~ 1100 K and 760 K, respectively.$^{29,30}$

- Geometric ferroelectrics, like BaNiF$_4$ or hexagonal YMnO$_3$, where the electric polarization is driven by a rotational instability of the polyhedra and displacement of the A-site cations.$^{31,32}$

- Spatial ordering of charges in a non-centrosymmetric arrangement, as was shown for the ordering temperature of Fe$^{2+}$ and Fe$^{3+}$ in LuFe$_2$O$_4$ at ~ 330 K.$^{33}$

- Ferroelectricity induced by the formation of a symmetry-lowering magnetic ground state that lacks inversion symmetry, such as TbMnO$_3$ or DyMnO$_3$.$^{3,34,35}$

Interest in materials with a magnetically-induced electric polarization increased dramatically in 2003 after Kimura et al. reported significant values of magnetocapacitance at low temperatures as a result of strong magnetoellectric coupling in TbMnO$_3$ (TMO) single crystal.$^3$ In TMO, an AFM transition at $T_N$ ~41 K with sinusoidal ordering of Mn$^{3+}$ moments with a noncollinear spiral spin ordering of Mn$^{3+}$ moments developing below $T_{lock}$ ~28 K (that results in a magnetoelastically induced lattice modulation and ferroelectricity) have been observed in addition to the ordering of Tb$^{3+}$ moments at ~7 K (Figure 1.4).$^3,36$ The origin of ferroelectricity at $T_{lock}$ is believed to be due to the atomic displacement of the O$^{2-}$ as a result of the inverse
Dzyaloshinskii-Moriya (DM) interaction.\textsuperscript{37–39} The DM interaction [antisymmetric exchange interaction of the form $D_{ij}(\mathbf{S}_i \times \mathbf{S}_j)$] causes a lattice displacement due to the canting of neighboring Mn$^{3+}$ moments that arises from the increased distortion in the Mn-O-Mn bond angle. Several materials with a net polarization resulting from similar spiral-spin ordering have since been discovered, such as CoCr$_2$O$_4$ \textsuperscript{34}, Ni$_3$V$_2$O$_8$ \textsuperscript{35}, and MnWO$_4$ \textsuperscript{40}, and the appearance of a ferroelectric polarization have also been explained through an antisymmetric exchange striction.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure14.png}
\caption{Temperature dependent (a) magnetization and specific heat versus temperature and (b) polarization for TbMnO$_3$ single crystal (from \textsuperscript{3}). (c) The spiral spin ordering of Mn$^{3+}$ moments (dots indicate Mn$^{3+}$ site and direction of moments indicated by arrows) in TbMnO$_3$ (from \textsuperscript{4}).}
\end{figure}

\subsection*{1.2.1. Linear magnetoelectric effect}

The free energy ($F$) can be written as an expansion in the form of a power series of electric field $\mathbf{E}$, magnetic field $\mathbf{H}$, or stress $\mathbf{T}$. A ferroic material possesses a contribution to $F$ that is linear in one parameter, while MFs posses a contribution that is bi-linear in these parameters. In magnetoelectric (ME) multiferroics, the free energy is expanded as:
\[ F(E,H) = F_0 - P^S i E_i - M^S j H_j - \frac{1}{2} \varepsilon_{ij} E_i E_j - \frac{1}{2} \mu_{ij} H_i H_j - \alpha_{ij} E_i H_j - \beta_{ijk} E_i E_j H_k - \frac{1}{2} \gamma_{ijk} H_i E_j E_k \ldots \]  

(1.3)

where \( P^S \) and \( M^S \) denote the spontaneous polarization and magnetization, and \( \varepsilon \) and \( \mu \) are the electric and magnetic susceptibilities, respectively.\(^{41} \) The tensor \( \alpha_{ij} \) results in a change in polarization with applied magnetic field or in magnetization with applied electric field and defines the linear magnetoelastic effect. It should be noted that the value of \( \alpha_{ij} \) is nonzero in only those materials that break both time-reversal and space-inversion symmetry. It has been demonstrated that the magnitude of this coupling term is limited by:

\[ \alpha^2_{ij} < \chi^E_{ij} \chi^M_{ij} \]

(1.4)

where \( \chi^E \) and \( \chi^M \) are the electric and magnetic susceptibilities, respectively.\(^{42} \) This suggests that the ME coupling is largest in materials with significant polarization and magnetization values. The ferroelectric (FE) polarization in TbMnO\(_3\) is considerably smaller (< 0.1 \( \mu \)Ccm\(^{-2}\)) than in a conventional FE material (1–100 \( \mu \)Ccm\(^{-2}\)).\(^{43} \) However, by applying a magnetic field of ~5 T a polarization flop is induced, changing the orientation of polarization in TbMnO\(_3\) from along the \( c \)-axis to along the \( a \)-axis, demonstrating ME control.\(^{3,44} \) Here, the coupling is said to be significant if the \( \alpha_{ij} E_i H_j \) term dominates the total free energy of the system.\(^{41} \)

1.2.2. A-site doped multiferroic RMnO\(_3\)

In RMnO\(_3\) with smaller rare-earth ions, the Mn\(^{3+}\) moments exhibit incommensurate sinusoidal ordering below \( T_N \).\(^{2} \) There is an additional lower-temperature transition from this spin configuration to either (i) A-type AFM, (ii) spiral spin ordering, or (iii) E-type AFM ordering depending on the ionic radius of R\(^{3+}\). To further examine the sensitivity of the ground state magnetic structure, several studies have investigated the effect of the average ionic radius at the
A-site ($<r_A>$) on the multiferroic properties of RMnO$_3$. For example, in Tb$_{1-x}$Gd$_x$MnO$_3$, region with a stable spiral spin ordering in the $ab$ plane (with polarization along the $a$-axis) was observed that had previously only been seen in GdMnO$_3$ with large applied magnetic fields. In addition, studies on Eu$_{1-x}$Y$_x$MnO$_3$ (where both rare-earth ions are non-magnetic) revealed a phase diagram similar to that of the RMnO$_3$ (Figure 1.3) as the value of $<r_A>$ is varied. However, several differences were also observed. In Eu$_{0.6}$Y$_{0.4}$MnO$_3$ that has the same average ionic radius at the A-site as TMO, spiral spin ordering in the $ab$ plane and a polarization parallel to $a$-axis was observed. Moreover, in the case of Eu$_{0.8}$Y$_{0.2}$MnO$_3$, a weakly ferromagnetic and weakly ferroelectric phase was revealed that is not present in any RMnO$_3$ multiferroic compounds. In these studies, the average ionic radius and magnetic properties of rare-earth ions were revealed to be crucial parameters in determining the magnetic and ferroelectric properties of multiferroic RMnO$_3$. There are fewer studies, however, focusing on the area near the phase boundary between spiral spin and E-type AFM ordering. Although the possibility of phase coexistence was proposed in Tb$_{1-x}$Ho$_x$MnO$_3$, it remains difficult to synthesize phase pure orthorhombic RMnO$_3$ with $<r_A>$ intermediate that of Tb$^{3+}$ and Ho$^{3+}$ without the formation of a hexagonal impurity phase. Thus, more studies are necessary to examine the effects of ionic radius and magnetism of the rare-earth ion at the A-site in this region of the phase diagram.

1.2.3. B-site doped RMnO$_3$

B-site doping in RMnO$_3$ is an appealing route not only to study the magnetic interactions present, but also to further understand how the noncollinear spiral spin develops in multiferroic RMnO$_3$. In addition, the introduction of FM interactions would also be desirable in order to increase the magnetic moment and therefore to achieve maximum theoretical ME coupling in
multiferroic RMnO$_3$. However, magnetic studies of TbMn$_{1-x}$Sc$_x$O$_3$ revealed a cluster glass behavior with no long-range magnetic order for samples with $x \geq 0.2$. In DyMn$_{1-x}$Fe$_x$O$_3$, static orbital ordering and thus magnetic behavior similar to DyMnO$_3$ was observed for $x \leq 0.2$ but for samples with higher Fe content, a G-type AFM structure similar to DyFeO$_3$ was revealed. Similarly, in Co- or Ru-doped TMO, after about 10% to 20% substitution in place of Mn$^{3+}$ the NSS ordering is suppressed in the material, which results in the loss of ferroelectricity. It would therefore be of interest to investigate a B-site dopant where both parent compounds are multiferroic. Coexistence of FE and FM-like ordering has been observed in orthorhombic YMn$_{1-x}$Cr$_x$O$_3$ with no reduction in polarization values and reversible polar behavior has recently been revealed below $T_N$ in the orthorhombic rare-earth chromites (RCrO$_3$). This suggests that Cr$^{3+}$ is a promising dopant to induce FM interactions in multiferroic TbMnO$_3$.

1.3. Colossal and Granular Magnetoresistance

![Figure 1.5. Resistivity normalized to the value at 0 T (zero field) versus applied magnetic field at various temperatures for (a) single crystal and (b) polycrystalline La$_{0.67}$Sr$_{0.33}$MnO$_3$ (from [5]).](image-url)
Magnetoresistance (MR) is defined as the relative change in electrical resistivity ($\rho$) with the application of a magnetic field. In this thesis, MR has been defined as:

$$\text{MR (\%)} = 100 \times \frac{\rho(H) - \rho(0 \ T)}{\rho(0 \ T)}$$  \hspace{1cm} (1.5)

This effect was first observed in iron and nickel when it was observed that discovered that the resistivity is maximum when the current is in the same direction as the magnetization and at a minimum when the current is perpendicular, as a result of the angular dependence of electron scattering processes. Giant magnetoresistance was later discovered in multilayers composed of alternating FM and non-magnetic layers, where the resistivity was lowered if the magnetization of adjacent FM layers were parallel. Colossal magnetoresistance (CMR), a change in the resistivity of several orders of magnitude (as seen in Figure 1.5a), is an intrinsic phenomenon that has been revealed in La$_{1-x}$Sr$_x$MnO$_3$ (LSMO) and La$_{1-x}$Ca$_x$MnO$_3$ (LCMO). To describe the mechanism of magnetoresistance in these materials, we must first consider intrinsic versus extrinsic effects, as well as additional interactions present in the doped manganites.

1.3.1. Single crystal vs. polycrystalline materials

![Figure 1.6. The microscopic arrangement of atoms in (a) a single crystalline and (b) a polycrystalline material. The dotted lines in (b) indicate the location of grain boundaries.](image)

A single crystal is formed by a continuous periodic array of atoms in the lattice (without grain boundaries), whereas polycrystalline are made up of a number of smaller grains with
different orientations (Figure 1.6). Properties that are said to be intrinsic to a material, resulting from the structure and the interactions present in a material, are best observed in single crystals. Some properties of the material may also be modified by the presence of grain boundaries (dislocations at the interfaces) that occur due to misorientation between neighboring grains. For example, the presence of grain boundaries (GBs) can scatter electrons and phonons and therefore reduce the electrical or thermal conductivity. This results in extrinsic contributions due to the shape and size of grains.

1.3.2. Double exchange

In doped manganites $R_{1-x}A_xMnO_3$, replacement of the rare-earth ion $R^{3+}$ by a divalent alkaline earth cation (such as $Sr^{2+}$ or $Ca^{2+}$) creates a $Mn^{3+}$ ($t_{2g}^{3} e_{g}^{1}$) - $Mn^{4+}$ ($t_{2g}^{3} e_{g}^{0}$) mixed valence to compensate the charge. This hole doping allows for an additional exchange interaction between $Mn^{3+}$ and $Mn^{4+}$ ions known as double exchange.\(^{59}\) As opposed to superexchange, which describes virtual electron transfer, double exchange represents a simultaneous jump of the $e_g$ electron of $Mn^{3+}$ to the $O p$-orbital and from the $O p$-orbital to the empty $e_g$ orbital of $Mn^{4+}$ (as shown in Figure 1.7). Assuming strong coupling between the $e_g$ and $t_{2g}$ spins according to Hund’s rule, and that the energy of that interaction exceeds the intersite hopping interaction $t_{ij}$ between neighboring sites, then:

$$t_{ij} = b_{ij} \cos\left(\frac{\theta_{ij}}{2}\right)$$

where $b_{ij}$ is a constant and $\theta_{ij}$ is the relative angle between neighboring spins.\(^{60,61}\) This indicates that the electron conduction is maximized when neighboring spins are aligned ($\theta_{ij} = 0$) and is therefore a FM interaction. This electron hopping allows delocalization of electrons and thus results result in metallic behavior in LSMO and LCMO.
1.3.3. Colossal magnetoresistance (CMR)

In single crystals or epitaxial manganite films, the ferromagnetic-paramagnetic transition temperature $T_C$, coincides with a metal-insulator transition ($T_{MI}$) as a result of the hopping of $e_g$ electrons due to double exchange.\textsuperscript{59,60} The largest values of MR are also observed near $T_C$. This intrinsic effect is due to the fact these materials are half-metallics, \textit{i.e.} the majority spins are conducting but the Fermi level lies in a gap for the antiparallel alignment.\textsuperscript{62} When the temperature is raised to near $T_C$, the configuration of the spin is dynamically disordered and hence local spins can be aligned by an externally applied magnetic field thereby reducing the resistivity. Such CMR behavior has been reported in LSMO and LCMO at high applied magnetic fields ($\geq 1$ T).\textsuperscript{16,63}

1.3.4. Low-field magnetoresistance

An extrinsic MR effect has been observed in ceramics and polycrystalline films at temperatures lower than $T_C$ with a reduction in resistivity values (and hence MR) at low applied fields ($\leq 0.5$ T) [Figure 1.5b].\textsuperscript{5,64} This ‘low-field’ magnetoresistance (LFMR) is thought to be a result of spin-polarized inter-grain tunneling that is closely associated with magnetic domain rotation. The sensitivity of the resistivity to low applied magnetic fields is attractive for use in magnetic field sensors.\textsuperscript{17} Artificial grain boundaries, chemical disorder, and the introduction of a

\begin{figure}[h]
\centering
\includegraphics[width=0.7\textwidth]{figure17.png}
\caption{(a) Schematic of superexchange interaction between neighboring Mn$^{3+}$ ions and (b) double exchange interaction between Mn$^{3+}$ and Mn$^{4+}$ ions.}
\end{figure}
secondary insulating phase have been shown to alter the magnetotransport properties of these materials and result in enhanced LFMR.\textsuperscript{65–68} For example, the presence of a non-magnetic or AFM insulating secondary phase, either at the grain boundaries or distributed within the bulk of the sample, have been shown to enhance LFMR in ceramic composites such as La\textsubscript{0.75}Sr\textsubscript{0.25}MnO\textsubscript{3}:TiO\textsubscript{2},\textsuperscript{66} La\textsubscript{0.67}Ca\textsubscript{0.33}MnO\textsubscript{3}:SrTiO\textsubscript{3},\textsuperscript{67} or La\textsubscript{0.7}Sr\textsubscript{0.3}MnO\textsubscript{3}:CeO\textsubscript{2} [ref. 68]. This is thought to be due to due to interfacial effects such as spin-polarized tunneling between GBs or spin-dependent scattering at the GBs due to the half metallic behavior of the mixed valence manganites.\textsuperscript{5,64,69}

<table>
<thead>
<tr>
<th>Composite Film</th>
<th>Maximum LFMR</th>
<th>Growth technique</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>La\textsubscript{0.7}Sr\textsubscript{0.3}MnO\textsubscript{3}:ZnO</td>
<td>-8% at 0.5 T and 77 K</td>
<td>PLD</td>
<td>70</td>
</tr>
<tr>
<td>(La\textsubscript{0.7}Sr\textsubscript{0.3}MnO\textsubscript{3})\textsubscript{0.5}:((ZnO)\textsubscript{0.5})</td>
<td>-11% at 0.3 T and 154 K</td>
<td>PLD</td>
<td>71</td>
</tr>
<tr>
<td>(La\textsubscript{0.7}Sr\textsubscript{0.3}MnO\textsubscript{3})\textsubscript{0.5}:((CeO\textsubscript{2})\textsubscript{0.5})</td>
<td>-15% at 0.5 T and 20 K</td>
<td>PLD</td>
<td>72</td>
</tr>
<tr>
<td>La\textsubscript{0.67}Sr\textsubscript{0.33}MnO\textsubscript{3}:Al\textsubscript{2}O\textsubscript{3}</td>
<td>-15% at 0.3 T and 86 K</td>
<td>PLD</td>
<td>73</td>
</tr>
<tr>
<td>La\textsubscript{0.7}Sr\textsubscript{0.3}MnO\textsubscript{3}:MgO</td>
<td>-25% at 0.5 T and 4.2 K</td>
<td>metalorganic aerosol deposition</td>
<td>74</td>
</tr>
<tr>
<td>La\textsubscript{0.7}Sr\textsubscript{0.3}MnO\textsubscript{3}:MgO</td>
<td>-32% at 0.5 T and 10 K</td>
<td>PLD on MgO nanowires</td>
<td>75</td>
</tr>
</tbody>
</table>

**Table 1.2.** A list of maximum low-field magnetoresistance (LFMR) values for a few manganite:insulator composite films in literature.

As compared to bulk ceramic composites, there has been limited studies on the LFMR response of thin films.\textsuperscript{70–74} Thin film studies however would be necessary for device integration.\textsuperscript{17} The focus of several recent studies on LFMR of nanocomposite films (as shown in Table 1.2) has been film deposition by pulsed laser deposition (PLD) or other methods requiring
high vacuum, but these techniques do not allow for large-area fabrication. Nanocomposites may be fabricated with different connectivity schemes such as nano-sized particulates embedded in a 3D matrix (3-0), vertically aligned nanorod array in a 3D matrix (3-1), or laminate composites (2-2). However, most of the composite films in the studies listed in Table 1.2 exhibit a columnar 3-1 type microstructure that cannot be maintained above a critical thickness and cannot be deposited in large areas using PLD. It should also be noted that in these composite films, studies of the MR are rather limited and/or focused on MR with fields $\geq 1$ T, which is not sensitive enough for sensor applications.\(^{76,77}\) As a result there is no clear picture of how the distribution of the two phases affects the transport properties in these films. Thus, studies are necessary to further understand the LFMR effect in films as well as to determine a route to enhance LFMR values.

1.4. Scope of Work

The work presented in this dissertation will focus on two areas: (i) the structural, magnetic, and ferroelectric properties of bulk TbMnO$_3$ and the effects of both A-site and B-site doping, and (ii) the structural, microstructural, magnetic, and magnetotransport properties of La$_{0.67}$Sr$_{0.33}$MnO$_3$:insulator composite thin films.

In Chapter 2, various techniques used for sample preparation and analysis are briefly introduced, including solution synthesis; structural characterization techniques such as x-ray diffraction, x-ray photoelectron spectroscopy, and Raman spectroscopy; resistivity, magnetization, and polarization measurements; and neutron diffraction.

In Chapter 3, the structural and magnetic properties of a bulk TbMnO$_3$ (TMO) sample are discussed. The effects of the synthesis route on the structural and magnetic properties are
examined. Anomalies in the DC and AC susceptibility corresponding to $T_N$, $T_{lock}$, and the ordering of Tb$^{3+}$ moments are observed. This is the first observation of the three transitions in the magnetization measurements of bulk samples.

In Chapter 4, the structural, magnetic, and ferroelectric properties of bulk TbMnO$_3$, Tb$_{0.67}$Y$_{0.33}$MnO$_3$, and Tb$_{0.67}$Ho$_{0.33}$MnO$_3$ samples are presented. The DC/AC magnetic measurements and temperature dependent polarization measurements reveal behavior attributed to a weak ferromagnetism and suggests a canted E-type AFM ordering in Tb$_{0.67}$Ho$_{0.33}$MnO$_3$ as compared to the noncollinear spiral spin ordering in TbMnO$_3$.

In Chapter 5, the investigation of the structural and magnetic properties of Tb$_{1-x}$A$_x$MnO$_3$ (A = Ca$^{2+}$, Sr$^{2+}$) is presented. Detailed DC and AC magnetic susceptibility reveals both long-range magnetic ordering as well as spin-glass-like transitions at low temperatures. The ionic-size mismatch at the A-site is found to play a crucial role in determining the magnetic properties of the mixed valence manganites.

In Chapter 6, the structure and magnetic structure of TbMn$_{1-x}$Cr$_x$O$_3$ bulk samples is revealed. DC and AC magnetic measurements for the complete solid solution are presented, as well as neutron diffraction studies and first-principles calculations for TbMn$_{0.5}$Cr$_{0.5}$O$_3$ sample. A magnetic phase diagram is proposed for the complete solid solution TbMn$_{1-x}$Cr$_x$O$_3$.

In Chapter 7, the effects of addition of ZnO and Mg(O) on the structure, microstructure, magnetic, and magnetotransport properties of La$_{0.67}$Sr$_{0.33}$MnO$_3$ are investigated. The structural (and possibly magnetic) disorder at the grain boundaries was found to modify both the FM transition temperature and the metal-insulator transition temperature. The introduction of a secondary phase results in an increase in magnetoresistance, especially at low applied magnetic fields. The biphasic composite samples have some of the highest LFMR values reported to date.
Chapter 2

Experimental Methods

2.1. Solution Synthesis

In general, solution synthesis of materials involves the preparation of a homogeneous solution of the necessary cations that can then be used to fabricate a thin film or to form a bulk powder. In addition to providing a high degree of compositional control, solution routes are easier and more cost-effective than other synthesis methods for the fabrication of both bulk and film as it does not require high-temperature processing or deposition in a high-vacuum chamber.\textsuperscript{74-78} Solution methods are also flexible, as one solution can be used to synthesize bulk ceramics, nanoparticles, thin films, or to draw nano-fibers by adjusting concentration, pH, viscosity, and solvents. There are several types of solution preparation routes,\textsuperscript{78,79} including:

- Sol-gel processes using alkoxide precursors and 2-methoxyethanol as a solvent and reactant.
- Metal-organic decomposition processes using water-insensitive metal carboxylate compounds.
- Chelating, or ‘hybrid’, routes that use modifying ligands.
- Hydrothermal routes that involve the crystallization of materials from high-temperature aqueous solutions at high vapor pressures.
- Pechini process or the related citrate route or nitrate route using nitrates dissolved in water with citric acid or ethylene glycol as a complexing agent.
In above mentioned methods, high-purity (99.99%) carboxylate, alkoxide, or nitrate precursors of the required cations are dissolved in an appropriate solvent in the desired stoichiometric ratio. The individual precursor solutions are then processed (mixed together, distilled, refluxed, etc.) to have a homogeneous final solution with uniform distribution of the cations. The solution is then either spin-coated on a substrate to synthesize a thin film or dried to form a bulk powder. This step is followed by a first heat treatment known as pyrolysis (between 200°C and 600°C), which involves the removal of organic material. This is then followed by annealing the sample at higher temperatures to allow for crystallization of the desired material. All the samples in this dissertation were synthesized in Dr. Menka Jain’s laboratory at the University of Connecticut.

2.1.1. Deposition of thin films by spin coating

Thin films can be fabricated via solution deposition by spin/dip or spray-coating the prepared solution on a substrate. The films in this work were prepared by a spin-coating technique and the steps of the process are shown in Figure 2.1. First, the substrate is held in place on the vacuum chuck of the spin coater. A drop of the precursor solution is placed on the substrate and the vacuum chuck is then accelerated rapidly to 3000–6000 rpm with a spinning time of 10 – 20 seconds to coat a wet/gel film on the substrate. The angular velocity and the spinning time together with the solution viscosity can be used to control the thickness of this ‘as-deposited’ film.
A multi-step process was used for pyrolysis and crystallization of the films. It has been proposed that this multi-step procedure allows for the removal of the organic materials prior to the collapse of the amorphous network, which may help to minimize cracking and blistering.\cite{78,79} Thus the as-deposited film first were pyrolyzed by heating the films in the tube furnace. The spinning and pyrolysis steps can be repeated several times until the desired film thickness is reached. After the final coating, the film is then annealed at higher temperatures to densify the film and for its crystallization (through a nucleation and growth process). The required annealing temperature was optimized to achieve desired structure, microstructure, and physical properties.

**Figure 2.1.** Spin-coating of a thin film on a substrate by solution deposition. A drop of solution is allowed to wet the substrate. The substrate is then spun at some angular velocity $\omega$ for several seconds to result in a thin film.
2.1.2. Nucleation and growth theory

A number of different phenomena can determine if the as-deposited film will convert into a single crystal like or a polycrystalline film. If the structure of the film and substrate are similar with relatively low mismatch in their in-plane lattice parameters, growth of a single-crystal-like film requires the growth of epitaxial grains located at the film/substrate interface. It has previously been demonstrated that the thermodynamics that govern the transformation from pyrolyzed film to the crystalline one play a role in defining the nucleation events that occur and therefore can define if the film is a polycrystal or single crystal after annealing. The energy barriers for homogeneous and heterogeneous nucleation are given by standard nucleation and growth theory:\(^{80}\)

\[
\Delta G_{\text{hom}}^* = \frac{16\pi \gamma^2}{3(\Delta G_v)^2} \tag{2.1}
\]

\[
\Delta G_{\text{hetero}}^* = \frac{16\pi \gamma^2}{3(\Delta G_v)^2} f(\theta) \tag{2.2}
\]

where \(\Delta G_v\) is difference in Gibbs free energy between the pyrolyzed and crystalline material, \(\gamma\) is the interfacial energy, and \(f(\theta)\) is a function related to the contact angle \(\theta\) that generally favors interfacial nucleation (\(\theta = 0\)). However, high crystallization driving forces or a change in the temperature such as when heated to the annealing temperature may result in enough energy to allow for other less favorable nucleation events resulting in grains with different orientations.

In the past, Schwartz\(^{78}\), Lange\(^{79}\), Bhuiyan\(^{81}\), and Brinker & Scherer\(^{82}\) presented detailed studies of the factors that influence grain nucleation in solution-derived films. The substrate, pyrolysis, and annealing conditions all play a role in determining if the resultant film would be polycrystalline, with preferential orientation, or single crystalline.
2.2. X-ray Diffraction

X-rays are electromagnetic radiation with a wavelength that is on the order of the interatomic distances in crystalline materials. This makes x-ray diffraction (XRD) a powerful technique for studying the arrangement of atoms in a lattice (i.e. the structure). In an x-ray tube, electrons are accelerated towards a target by applying a large voltage difference between two metal electrodes. This results in both bremsstrahlung radiation from the inelastic scattering with the outer electron clouds of the target and characteristic radiation resulting from the excitation of electrons in the inner shells. In particular, the copper Kα characteristic radiation resulting from the 2p – 1s transition (λ = 1.54 Å) is utilized for the x-ray diffractometers available at the Institute of Materials Science at the University of Connecticut. A Bruker D-5 diffractometer with Bragg–Brentano "θ - θ" geometry, where the x-ray tube and detector rotate around the sample with an angle between them of 2θ, was used for phase identification and to identify the lattice parameters of powder samples. This setup was also utilized to investigate the orientation and out-of-plane lattice parameters of thin film samples.

2.2.1. Bragg’s law

![Figure 2.2.](image)

**Figure 2.2.** The diffraction of x-rays at an angle θ from a periodic crystal lattice. The difference between planes of atoms is d and the path difference between the scattered rays is 2d sin θ.
Diffraction is due to the existence of phase relationships between two or more waves. By considering elastic scattering of x-rays in an ordered lattice (as shown in Figure 2.2) we can see that atoms located at lattice points will act as scattering centers for the x-rays. Between any two x-ray beams scattered from different atoms, there will be some path difference that will result in a phase shift between the two diffracted rays. The path difference for two rays scattered in the same plane is always zero and therefore contributions from each plane are in phase and contribute to the diffracted beam. The path difference for rays scattered by atoms in different planes is \(2d\sin\theta\). The conditions for constructive interference, which will result in a peak in the \(\theta-2\theta\) plot, are given by Bragg’s Law:

\[
2d' \sin \theta = n\lambda
\]

(2.3)

where \(\lambda\) is the wavelength of the x-ray source and \(n\) is the order of the reflection and is equal to the number of wavelengths in the path difference between rays. We can consider a reflection of any order as a first order reflection from planes spaced at a distance \(1/n\) of the previous spacing. In general, an \(n^{th}\) order reflection may be considered as a first order reflection of the \((nh\ nk\ nl)\) planes of spacing \(d = d'/n\). Therefore, the equation can be re-written in the commonly used form:

\[
2d \sin \theta = \lambda
\]

(2.4)

The value of \(d\) is related to the Miller indices and crystal structure and is given by:

\[
\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}
\]

(2.5)

where \(h, k, l\) are the Miller indices and \(a, b,\) and \(c\) are the lattice parameters of the unit cell. It should be noted that the angle between the diffracted beam and the transmitted beam is always \(2\theta\), which is the parameter that is measured experimentally. By measurements of the diffraction
directions, the shape and size of the unit cell can be determined. This theory of elastic scattering and the Bragg’s law described above is applicable to both x-ray and neutron diffraction.

2.2.2. Structure factors and Rietveld refinement

The integrated intensity ($I_{hkl}$) of a XRD peak is determined by the multiplicity of the reflection (number of planes having the same spacing), the Lorentz factor, and the structure factor ($F_{hkl}$). The $F_{hkl}$ is the Fourier transform of the electron density in a crystal and can be determined by summing over all atoms in the crystal:

$$F_{hkl} = \sum f_j \exp[2\pi i (hx_j + ky_j + lz_j)]$$

(2.6)

where the form factor, $f_j$, represents the scattering power of a particular atom and depends on the number of electrons in an atom, the wavelength ($\lambda$), and the scattering angle ($\theta$). The integrated intensity of an XRD peak is directly proportional to the amplitude of this complex function $F_{hkl}$, i.e.:

$$I_{hkl} \propto |F_{hkl}|^2$$

(2.7)

It should be noted that depending on the symmetry of the lattice, $|e^{2\pi i \phi}|^2$ can be zero for certain values of $h$, $k$, and $l$, resulting in zero intensity at what are known as ‘forbidden’ reflections. By combining this model of intensity with the determination of allowed $2\theta$ values from Bragg’s law, information about the lattice shape/size and the position of atoms within the unit cell can be obtained by modeling the position and intensities of peaks in a $\theta$-2$\theta$ plot.

One method for evaluating the crystal structure from XRD data is Rietveld refinement. The principle of the Rietveld method is to minimize a function $M$, which represents the difference between a calculated profile and the measured data through an iterative least-squares method. Creating a calculated profile requires the input of the space group and corresponding
lattice symmetries as well as a starting point for the lattice parameters and atomic positions within the lattice. The program uses the space group to generate a reflection list and then computes the lattice parameters and $F_{hkl}$ from the provided model to match peak positions and amplitudes. These parameters are then optimized to improve the reliability factor of the fit. In this dissertation, the FullProf program was used to refine XRD data of bulk samples.\textsuperscript{84}

### 2.3. X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a technique that can be used to determine not only the elemental composition but also the valence state of ions in a material. It is based on the photoelectric effect, where electrons are emitted from a solid when atom absorbs a photon with energy greater than the work function. By using an x-ray with a known wavelength, the binding energy of the emitted electrons can be calculated by measuring the kinetic energy of the ejected electrons. The values are related through conservation of energy:

$$h\nu = E_B + \Phi_0 + E_K$$ \hspace{1cm} (2.8)

where $E_B$ is the binding energy with respect to the Fermi level, $\Phi_0$ is the work function of the material (\textit{i.e.} the minimum energy required to eject an electron), and $E_K$ is the kinetic energy of the emitted electron.

For the work presented in this dissertation, XPS measurements were carried out in facilities available in the Institute of Materials Science at the University of Connecticut. The surface of a material is irradiated with a beam of x-rays in ultra-high vacuum, and the kinetic energy and number of electrons that escape are measured. These electrons are from the top 1 – 10 nm of the material. Although the x-rays penetrate deeper in the sample, these photo-emitted electrons are recaptured or trapped by other ions in the material. The characteristic peaks
correspond to the valence of the ejected electrons, eg. 1s, 2s, 2p, etc.. The kinetic energies of ejected electrons are therefore directly related to the number of protons and electrons as well as the electron configuration.

2.4. Raman Spectroscopy

Raman scattering is a process where light induces an oscillating dipole due to the interaction with the polarizability (that can be described by the electron cloud) of a vibrating molecule. The wavelength of the light used for the excitations is generally too large to allow for transitions between electronic states, and therefore excites stretching modes or vibrations of heavier atoms in molecules, or phonons in a lattice. A phonon is defined as an excited state of vibrational motion in which atoms in a lattice collectively oscillates at a single frequency. The photons excite the molecule to a virtual energy state from which it then relaxes to a different energy state and emits a photon corresponding to the energy loss (as shown in Figure 2.3). The difference in energy between the initial and final state leads to a shift in the frequency of the emitted photon. By plotting the change in frequency with respect to the excitation frequency, the frequency of the excited vibrational state (or the phonon mode) can be determined:

\[ \Delta \omega = \omega_f - \omega_i = \Omega \]  

(2.9)

Raman shift \( \Delta \omega \) is therefore the quantity that is typically plotted, and conventionally expressed in terms of wavenumbers with the units cm\(^{-1}\), given by \( \Omega/(2\pi c) \) where \( c \) is the speed of light. Similar to XRD, analysis of Raman measurements can determine the structure of a sample and Raman spectra for different materials and different structures are unique. In this work, room temperature Raman measurements were carried out in the Institute of Materials Science at University of Connecticut with a Renishaw Ramascope using the 514.5 nm laser as the excitation
beam. For the measurements, the laser light is focused on a small area of the sample using a microscope and the scattered light is sent through a monochromator to a detector.

![Diagram of Raman spectroscopy](image)

**Figure 2.3.** Raman excitation from an initial state (i) to a virtual excited state (v) by a photon of energy $\hbar \omega_i$ and finally to a final excited vibrational state (f). The energy of the final excited phonon mode is $\hbar \Omega$.

### 2.5. Electron Microscopy

An electron microscope uses a focused electron beam to image structures down to 1 nm in size. The electron beam is accelerated through a large potential difference, the beam is focused, and then hits the sample where some electrons are scattered and some are transmitted if the sample is thin enough (that are utilized in transmission electron microscopy) or go through secondary scattering processes if the sample is thicker (that are utilized in scanning electron microscopy). The electron wavelength $\lambda$ as determined by the equation

$$\lambda = \frac{\hbar}{p} = \frac{\hbar}{\sqrt{2mE}}$$

(2.10)

where $\hbar$ is Planck’s constant, $m$ is the mass of the electron, and the energy $E$ directly depends on the voltage used for acceleration., is generally ~10,000 times shorter than visible light allowing for much higher resolution imaging.
In this work, scanning electron microscopy (SEM) images were taken at the University of Connecticut using a JEOL 6335F Field Emission SEM, in collaboration with Dr. Haiyong Gao and Dr. Pu-Xian Gao. Transmission electron microscopy (TEM) was performed in collaboration with Dr. Claudia Cantoni at Oak Ridge National Laboratory using a FEI/Philips CM200 TEM/scanning TEM (STEM) microscope and an energy-dispersive x-ray (EDX) spectroscopy R-TEM Si(Li) x-ray spectrometer, and a Fischione Z-contrast STEM detector.

2.6. Resistivity and Magnetotransport

Direct current (DC) resistivity measurements were performed using a four point contact measurement. In this setup, two separate leads pass a fixed current \( I \) through the sample and two separate leads measure the voltage \( V \). The voltmeter has high impedance and draws little current. Therefore, it is possible to know to a high degree of certainty both the current and voltage drop across the sample. The resistance \( R \) is then accurately calculated by Ohm’s Law:

\[
R = \frac{V}{I}
\]

This can then be converted to resistivity \( \rho \):

\[
\rho = \frac{RA}{l}
\]

where \( A \) is the cross-sectional area (as determined by the electrodes) and \( l \) is the conductor length between the voltage probes.

2.6.1. Temperature and magnetic field dependent resistivity

Measurement of resistivity as a function of temperature or magnetic field was measured with an Evercool Physical Property Measurement System (PPMS) by Quantum Design, available
in Dr. Menka Jain’s laboratory at the University of Connecticut. The PPMS consists of a dewar containing a liquid helium bath in which the probe is immersed. The probe contains temperature control hardware, a 12 pin connector to install sample pucks, and a 9 T niobium-titanium alloy superconducting magnet. The temperature range that can be achieved is 1.9 K – 400 K. This allows the resistivity to be measured as a function of temperature as well as applied magnetic field.

![Figure 2.4](image)

**Figure 2.4.** (a) The probe inside the PPMS dewar and cross-section of the probe showing the 9 T magnet, thermometer, cooling annulus, heaters, and the sample puck for resistivity measurements connected to the 12 pin connector. (b) A photo of the PPMS setup in Dr. Menka Jain’s laboratory at the University of Connecticut, with the vibrating sample magnetometer option connected.

When the resistivity option is connected, four wires connected to the sample by a conducting paste are soldered to a user bridge that connects with the 12 pin connector at the bottom of the probe. The user bridge board applies two consecutive DC excitations to the sample. The initial excitation current used is generally the specified current limit. The potential drop across the sample is measured for each excitation, and the voltage readings are averaged. The user bridge also applies an identical current to an appropriate calibration resistor, permitting for the compensation of drift or offset errors.
2.7. DC Magnetic Measurements

A vibrating sample magnetometer (VSM) can be used to accurately detect the bulk magnetization of a sample. VSM measurements are based on Faraday’s law of electromagnetic induction and are performed by oscillating the sample near a pickup coil and detecting the induced voltage. The change in induction as the sample is vibrated is:

\[ V_{\text{coil}} = -NA \frac{d\vec{B}}{dT} = -NA \left( \frac{d\vec{B}}{dz} \right) \left( \frac{dz}{dt} \right) \]  \hspace{1cm} (2.13)

where \( N \) is the number of turns, \( A \) is cross sectional area of the coil, \( B \) is the magnetic field or ‘magnetic flux density’, and \( z \) is the vertical position of the sample with respect to the coil. As the sample is moved in and out of the pickup coil, the change in \( B \):

\[ \Delta B = \mu_0 (H + M) - \mu_0 H = \mu_0 M \]  \hspace{1cm} (2.14)

This method thus provides a direct measurement of the magnetization \( M \) that is not dependent on the magnetic field strength \( H \). The induced e.m.f. resulting from this change in flux when the sample is sinusoidally oscillated is:

\[ V_{\text{coil}} = 2\pi f CMA \sin(2\pi f t) \]  \hspace{1cm} (2.15)

for a sinusoidally oscillating sample position, where \( C \) is a coupling constant and \( M \) is the DC magnetic moment of the sample.

In this dissertation work, temperature and field dependent DC magnetization measurements were performed using the VSM option of the PPMS. The sample is attached to the end of a sample rod that is driven sinusoidally by the VSM linear motor. The center of oscillation is positioned at the center of a gradiometer pickup coil. Previous to the measurement, the location of the sample in the sample holder is determined through a centering procedure that measures the response of the pickup coil as a function of position relative to the end of the
sample holder. This is an important step, as accurate measurements require that the sample oscillates directly in the center and that the centering position be kept stable to within about 0.1 mm at the center of the pickup coil. This stability is maintained by 'touchdown' operations that adjust for changes in the sample position by determining the location of the bottom of the sample holder with respect to the pickup coil. The position and amplitude of oscillation during measurement is controlled using an optical linear encoder signal readback from the linear motor transport. The VSM utilizes a peak oscillation amplitude of 1-3 mm and a frequency of 40 Hz that resolves magnetization changes of $10^{-5}$ emu.

2.7.1. Temperature dependent magnetization

![Diagram of magnetic materials]

*Figure 2.5.* The DC susceptibility ($\chi = M/H$) and the corresponding Curie-Weiss law for paramagnetic, ferromagnetic, and antiferromagnetic materials (from [6]).

Measurements of the temperature dependence of the magnetization $\{M(T)\}$ with the VSM can be used to identify both the magnetic transition temperature, as well as the nature of the magnetic ordering in a material as shown in Figure 2.4. An increase in the magnetization values below Curie temperature ($T_C$) is expected in ferromagnetic (FM) materials due to the onset of a spontaneous magnetization. A peak in the $M(T)$ data is generally observed at the antiferromagnetic (AFM) ordering temperature ($T_N$). However, this peak may be very weak and
obscured by paramagnetic or diamagnetic contributions. The classification of the magnetic ordering in a material as FM or AFM can be achieved by fitting the DC susceptibility ($\chi_{dc}$) in the paramagnetic region with Curie-Weiss law:

$$\chi_{dc} = \frac{C}{T - \Theta}$$  \hspace{1cm} (2.16)

where $\Theta$ is Curie-Weiss temperature, and $C$ is Curie constant:

$$C = \frac{NgJ(J + 1)\mu_B^2}{3k_B T} = \frac{\mu^2_{\text{eff}}}{3k_B T}$$  \hspace{1cm} (2.17)

where $k_B$ is the Boltzmann constant and the effective magnetic moment ($\mu_{\text{eff}}$) is defined by the number of atoms per unit volume ($N$) and the effective number of Bohr magnetons, $gJ(J + 1)$. The value of $\Theta$ can be used to identify the magnetic order:\(^6\)

1. $\Theta = 0$ for paramagnetic ordering.
2. $\Theta > 0$ and $= T_C$ for FM ordering.
3. $\Theta < 0$ but $\neq T_N$ for AFM ordering.

The general measurement procedure is to cool the sample from above the magnetic ordering temperature. A magnetic field is then applied to align the magnetic domains, and the magnetization is measured during warming to obtain the zero-field cooled (ZFC) magnetization data. With the field still on, the magnetization is then measured while cooling through the transition again to obtain the field cooled (FC) magnetization data. The ZFC data is dominated by thermal fluctuations whereas the FC data is more sensitive to the temperature dependence of the spontaneous moment.\(^{85}\) This allows the two curves to separate (‘bifurcate’) at an irreversibility temperature $T_{irr}$ that can be observed in inhomogeneous materials such as cluster glasses, spin glasses, or polycrystalline samples that have FM or FM-like (canted AFM or ferrimagnetic) ordering.\(^{86,87}\)
2.7.2. Magnetic field dependent magnetization

In the paramagnetic phase, the magnetization $M$ varies linearly with applied magnetic field $H$. However, in a ferromagnet, the formation of magnetic domains that have net moments in different directions results in an applied magnetic field necessary to reach the saturation magnetization by aligning the domains. The growth of magnetic domains that are favorably aligned to the field and the rotation of domains to align with the field in FM materials results in a characteristic hysteresis loop in the $M$ vs. $H$ data (as shown in Figure 2.5). Two important quantities are noted in this figure: (i) the remanent magnetization ($M_R$) once the field is removed after saturation and (ii) the coercive field ($H_C$), which is the applied field required to reduce the magnetization to zero starting from saturation.

The directional dependence of the magnetic properties, may occur in FM thin films due to magnetocrystalline anisotropy or shape anisotropy. Magnetic anisotropy results in the direction of the moment being favored along one of the crystallographic axes, resulting in an

![Figure 2.6. A characteristic hysteresis loop in the field dependent magnetization data with the remanent magnetization ($M_R$) and coercive field ($H_C$) as marked.](image)
easy axis (direction of lowest energy) that will produce a hysteresis loop with low $H_c$ that quickly reaches saturation when the field is applied in that direction.

2.8. AC Magnetic Measurements

Alternating current (AC) susceptibility ($\chi_{ac}$) is measured using a similar method to VSM, but the sample is not removed from the coil and therefore an AC susceptometer does not directly measure the magnetic moment. Rather, a small alternating magnetic field is applied and the response of the pickup coil is compared to the original signal to determine the AC susceptibility:

$$\chi_{ac} = \frac{dM}{dH} \quad (2.18)$$

This is different than the true value of susceptibility that can be determined from the DC magnetization:

$$\chi_{dc} = \frac{M}{H} \quad (2.19)$$

Both the amplitude and phase of the response, or the in-phase and the out-of-phase components are reported. This gives the real ($\chi'$) and complex ($\chi''$) components of the total susceptibility $\chi_{ac}$.

For this dissertation work, AC susceptibility measurements were performed using the AC measurement system (ACMS), attached to the PPMS in Dr. Menka Jain’s lab. It is important to separate sample phase shift from instrumental phase shift. With the ACMS, this is accomplished by a five point measurement that measures the instrument-dependent phase shift for each data point. There are two detection coils in the ACMS setup. To ensure an accurate measurement, the sample must be centered by applying a constant AC magnetic field and sweeping the sample position between the two detection coils. The first three readings are with the sample positioned in one of the two detection coils. The data points are fitted and compared to the driving signal to determine real and imaginary components and saved in terms of a complex vector. The sample is
then placed at the center of the detection coil array. Two more readings are taken with a low-
inductance calibration coil switched into the detection coil circuit with opposite polarities. By
subtracting the two calibration readings, a complex calibration vector is obtained that does not
depend on the sample signal. This calibration vector is then used to accurately determine proper
orientation and scaling for the sample vector. This procedure allows for the reporting of $\chi'$ and
$\chi''$ as determined from the real and imaginary components of the complex vector.$^{88}$

2.8.1. Temperature dependent AC susceptibility

AC susceptibility is a sensitive probe of the magnetic order in a sample as peaks in the
temperature dependent $\chi'$ and $\chi''$ data can be used to accurately detect FM or AFM transition
temperatures. In addition, frequency dependence of the susceptibility is observed in several
systems such as superparamagnetic particles or in spin glasses and cluster glasses. The relative
change of the peak position ($T_{\text{peak}}$) in $\chi'$ with frequency ($f$) can be used to separate FM or AFM
ordering from superparamagnetism or spin-glass systems$^{86}$:

$$K = \frac{\Delta T_{\text{peak}}}{T_{\text{peak}} \Delta \log f}$$  \hspace{1cm} (2.20)$$

where $K \sim 0.1$ for paramagnetic materials and $\sim 0.01$ for spin-glass or cluster-glass systems. For
$K < 0.01$, the peak is thus referred to as ‘frequency-independent’ and it is assumed that the peak
is a result of FM or AFM ordering transition.
2.9. Pyrocurrent Measurements

A material is pyroelectric when a change in temperature can induce an atomic displacement within the crystal structure, giving rise to a polarization and therefore a voltage across the material. If the direction of the polarization can be switched by applying an electric field, the material is ferroelectric. Although not all pyroelectric materials are FE, all FE materials will exhibit a pyrocurrent. The pyroelectric coefficient $p_i$ is defined as:

$$p_i = \frac{\partial P_{S,i}}{\partial T}$$  \hspace{1cm} (2.20)

where $P_S$ is the spontaneous polarization. The polarization is therefore determined by integrating the pyroelectric current with respect to temperature and normalizing by the area of the sample.

Temperature dependent pyrocurrent measurements were performed using a Keithley 6517A electrometer with temperature control provided by a PPMS in collaboration with Dr. Gavin Lawes’ group at Wayne State University. The electrometer can detect a current up to 1 fA. Prior to these measurements, the samples were poled with 200 V on cooling to align the domains. Once the sample was cooled, this field was removed resulting in a remanent polarization. The current was then measured on warming the sample to above the ferroelectric transition temperature. The reversibility of the polarization was confirmed by poling the sample with 200 V and measuring the current while cooling.

2.10. Neutron Diffraction

Neutron diffraction is similar to XRD and can be used to evaluate the composition and structure of a material. Production of neutrons occurs in a nuclear reactor with enriched uranium-
235 as fuel. The wavelength of a neutron beam \( \lambda \) can be comparable to that of x-rays, and is determined by equation (2.10) where now \( m \) is the mass of the neutron and \( E \) is the energy of the neutron source. However, neutrons are magnetic with spin \( \frac{1}{2} \) but are uncharged, allowing the neutron to penetrate the sample and not be affected by Coulomb repulsion. There are two important consequences of these properties. First, the neutrons interact directly with the nucleus of the atoms, as opposed to x-rays that interact with the electron cloud. This allows for the detection of light elements such as oxygen or hydrogen. Secondly, since they carry spin, they can interact with local magnetic moments in the sample and reveal the microscopic magnetic structure. In the case of long-range magnetic order, new Bragg peaks relating to the periodicity of the magnetic order are observed.

**Figure 2.7.** (a) A diagram of the setup and (b) a photo of the powder diffractometer at the HB-2A beamline at Oak Ridge National Laboratory.

Powder neutron diffraction was performed at the HB-2A beamline at the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory in collaboration with Dr. Clarina dela Cruz. The beamline is set up as shown in Figure 2.6. The powder diffractometer has a Debye-Scherrer geometry, which uses a parallel beam where the sample is contained in a cylindrical
aluminum tube. The detector bank has 44 Helim-3 tubes with a high absorption cross-section for free neutrons, where the intensity is detected by the reaction:

$$n + ^3\text{He} \rightarrow ^3\text{H} + ^1\text{H} + Q$$

where $Q = 0.764$ MeV for thermal neutrons. Each $^3\text{He}$ detector has 6 ft Soller slits to collimate the beam and to correct for geometrical aberrations. The scattering angle $2\theta$ can be scanned between $0^\circ$ and $155^\circ$ by moving the detector bank. A germanium wafer-stack monochromator vertically focuses the neutron beam and can tune the wavelength through Bragg diffraction of the (113), (115), or (117) reflections. The monochromator can provide one of three principal wavelengths depending on which reflection is in the diffracting condition. In this study, the (113) reflection with $\lambda = 2.4095$ Å was utilized that provides a higher resolution than shorter wavelength beams. The data was analyzed by Rietveld refinement using FullProf, as described in section 2.2.
Chapter 3

Solution Synthesis of Bulk TbMnO₃

3.1. Introduction

Single crystals of TbMnO₃ (TMO) exhibit peaks in the magnetization corresponding to an AFM transition ($T_N$) $\approx$41 K (sinusoidal ordering of Mn$^{3+}$ moments) and an incommensurate-commensurate transition ($T_{lock}$) $\approx$28 K (the modulated magnetic ordered phase is accompanied by magnetoelastically induced lattice modulation and appearance of ferroelectricity) in addition to the ordering of Tb$^{3+}$ moments $\approx$7 K. However, in bulk TMO the Mn$^{3+}$ transitions $\approx$41 K and 28 K have not been observed in magnetization data due to the large contribution of the paramagnetic Tb$^{3+}$ moment.$^{54,91-93}$ In the past several years, several studies have examined the size effects in magnetic TMO nanoparticles (NPs). For TMO NPs with a diameter 40-60 nm, Dyakonov et al. also did not observe any anomaly related to these two transitions.$^{94}$ Recently, Kharrazi et al. reported only $T_N$ $\approx$41 K for $\sim$40 nm TMO NPs [ref. 95] and furthermore, Das et al. reported an anomaly at $T_{lock}$ $\approx$27 K and $T_N$ at 45 K for $\sim$25 nm TMO NPs [ref. 96].

Considering atomic displacement of the O$^{2-}$ (a result of the Dzyaloshinkii-Moriya (DM) interaction) as the origin of ferroelectricity,$^{37-39}$ it may be inferred that the lattice parameters of TMO would impact the magnetic and therefore the ferroelectric properties. It should be noted that the lattice parameter ($c$) of bulk TMO has been shown to depend on the synthesis method.$^{91,93}$ However, the implications of the modification of the structure of pure TMO (through various synthesis routes) on the magnetic properties have only been commented on but not fully investigated. Most of the previously reported TMO bulk samples have been prepared via solid state synthesis that requires high processing temperatures ($> 1200^\circ$C). In this work, a
facile solution method is utilized to prepare bulk TMO at comparatively lower temperature and the structural and magnetic properties are compared with previous results.

3.2. Sample Synthesis

High purity precursors were mixed in stoichiometric ratio Tb(1)Mn(1) in acetic acid for several hours. The precursor solution was then dried at 60 °C in an oven and then one part of the sample was annealed at 800 °C and another part at 900 °C both in oxygen for 2 h.

3.3. Structural and Microstructural Characterizations

![XRD graphs for TbMnO3 bulk annealed at 800°C and 900°C.](image)

**Figure 3.1.** The XRD θ-2θ scans for TbMnO3 bulk annealed at (a) 900°C and (b) 800°C. The impurity peaks (possibly due to MnO2 or Mn2O3) are marked with * in part (b).

The XRD θ-2θ data of the samples annealed at 800°C and 900°C is shown in Figure 3.1. TbMnO3 is an orthorhombically distorted perovskite with space group *Pbnm*. The 800°C
annealed TMO sample shows the presence of impurity peaks that may correspond to those of MnO₂ or Mn₃O₄ in addition to peaks due to TMO phase. However, in the 900°C annealed sample, only the peaks of the TMO phase [JCPDS #72-379] were preset confirming that this sample is phase pure. This may indicate the development of a metastable intermediate phase that forms at lower temperatures. Similar metastable phases have been previously demonstrated to lower crystallization energy in solution grown samples. The lattice structure was determined by Rietveld refinement of the XRD data for the phase pure sample and the lattice parameters and bond lengths/angles are given in Table 3.1. The values of a and b parameters of the present TMO are comparable to those previously observed in other single crystal and polycrystalline samples. The out-of-plane lattice parameter (c) is comparable to some previously reported values [91,92] but slightly higher than others [93,97]. This discrepancy in the value of c is observed in TbMnO₃ samples synthesized by different methods (i.e. solid state reaction versus soft-chemistry). A slight increase in c value has been noted in related manganites due to the formation of oxygen vacancies, which would result in the conversion of some of the Mn³⁺ to Mn²⁺ to compensate the charge and would also significantly impact the magnetic properties.

To verify the valence state in the present TMO, x-ray photoemission spectroscopy (XPS) was performed for the Mn 2p peaks (2p¹/₂ and 2p³/₂) as shown in Figure 3.2. The XPS data fitted well with one peak (no asymmetry was detected that would require a secondary peak) that corresponds to a 3⁺ valence state of Mn in the material. This confirms the absence of Mn²⁺ in the present sample and therefore no oxygen vacancies are expected.
Table 3.1. The lattice parameters, Mn – O bond lengths and bond angle from Rietveld refinement of the XRD data.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameters (Å)</td>
<td></td>
</tr>
<tr>
<td>(a)</td>
<td>5.299</td>
</tr>
<tr>
<td>(b)</td>
<td>5.817</td>
</tr>
<tr>
<td>(c)</td>
<td>7.415</td>
</tr>
<tr>
<td>(d_{\text{Mn-O}}) (Å)</td>
<td>1.80(3)</td>
</tr>
<tr>
<td>(d_{\text{Mn-O}}) (Å)</td>
<td>2.34(3)</td>
</tr>
<tr>
<td>Mn – O – Mn bond angle</td>
<td>144.9(12)°</td>
</tr>
<tr>
<td>(\chi^2)</td>
<td>2.05</td>
</tr>
</tbody>
</table>

Figure 3.2. X-ray photoemission spectrum for Mn 2p peaks. The \(2p^{1/2}\) and \(2p^{3/2}\) peaks are labeled with position.
The phase purity of the sample was also examined with Raman spectroscopy. 24 Raman active modes have been identified in orthorhombic TbMnO$_3$ by group theory calculations: $\Gamma = 7A_g + 7B_{1g} + 5B_{2g} + 5B_{3g}$. Room temperature Raman spectroscopic data for the present TMO sample is shown in Figure 3.3. Raman active peaks were identified at (i) $\sim$275 cm$^{-1}$ that corresponds to an $A_g$ in-phase rotation of the MnO$_6$ octahedra, (ii) $\sim$373 cm$^{-1}$ that corresponds to an $A_g$ tilting mode of the MnO$_6$ octahedra, (iii) $\sim$479 cm$^{-1}$ that corresponds to an $A_g$ asymmetric Jahn-Teller mode, (iv) $\sim$521.5 cm$^{-1}$ that corresponds to $(A_g + B_{1g})$, and (v) $\sim$607.4 cm$^{-1}$ that has been assigned to the in-phase oxygen stretching. Two additional low-frequency modes are observed ($A_g$ mode at 137.4 cm$^{-1}$ and $B_{1g}$ mode at 158.6 cm$^{-1}$) that correspond to the vibrational modes of the Tb$^{3+}$ ions. The peaks $\sim$479 and 607.4 cm$^{-1}$ related to the modes involving Mn – O bond stretching vary when a mixed Mn valence is present, further confirming the absence of oxygen vacancies in the present TMO sample.

![Raman spectroscopy data](image-url)

**Figure 3.3.** Room temperature Raman spectroscopic data of bulk TbMnO$_3$ sample with peaks corresponding to Raman modes indicated by arrows.
As the magnetic properties also depend on the particle, it is essential to determine the average size of TMO grains. The average grain size of the present TMO bulk sample was ~100 nm as determined by scanning electron microscopy as shown in Figure 3.4.

![Scanning electron microscopy image of TbMnO₃ bulk powder.](image)

**Figure 3.4.** Scanning electron microscopy image of TbMnO₃ bulk powder.

### 3.4. Magnetic Measurements

The temperature dependent ZFC and FC DC susceptibility data \(\{\chi_{dc}(T)\}\) of the TMO sample (annealed at 900°C) with 50 Oe applied magnetic field is shown in Figure 3.5a. A clear anomaly ~7 K due to the ordering of Tb\(^{3+}\) moments is observed in the ZFC and FC curves. A small peak ~40 K below the bifurcation of the ZFC and FC data may be a signature of the AFM ordering of Mn\(^{3+}\) moments. The onset of the ordering, as determined by a peak in the \(d\chi_{dc}/dT\) plot, gives \(T_N\) ~41 K in the present TMO sample that is consistent with previous results for bulk and single crystals. It should be noted that previously, a bifurcation observed in the FC and ZFC data was ascribed to the AFM ordering at \(T_N\).\(^{92,96,102}\) However, this bifurcation in TMO is an extrinsic effect that is related to uncompensated moments at the grain boundaries and depends on the applied magnetic field, as shown in Figure 3.5 (b) and (c).
TMO NPs with average diameter ~25 nm and ~40 nm have previously demonstrated anomalies at $T_N$ that was not observed for particles with larger size.\textsuperscript{94–96} However, the grains in the present TMO sample are not nano-sized as observed in Figure 3.4, suggesting that the appearance of the above mentioned anomaly is not related to grain-size effects. The FC susceptibility data in the range 60 K - 300 K fitted well with Curie-Weiss law. The values of Curie constant ($C$) and Curie-Weiss temperature ($\Theta$) were found to be 0.028 emuK/gOe and -38.8 K, respectively. The negative value of $\Theta$ confirms AFM ordering at low temperatures (below $T_N$) in the present TMO sample. These values are comparable to several other reports in bulk TMO.\textsuperscript{91,94}

The magnetic field dependent isothermal magnetization curves are shown in Figure 3.6a at temperatures between 5 K and 50 K. As the temperature is increased, the sample displays paramagnetic behavior. At 5 K, a metamagnetic transition is observed $\sim$1.7 T that is shown.
clearly in the dM/dH versus field data as shown in Figure 3.6b. Similar changes in slope are also reported for other bulk samples. Metamagnetic transitions are also observed at low temperatures in single crystal TMO, and the field at which such transitions occur depends on the orientation of the crystallographic axes to the applied magnetic field. These transitions are consistent with the magnetic reversal of Ising Tb\textsuperscript{3+} moments as observed in the orthoferrite TbFeO\textsubscript{3}.\textsuperscript{104,105}

![Figure 3.6. (a) The field dependent magnetization curves at temperatures between 5 K and 50 K. and (b) the dM/dH versus magnetic field data at 5 K.](image)

The temperature dependent AC susceptibility data in Figure 3.7 shows frequency dependence of both the real (\(\chi'\)) and complex (\(\chi''\)) components for the TMO sample and the ordering of Tb\textsuperscript{3+} moments was observed at \(\sim 7\) K through a peak in \(\chi'\) data and an increase in susceptibility values in \(\chi''\) data. Similar increase in \(\chi''(T)\) below 7 K has been observed in other bulk TMO samples.\textsuperscript{97} A peak with an onset \(\sim 41.5\) K (as determined by \(d\chi''/dT\)) was observed in \(\chi''(T)\) data. Similar peaks are reported in LaMnO\textsubscript{3} [106] and YbMnO\textsubscript{3} [107] where the onset of the anomaly is defined as \(T_N\). This corresponds to the anomaly observed in \(\chi_{dc}(T)\) data and is comparable to previously reported values of \(T_N\) in TMO bulk and single crystals.\textsuperscript{3,54} A distinct
change in the $\chi''(T)$ behavior of the present sample at lower temperatures with an onset $\sim 28$ K (as determined by $d \chi''/dT$) indicates the presence of a change in the magnetic order. This peak position does not appear to be frequency-dependent and therefore the possibility of a spin-glass state is ruled out; however it may be due to the noncollinear spiral spin ordering at $T_{lock} = 28$ K. Transitions to similar cycloidal spin states have previously been observed as an anomaly in the AC susceptibility data in single crystal DyMnO$_3$ and bulk magnetoelectric FeV$_2$O$_4$.\textsuperscript{108,109}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.7.png}
\caption{The real ($\chi'$) and complex ($\chi''$) components of the temperature dependent AC susceptibility data at several frequencies for TbMnO$_3$.}
\end{figure}

It should be noted that no anomalies at $T_N$ or $T_{lock}$ were present in the AC susceptibility data of bulk TMO synthesized by solid state reaction or soft-chemistry methods.\textsuperscript{93,97} These results are therefore the first observation of signatures due to Mn$^{3+}$ ordering at both $T_N$ and $T_{lock}$ in the susceptibility data of bulk TbMnO$_3$. The present hybrid solution route is therefore a promising synthesis method for fabricating the multiferroic manganites due not only as it lowers the required processing temperatures, but in addition results in the modulation of the
orthorhombic structure through modifying the lattice parameters and thus the magnetic properties.

3.5. Conclusions

In conclusion, phase-pure orthorhombic bulk TbMnO$_3$ sample was prepared via solution route by annealing at 900°C. The possibility of oxygen vacancies was disregarded for the present sample. The DC susceptibility data showed anomalies related to ordering of Tb$^{3+}$ moments $\sim$ 7 K and an anomaly that corresponds to the sinusoidal ordering of Mn$^{3+}$ moments at Néel temperature. The AC susceptibility data also revealed anomalies at both $T_N$ and the noncollinear spiral spin ordering at $T_{lock}$. The present solution synthesis route modulated the structure that may have impacted the magnetic properties of bulk TbMnO$_3$. 
Chapter 4

Multiferroic Properties of Tb$_{0.67}$R$_{0.33}$MnO$_3$ (R = Ho$^{3+}$ and Y$^{3+}$)

4.1. Introduction

As mentioned in Chapter 1, rare-earth manganites (RMnO$_3$) with orthorhombically distorted perovskite structure exhibit magnetic properties that vary with the ionic radius (or for R$_{1-x}$R$'_{x}$MnO$_3$, the average ionic radius) at the A-site.$^{2,110}$ Metastable orthorhombic HoMnO$_3$ (o-HMO) exhibits sinusoidal ordering below $T_N$ $\sim$ 41 K and E-type AFM ordering (as shown in Figure 4.1a) below $T_{lock}$ $\sim$ 26 K.$^{111}$ Multiferroicity in o-HMO was theoretically predicted to arise as a result of displacement of O$^{2-}$ due to a symmetric $S_i \cdot S_j$ Mn – Mn exchange striction$^{112}$ and was later confirmed experimentally with a spontaneous polarization developing below $T_{lock}$ (Figure 4.1b).$^7,113$ It should be noted that an increase in the polarization was observed below 15 K resulting from an additional Ho – Mn exchange interaction due to the noncollinear configuration of the Ho$^{3+}$ moments. This indicates that interesting new magnetic or multiferroic properties may arise due to the magnetic moment of the rare-earth (or substituted rare-earth) ion.

![Figure 4.1.](image)

Figure 4.1. (a) Spin configuration in E-type AFM ordering (plus and minus represent Mn$^{3+}$ spins up and down, respectively) and (b) temperature dependent polarization values showing the onset of a spontaneous polarization at the E-type AFM ordering temperature ($T_L$) and the Ho$^{3+}$ ordering temperature ($T_{NC}$), from [7].
The possibility of using Ho$^{3+}$ substitution to enhance the polarization of the multiferroic rare-earth manganites (RMnO$_3$, R = Gd, Tb, Dy) has previously been investigated. However, magnetic studies of these materials have not been presented. Both the ferroelectric and magnetic results of samples with average ionic radii intermediate those of Tb and Ho are necessary to experimentally investigate the competition between the noncollinear spiral spin (NSS) and the E-type AFM ordering, as well as the possibility of phase coexistence of these two magnetic orders. In addition, as there are several parameters that can modulate the properties in the manganites (such as relative size and moment of the dopant cation), comparison of a magnetic versus non-magnetic dopant with similar ionic radii may provide insight as to the role the ordering of Ho$^{3+}$ moments plays in determining the multiferroic properties. Thus, in this chapter the structural, magnetic, and electric properties of TMO, Ho-doped TMO, and Y-doped TMO (as Y$^{3+}$ has an ionic radius very close to that of Ho$^{3+}$ but with zero magnetic moment) are examined.

4.2. Sample Synthesis

Bulk ceramic samples were prepared via citrate route. High-purity precursors were mixed with stoichiometric ratios of Tb(1)Mn(1), Tb(0.67)Ho(0.33)Mn(1), and Tb(0.67)Y(0.33)Mn(1) in solvent with citric acid. The resultant solutions were dried to form a powder, which were then annealed at 900$^\circ$C for 2 hours. The TbMnO$_3$ (TMO) and Tb$_{0.67}$Ho$_{0.33}$MnO$_3$ (THMO) samples were prepared in oxygen, and part of the Tb$_{0.67}$Y$_{0.33}$MnO$_3$ sample was annealed in oxygen and part in air.
4.3. Structural Characterizations

The XRD $\theta$-2$\theta$ scans for (a) TMO and THMO, and (b) Y-doped TMO annealed in oxygen and in air. The subscript ‘h’ denotes peaks of the hexagonal impurity phase.

The XRD $\theta$-2$\theta$ scans for TMO, THMO, and Y-doped TMO are shown in Figure 4.2. Peaks corresponding to only orthorhombic TMO and THMO are observed (as in JCPDS file #72-379 for TMO) in Figure 4.2a, indicating that the samples are phase pure. The Y-doped sample annealed in oxygen reveals peaks that can be indexed to a hexagonal manganite phase (as marked with subscript ‘h’ in Figure 4.2b). However, annealing in air results in a phase pure orthorhombic sample. Here, the phase pure sample will be referred to as TYMO; the sample with hexagonal impurities will not be discussed further. Rietveld refinement of the XRD data was used to evaluate the structure of the samples, and the results are presented in Table 4.1.
The values of $a$, $b$, and $c$ lattice parameters for the pure TMO are comparable to values reported for bulk TMO synthesized by soft-chemistry solid state reaction\textsuperscript{93,97} and the value of $c$ is smaller than those observed for TMO synthesized by hybrid route (see section 3.3) suggesting that these values depend on synthesis route. The lattice parameters decreased upon substitution of Ho$^{3+}$ or Y$^{3+}$ for Tb$^{3+}$ in TMO lattice, which is as expected due to the smaller ionic radii of Ho$^{3+}$ and Y$^{3+}$ as compared to Tb$^{3+}$ (1.072 Å and 1.075 Å as compared to 1.095 Å, respectively). The average ionic radius at the A-site {$<r_A>$} is decreased to 1.088 Å and 1.087 Å for TYMO and THMO samples, respectively. The reduction in {$<r_A>$} values may explain the lowering of $a$, $b$, and $c$ lattice parameters as well as the change in unit cell volume.

<table>
<thead>
<tr>
<th></th>
<th>TbMnO$_3$</th>
<th>Tb$<em>{0.67}$Y$</em>{0.33}$MnO$_3$</th>
<th>Tb$<em>{0.67}$Ho$</em>{0.33}$MnO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>5.2981(1)</td>
<td>5.2851(4)</td>
<td>5.2817(1)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>5.8409(2)</td>
<td>5.8406(1)</td>
<td>5.8239(3)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>7.4034(1)</td>
<td>7.3859(1)</td>
<td>7.3964(1)</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
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<td>227.99(1)</td>
<td>227.51(2)</td>
</tr>
<tr>
<td>$d_{\text{Mn-O}}$</td>
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<td>1.964</td>
<td>1.888</td>
</tr>
<tr>
<td>$d_{\text{Mn-O}}$</td>
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<td>2.158</td>
<td>2.254</td>
</tr>
<tr>
<td>Mn – O – Mn</td>
<td>145.27</td>
<td>145.56</td>
<td>144.13</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>2.14</td>
<td>1.99</td>
<td>2.05</td>
</tr>
</tbody>
</table>

Table 4.1. Structural parameters for TMO, TYMO, and THMO samples derived from Rietveld refinement of the XRD data.
Room temperature Raman spectroscopic data of all samples are shown in Figure 4.3. As previously mentioned, orthorhombic RMnO$_3$ have 24 Raman active modes classified as $\Gamma = 7A_g + 7B_{1g} + 5B_{2g} + 5B_{3g}$. The observed Raman spectrum of TMO/TYMO/THMO reveals the presence of (i) a $B_{1g}$ symmetric oxygen stretching mode at 608/605/611 cm$^{-1}$, (ii) $A_g + B_{1g}$ mode at 503/521/528 cm$^{-1}$, (iii) an $A_g$ antisymmetric Jahn-Teller mode at 482/480/491 cm$^{-1}$, (iv) an $A_g$ tilting mode of the MnO$_6$ octahedra at 372/373/379 cm$^{-1}$, and (v) an $A_g$ in-phase rotation of the MnO$_6$ octahedra at 271/266/280 cm$^{-1}$ as well as two low-frequency modes corresponding to the movement of the rare-earth ions. These modes are suppressed in TYMO sample due to much lower atomic mass of Y$^{3+}$ as compared to Tb$^{3+}$ or Ho$^{3+}$. The shifts in peak position in TYMO and THMO are consistent with the change in the Mn – O bond lengths and the tilting of the MnO$_6$ octahedra as suggested by the decreased Mn – O – Mn bond angle. In comparison, group-theoretical analysis has determined 38 Raman active modes in hexagonal YMnO$_3$ and HoMnO$_3$: 

Figure 4.3. Room temperature Raman spectroscopic data of TMO, TYMO and THMO bulk samples with Raman modes as indicated by arrows.
\[ \Gamma = 9A_g + 14E_{1g} + 15E_{2g} \] In o-YMnO$_3$, the presence of a small (~12\%) hexagonal impurity phase resulted in a strong peak ~685 cm$^{-1}$ in Raman spectrum.\textsuperscript{119} No such peak was observed for the present THMO and TYMO bulk samples and therefore the presence of a hexagonal impurity phase is disregarded supporting the XRD results of these samples.

### 4.4. Magnetic Measurements

![Graph](https://via.placeholder.com/150)

**Figure 4.4.** The temperature dependent (a) ZFC and FC DC susceptibility ($\chi_{dc}$) and (b) real ($\chi'$) and complex ($\chi''$) components of the AC susceptibility data for TMO sample.

The temperature dependent ZFC and FC DC susceptibility data ($\chi_{dc}$) with 50 Oe applied magnetic field for TMO (Figure 4.4a) shows only an anomaly ~7 K due to the ordering of Tb$^{3+}$ moments. No anomalies related to ordering of Mn$^{3+}$ at $T_N$ or $T_{lock}$ are observed; the discrepancy between the present TMO and the results presented in Chapter 3 may be due to the difference in lattice parameters as previously mentioned. However, these results are consistent with previous reports on bulk TMO and may be due to the large paramagnetic moment of Tb$^{3+}$ dominating the
bulk magnetization response. Similar features to those seen in $\chi_{dc}(T)$ data are also observed in the real ($\chi'$) component of AC susceptibility data as shown in Figure 4.4b, with a clear anomaly ~7 K. An increase in amplitude of the complex ($\chi''$) component of AC susceptibility data is also revealed at the Tb$^{3+}$ ordering temperature. Similar features are observed in the DC and AC susceptibility data of TYMO in Figure 4.5, i.e. a peak ~7 K is observed but the feature appears to be broader, which may be due to dilution of Tb$^{3+}$ ordering due to Y substitution.

![Graph](image)

**Figure 4.5.** The temperature dependent (a) ZFC and FC DC susceptibility and (b) real and complex components of the AC susceptibility data for TYMO.
Upon the substitution of Ho\(^{3+}\) at the Tb-site, interesting features arise in both DC and AC susceptibility as seen in Figure 4.6. A bifurcation of the ZFC and FC curves is observed at ~70 K, below which a broad peak in the ZFC data develops ~40 K. A change in the ZFC $\chi_{dc}$ behavior is observed ~24 K along with the peak due to Tb\(^{3+}\) ordering as observed in TYMO sample. An upturn in $\chi_{dc}$ data at 24 K may be due to the onset of the NSS ordering of the Mn moments in the THMO sample. Curie-Weiss law fitted the data well for all samples (between 60 K and 300 K for TMO and TYMO, and between 100 K and 300 K for THMO) as shown in Figure 4.7. The values of Curie constant ($C$) and Curie-Weiss temperature ($\Theta$) are given in Table 4.2.

**Figure 4.6.** The temperature dependent (a) ZFC and FC DC susceptibility and (b) real and complex components of the AC susceptibility data for THMO.
A lower value of the effective moment ($\mu_{\text{eff}}$, as calculated from Curie constant) is observed for both THMO and TYMO samples as compared to pure TMO. This is expected in TYMO as the magnetic moment of the rare-earth ion contributes to the net moment. The magnetic moment of Tb$^{3+}$ is 9.7 $\mu_B$ and Ho$^{3+}$ is 10.6 $\mu_B$. Thus, a reduction of the net effective magnetic moment in THMO may indicate unusual magnetic behavior in this sample. Negative values of $\Theta$ for all samples indicate that the dominant magnetic interactions are AFM. A larger negative value in TYMO and a smaller negative value in THMO suggest a modulation of the interaction strength with A-site doping, and could indicate the presence of a weakly FM interaction in THMO.

Table 4.2. The fitting parameters from Curie-Weiss fit of the $\chi_{dc}(T)$ data.

<table>
<thead>
<tr>
<th></th>
<th>TbMnO$_3$</th>
<th>Tb$<em>{0.67}$Y$</em>{0.33}$MnO$_3$</th>
<th>Tb$<em>{0.67}$Ho$</em>{0.33}$MnO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{\text{eff}}$ ($\mu_B$)</td>
<td>9.37</td>
<td>7.89</td>
<td>9.20</td>
</tr>
<tr>
<td>$\Theta$ (K)</td>
<td>-33.94</td>
<td>-39.18</td>
<td>-24.33</td>
</tr>
</tbody>
</table>

Figure 4.7. The temperature dependent $1/\chi_{dc}$ data and Curie-Weiss fittings for TMO, TYMO, and THMO samples. The THMO data has been multiplied by a factor of 1.5 for clarity.
The complex AC susceptibility data $\chi''(T)$ of THMO reveals two distinct peaks $\sim47$ K and $\sim25$ K. The peak $\sim25$ K is relatively frequency-independent (with a relative change of the peak position with frequency $K \sim 0.001$ that is an order of magnitude lower than that observed in spin glasses) and is thus attributed to the NSS ordering at $T_{lock}$. Similar transitions have been observed as a peak in $\chi''(T)$ in single crystal DyMnO$_3$ [ref. 108] as well as the bulk TbMnO$_3$ sample presented in Chapter 3. The broad peak $\sim47$ K is similar to the feature observed in the ZFC DC susceptibility data and could be related to a transition from paramagnetic to AFM or possibly weak FM ordering. This peak is therefore ascribed to the sinusoidal ordering of Mn$^{3+}$ at $T_N$. In La-doped $\delta$-HMO, a similar broad peak centered $\sim130$ K was attributed to a weak ferromagnetism arising from the alteration of AFM and FM superexchange interactions.$^{120}$ In THMO, the onset of this feature corresponds to the bifurcation of the ZFC and FC data and is therefore a signature of a weak FM ordering near $T_N$.

![Figure 4.8](image)

**Figure 4.8.** (a) The field dependent magnetization ($M$) data for TMO, TYMO, and THMO at 5 K. The $dM/dH$ versus field plot is shown in the inset. (b) The temperature dependent coercive field for THMO.

To further compare the magnetic properties, the field dependent magnetization data of TMO, TYMO, and THMO samples at 5 K was measured and is shown in Figure 4.8a. The
metamagnetic transition due to the magnetic reversal of Ising Tb$^{3+}$ moments is again observed \(~1.7 \text{ T}\) for pure TMO sample as presented in the inset of Figure 4.8a. This reversal is also observed in TYMO and THMO but the magnitude of the peak is lowered and the peak position shifted to lower applied fields \(\sim 1.3 \text{ T}\). This further confirms that the present metamagnetic transition corresponds to a rotation of Tb$^{3+}$ moments, as it would be expected that the substitution of Y$^{3+}$ or Ho$^{3+}$ dilutes Tb ordering. The coercive field \(H_C\) is negligible in TMO and TYMO data; however, a small but measurable remanent magnetization and \(H_C \sim 380 \text{ Oe at } 5 \text{ K}\) is observed in THMO as plotted in Figure 4.8b. The behavior in THMO is typical of FM-like ordering, confirming the susceptibility data. Weak ferromagnetism has not previously been observed in bulk TMO or o-HMO. However, it has been demonstrated that a coexistence of the NSS and E-type AFM ordering may occur for Mn-O-Mn bond angles intermediate the two.$^{116,117,121}$ Furthermore, a canting of the sinusoidal ordering at \(T_N\) in strained thin films of YMnO$_3$ was experimentally observed, and a spiral modulation or canting of the E-type AFM ordering has been theoretically predicted. Thus, an FM-like ordering is most likely due to a canted ordering of the Mn$^{3+}$ moments, which is consistent with the magnetization data as the value at \(9 \text{ T}\) applied field of 4.3 \(\mu_B\) is much lower than the theoretical value of 13 \(\mu_B\) if all Tb, Ho, and Y moments are aligned with the field. It is interesting to note that THMO sample exhibits this behavior but TYMO does not. This may be related to a small difference in the average ionic radii, or more likely is due to effects of magnetic versus non-magnetic dopants that may further modulate the exchange interactions and also control the canting of Mn$^{3+}$ spins.
4.5. Ferroelectric Measurements

Figure 4.9. The temperature dependent polarization values (normalized to the polarization at 0 T and 10 K) (a) with ±4 kV/cm applied electric field showing reversibility of polarization in TMO and THMO, and with applied magnetic fields for (b) TMO and (c) THMO samples.

The temperature dependent ferroelectric polarization values \( \{P(T)\} \) of TMO and THMO were determined from the pyroelectric current measurements with the samples poled with a 4 kV/cm applied electric field on cooling to align the ferroelectric domains. As the samples are polycrystalline, the measurement represents an average of the polarization values over all possible grain orientations and is therefore lower than the intrinsic polarization values for a single grain or domain as \( P \) is expected to lie along one of the crystallographic axes in TbMnO\(_3\). The magnitude of the polarization values for the present samples have therefore been normalized to the maximum polarization values with 0 T applied field, as shown in Figure 4.9a. Reversibility of the polarization upon cooling with a -4 kV/cm poling field was observed for both TMO and THMO samples, confirming true ferroelectric ordering. The onset of a spontaneous polarization (as determined by a peak in \( dP/dT \)) gives \( T_{\text{lock}} \sim 28 \) K in pure TMO, which is consistent with previous reports for bulk and single crystal samples. The ferroelectric transition temperature...
decreases to \(\sim 25\) K in THMO, verifying that the peak observed in the \(\chi''(T)\) data is related to the magnetic ordering that results in multiferroicity in this sample. The values of \(P\) at 10 K (and 0 T) are 7.7 \(\mu\)C/m\(^2\) and 5.0 \(\mu\)C/m\(^2\) for TMO and THMO, respectively. The smaller ferroelectric polarization in the present THMO sample is in contrast with a previous report revealing an enhancement in polarization values with 20\% - 40\% Ho substitution in TMO.\(^{48}\)

Considering this discrepancy, first-principles calculations were performed by Dr. Vinit Sharma and Dr. Rampi Ramprasad at the University of Connecticut. The full structural optimization and electronic polarization calculations are performed using Vienna ‘ab-initio’ simulation package (VASP) with the projector augmented plane wave basis functions. The exchange interaction is treated within the generalized gradient approximation (GGA). As these GGA calculations show that TbMnO\(_3\) is metallic, the on-site repulsion \(U\) must also be taken into account (GGA+\(U\)) to give the correct ground state for the pure material. This model was then applied to Tb\(_{0.75}\)Ho\(_{0.25}\)MnO\(_3\) considering both the spiral spin and E-type AFM arrangements. The E-type AFM is determined as the energetically favorable ground state of the Ho-doped TMO. The ferroelectric polarization was found to decrease to 155 \(\mu\)C/m\(^2\) as compared to pure TMO (430 \(\mu\)C/m\(^2\)), which is consistent with the trend observed in the present TMO and THMO samples.

The \(P(T)\) values increased with the application of magnetic fields of 2.5 T and 5 T in TMO (as shown in Figure 4.9b) and is consistent with reports for other bulk samples.\(^{48}\) This is thought to associated with the presence of multiple domains and a reorientation from \(P//c\) to \(P//a\) with applied magnetic field. However, a decrease of polarization values is observed in THMO with application of a magnetic field (Figure 4.9c). A similar reduction has previously been reported in pure \(o\)-HMO and another Ho-doped TMO sample, and is thought to be due to a
metamagnetic transition of Ho$^{3+}$ that modifies the Ho-Mn exchange striction and therefore the polarization.\textsuperscript{7,48,113} This exchange striction plays a role with 33% Ho substitution as evidenced by an anomaly in the P(T) data $\sim$15 K (a jump in polarization values near the Ho$^{3+}$ ordering temperature) that is also observed in single crystal and bulk $\alpha$-HMO.\textsuperscript{7,113} No evidence of this transition is observed in the pure TMO sample, suggesting that this feature does arise from the substitution of Ho for Tb. It should be noted that this may also be an indication of coexistence between NSS and E-type AFM ordering in the samples, but measurements on single crystals would be necessary to determine the dominant mechanism of polarization.

4.6. Conclusions

Phase pure orthorhombic TbMnO$_3$, Tb$_{0.67}$Ho$_{0.33}$MnO$_3$, and Tb$_{0.67}$Y$_{0.33}$MnO$_3$ bulk samples were synthesized via solution route. Raman modes were shifted in doped TMO samples corresponding to change in Mn – O – Mn bond angle. Both DC and AC susceptibility data of Y-doped TMO was similar to that of pure TMO, but for Ho-doped TMO a weak ferromagnetic ordering was revealed. In addition, polarization measurements demonstrated ferroelectricity and magnetoelectric coupling in TMO and Ho-doped TMO samples. First-principles calculations suggested E-type AFM ordering in Ho-doped TMO that may lead to a canted antiferromagnetism. Thus the DC/AC susceptibility data and polarization measurements reveal that not only the average ionic radius at the A(Tb)-site but the magnetic moment of the rare-earth ions strongly affects both the magnetic and ferroelectric properties of the multiferroic TbMnO$_3$. 
Chapter 5

Magnetic Properties of Tb$_{1-x}$M$_x$MnO$_3$ (M = Ca$^{2+}$ and Sr$^{2+}$)

5.1. Introduction

As previously mentioned, substitution of the rare-earth in RMnO$_3$ with a divalent alkaline earth cation results in the conversion of some of the Mn$^{3+}$ ions to Mn$^{4+}$. The physical properties of these R$_{1-x}$M$_x$MnO$_3$ (M = Ca$^{2+}$ or Sr$^{2+}$) systems depend on several factors, including the Mn$^{3+}$/Mn$^{4+}$ ratio (as determined by the doping level $x$), the average ionic radius of the A-site cation $\langle r_A \rangle$, and the ionic-size mismatch at the A-site defined by the variance $\sigma^2$ where:

$$\sigma^2 = \Sigma y_i r_i^2 - \langle r_A \rangle^2$$

(5.1)

where $y_i$ is the fractional occupancy and $r_i$ is the ionic radius for a particular cation at the A-site.$^{123-125}$ Several studies are present focusing on the magnetic and magnetotransport properties of these systems for larger rare-earth ions (R = La, Pr, Nd).$^{16,63,123,126}$ There are currently only a few studies on the mixed valence manganites when the parent compound is multiferroic (R = Gd, Tb, Dy, Ho, etc.).$^{3,13}$ It should be noted that in contrast to doped LaMnO$_3$ or PrMnO$_3$, these materials (i) grant access to a much broader range of average ionic radii and variance, allowing for understanding of a more complete picture of how these parameters affect the properties, and (ii) have rare-earth with large magnetic moments that could play an important role in modulating their magnetic properties due to additional coupling between the Mn and R moments. For example, in Ca- or Sr-doped GdMnO$_3$ and DyMnO$_3$ (for $0.2 \leq x \leq 0.4$), bulk magnetization data suggests that the Gd or Dy moments align antiparallel to the FM Mn moments, resulting in negative magnetization values and ferrimagnetic ordering.$^{127-130}$ However, for a similar doping range ($0.1 \leq x \leq 0.33$), a spin-glass-like state was reported for Tb$_{1-x}$Ca$_x$MnO$_3$ due to the
formation of FM clusters without developing a long-range magnetic ordering reported in Gd$_{1-x}$A$_x$MnO$_3$ or Dy$_{1-x}$A$_x$MnO$_3$ (A = Ca, Sr). This behavior is rather unexpected since the ionic radius and magnetic moment of Tb$^{3+}$ are intermediate those for Gd$^{3+}$ and Dy$^{3+}$. Thus, further investigation in these R$_{1-x}$A$_x$MnO$_3$ systems is necessary to fully understand the effects of the variance at the A-site and magnetic moment of the rare-earth ion on their magnetic properties.

5.2. Sample Synthesis

Bulk ceramic samples were prepared via citrate route. High-purity precursors were mixed in stoichiometric ratios Tb(0.67)Ca(0.33)Mn(1), Tb(0.67)Sr(0.33)Mn(1), and Tb(0.75)Sr(0.25)Mn(1) in solvent with citric acid. The resultant solutions were dried to form a powder, which were then annealed at 900°C in oxygen for 2 hours.

5.3. Structural Characterizations

Figure 5.1. The XRD $\theta$-2$\theta$ scans for TCMO, TSMO, and TSMO25 samples.
The XRD $\theta$-2$\theta$ scans for all three samples shown in Figure 5.1 indicates that $\text{Tb}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ (TCMO), $\text{Tb}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (TSMO), and $\text{Tb}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ (TSMO25) samples are of single phase and have orthorhombic structure. The lattice parameters calculated from the XRD data as well as a comparison of the average ionic radius at the A-site <$r_A$> and the variance $\sigma^2$ for all samples are presented in Table 5.1.

<table>
<thead>
<tr>
<th></th>
<th>$\text{Tb}<em>{0.67}\text{Ca}</em>{0.33}\text{MnO}_3$</th>
<th>$\text{Tb}<em>{0.67}\text{Sr}</em>{0.33}\text{MnO}_3$</th>
<th>$\text{Tb}<em>{0.75}\text{Sr}</em>{0.25}\text{MnO}_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>5.32</td>
<td>5.36</td>
<td>5.29</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>5.78</td>
<td>5.77</td>
<td>5.78</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>7.48</td>
<td>7.32</td>
<td>7.40</td>
</tr>
<tr>
<td>$b/a$</td>
<td>1.088</td>
<td>1.077</td>
<td>1.094</td>
</tr>
<tr>
<td>&lt;$r_A$&gt; (Å)</td>
<td>1.123</td>
<td>1.165</td>
<td>1.148</td>
</tr>
<tr>
<td>$\sigma^2 = \sum y_i r_{i1}^2 - &lt;r_A&gt;^2 (10^{-3} \text{Å}^2)$</td>
<td>1.6</td>
<td>10.2</td>
<td>8.7</td>
</tr>
</tbody>
</table>

Table 5.1. The structural parameters and calculated values for TCMO, TSMO, and TSMO25 samples.

In the present samples, an increment in the lattice parameter $a$ and a reduction in the lattice parameter $b$ as compared to pure TbMnO$_3$ was observed.$^{93,97}$ The orthorhombic distortion in TbMnO$_3$ is correlated with Jahn-Teller (JT) distortion of Mn$^{3+}$ in the MnO$_6$ octahedra.$^{132}$ With the substitution of Ca$^{2+}$ or Sr$^{2+}$ in place of Tb$^{3+}$, the tolerance factor increases due to the increase in <$r_A$>. In addition, the introduction of non-JT active Mn$^{4+}$ ions gives rise to a decrease in the lattice parameter $b$ and an overall decrease in the $b/a$ ratio (as compared to 1.102 for TbMnO$_3$ [97]). The introduction of Mn$^{4+}$ is considered to be the most important factor in the modification of the lattice parameters,$^{97}$ which explains the larger orthorhombicity in TSMO25 with smaller Mn$^{3+}$/Mn$^{4+}$ ratio. This behavior is similar to that reported in Gd$_{1-x}$Ca$_x$MnO$_3$ or Dy$_{1-x}$Ca$_x$MnO$_3$. 

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with increasing $x$, although the values of $b$ observed in the present Ca- and Sr- substituted TbMnO$_3$ samples are higher than that in previous reports for similar compositions.\textsuperscript{97,128,129} This discrepancy may result from a difference in synthesis route, as discussed for pure TbMnO$_3$ in Chapter 3. It should be noted that for TCMO and TSMO samples, the Mn$^{3+}$/Mn$^{4+}$ ratio is expected to be the same and therefore any differences in their magnetic properties are expected to arise as a result of differences in the orthorhombic distortion, $<r_A>$, or $\sigma^2$.

5.3. Magnetic Measurements

The temperature dependent ZFC and FC DC susceptibility data ($\chi_{dc}$) of TCMO (Figure 5.2a) shows several interesting features that includes (i) a large change in slope (observed as a peak in $d\chi_{dc}/dT$) $\sim$78 K, (ii) a peak $\sim$ 50 K in both FC and ZFC data, and (iii) an inflection point (local minimum) in the ZFC data corresponding to a switch from positive to negative FC susceptibility values $\sim$15 K. The magnetic behavior of the present TCMO sample is markedly different as compared to the previous report on Tb$_{1-x}$Ca$_x$MnO$_3$.\textsuperscript{97} However, similar features have been observed in the $\chi_{dc}(T)$ of the related materials Gd$_{1-x}$Ca$_x$MnO$_3$ and Dy$_{1-x}$Sr$_x$MnO$_3$ with comparable Mn$^{3+}$/Mn$^{4+}$ ratios.\textsuperscript{127–129} Through comparison of these previous reports and the data for present TCMO sample, it is believed that the ferromagnetic-like ordering of the Mn sublattice occurs at $T_C \sim$ 78 K, below which it imposes an internal field ($H_{int}$) on the Tb sublattice. As the temperature is lowered below $T_C$, the Tb$^{3+}$ ions behave like paramagnetic spins reacting to the $H_{int}$, resulting in a peak $\sim$ 50 K due to the ferrimagnetic ordering of the Mn and Tb sublattices. The Mn$^{3+}$ (Tb$^{3+}$) moments dominate the net magnetization above (below) the compensation temperature $T_{comp} \sim$ 15 K. In contrast to previous studies, the present TCMO sample exhibits characteristics of a long-range magnetic ordering.\textsuperscript{97,133}
Figure 5.2. The temperature dependent DC susceptibility data ($\chi_{dc}$) for (a) TCMO, (b) TSMO, and (c) TSMO25 samples.
The DC susceptibility data of TSMO (Figure 5.2b) shows a clear FM-like transition in both ZFC and FC susceptibility with an onset ~87 K. A broader feature in the ZFC data is also observed ~50 K that may indicate a transition to a spin-glass-like state, the possibility of which will be investigated in more detail later. The DC susceptibility data of TSMO25 (Figure 5.2c) is similar, with a change in slope ~83 K and a broad peak ~35 K. Curie-Weiss law fits the data well in the temperature range 100 K - 300 K for all three samples. The values of effective moment ($\mu_{\text{eff}}$ as derived from Curie constant $C$) and Curie-Weiss temperature ($\Theta$) are given in Table 5.2.

<table>
<thead>
<tr>
<th></th>
<th>Tb$<em>{0.67}$Ca$</em>{0.33}$MnO$_3$</th>
<th>Tb$<em>{0.67}$Sr$</em>{0.33}$MnO$_3$</th>
<th>Tb$<em>{0.75}$Sr$</em>{0.25}$MnO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{\text{eff}}$ ($\mu_B$)</td>
<td>7.62</td>
<td>7.46</td>
<td>7.79</td>
</tr>
<tr>
<td>$\Theta$ (K)</td>
<td>9.5</td>
<td>-21.7</td>
<td>2.5</td>
</tr>
<tr>
<td>$T_C$ (K)</td>
<td>78</td>
<td>87</td>
<td>83</td>
</tr>
</tbody>
</table>

**Table 5.2.** The magnetic properties of TCMO, TSMO, and TSMO25 as derived from the fit.

The value of $\Theta$ is positive (but not equal to $T_C$) for TCMO and negative for TSMO and TSMO25 samples. All $\Theta$ values are lower than that found for pure TbMnO$_3$ synthesized by citrate route in similar conditions as presented in Chapter 4. This suggests that below $T_C$, the present samples have a FM-like macroscopic magnetic response but the microscopic magnetic order is a canted antiferromagnetism (c-AFM) similar to Pr$_{0.67}$Ca$_{0.33}$MnO$_3$ [134] rather than simple ferromagnets like La$_{0.67}$Ca$_{0.33}$MnO$_3$ [135].
To further examine the nature of the magnetic interactions, the field dependent magnetization data was measured in a range of temperatures. The data for all samples at 5 K is shown in Figure 5.3a. Significant coercivity is observed at low temperatures with values of coercive field ($H_C$) that decrease with increasing temperature and disappear above $T_C$ as shown in Figure 5.3b, confirming FM-like ordering of the Mn moments. The values of $H_C$ are similar to previously reported values for Ca-doped GdMnO$_3$ or DyMnO$_3$\textsuperscript{128,136} Saturation was not observed in magnetization even with applied fields up to 9 T, which is consistent with a large field-dependent magnetization at low temperatures that has been previously demonstrated in canted AFM or ferrimagnetic systems.\textsuperscript{137,138} The law of approach to saturation,

$$M(H) = M_S(1-aH^1-bH^2) - \chi$$

where $a$, $b$, and $c$ are constant fitting parameters, can therefore be used to determine the saturation magnetization ($M_S$).\textsuperscript{139} The values of $M_S$ at 5 K were determined to be 4.65 $\mu_B$, 3.39 $\mu_B$, and 3.66 $\mu_B$ for TCMO, TSMO, and TSMO25 samples respectively. The theoretical value is $M_S = g_J\mu_BJ = 12.03$ $\mu_B$, assuming that the Mn$^{3+}$ moments and the paramagnetic moments of Tb$^{3+}$ are aligned for large externally applied magnetic fields ($H_{ext} > H_{int}$). The lower values of $M_S$ in
the present samples further suggest that the macroscopic FM-like ordering in TCMO, TSMO, and TSMO25 is in fact a canted AFM similar to that observed in Pr$_{1-x}$Ca$_x$MnO$_3$ [ref. 134] and could also indicate the presence of AFM clusters.

Temperature dependent real ($\chi'$) and complex ($\chi''$) AC susceptibility data for TCMO, TSMO, and TSMO25 are shown in Figure 5.4. Features in the temperature range 70 - 90 K similar to those observed in the ZFC $\chi_{dc}$ data are observed in the real component of the AC susceptibility. In addition, the onset of a finite complex susceptibility (as determined by $d\chi''/dT$) is observed for all samples at temperatures near the peak in $d\chi_{dc}/dT$ data. These peaks are therefore due to the onset of c-AFM ordering at $T_C = 78$ K, 87 K, and 83 K for TCMO, TSMO, and TSMO25 samples respectively. A second peak at lower temperatures (~25 – 55 K) is also present for all samples that exhibits clear frequency dependence of the peak position. This is a signature of a spin-glass transition with an onset of ~36 K, ~55 K, and ~40 K in TCMO, TSMO, and TSMO25. This spin-glass-like behavior occurs at a similar transition temperature as previously reported in TCMO, although this sample did not show the frequency-independent peak indicating long-range order. The competition between FM and AFM ordering in mixed-valence manganites leads to complex phase diagrams and possibly multiple magnetic transitions in a single material. It is possible that the values of $<r_A>$ or $\sigma^2$ in the present samples are close to a phase boundary between long-range ordering and spin-glass states, resulting in the lower-temperature transition.
Figure 5.4. The real ($\chi'$) and complex ($\chi''$) components of AC susceptibility data for (a) TCMO, (b) TSMO, and (c) TSMO25 samples at selected frequencies.
The apparent onset of glassy behavior at finite periodicity $\tau$ (at $T_{\text{peak}}$) was determined by subtracting a background contribution from the $\chi'(T)$ data due to the paramagnetic contribution of Tb (similar to the method for Dy$_{0.5}$Sr$_{0.5}$MnO$_3$ in ref. 141) and fitting the resulting data to obtain the peak position. For a spin glass or cluster glass, the values of $T_{\text{peak}}$ should obey critical scaling near the spin-glass transition $T_{SG}$ as described by the power law:

$$T_{\text{peak}} = T_{SG}(1 + (\tau_0/\tau)^{1/zv})$$

(5.3)

where $\tau$ is the time scale of the measurement and is equal to $1/f$, $zv$ is a critical exponent, and $\tau_0$ is a characteristic spin-flip time. This equation fits the data well for all samples with frequencies between 100 Hz and 5000 Hz, as shown in Figure 5.5.

![Figure 5.5. The $T_{\text{peak}}$ versus ln$\tau$ data and the resultant power law $\{T_{\text{peak}} = T_{SG}(1 + (\tau_0/\tau)^{1/zv})\}$ fitting for (a) TCMO, (b) TSMO, and (c) TSMO25 samples.](image)

<table>
<thead>
<tr>
<th>$T_{SG}$ (K)</th>
<th>$zv$</th>
<th>$\tau_0$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb$<em>{0.67}$Ca$</em>{0.33}$MnO$_3$</td>
<td>26</td>
<td>1.8</td>
</tr>
<tr>
<td>Tb$<em>{0.75}$Sr$</em>{0.25}$MnO$_3$</td>
<td>34</td>
<td>2.4</td>
</tr>
<tr>
<td>Tb$<em>{0.67}$Sr$</em>{0.33}$MnO$_3$</td>
<td>49</td>
<td>5.6</td>
</tr>
</tbody>
</table>

**Table 5.3.** The parameters derived from the power law $\{T_{\text{peak}} = T_{SG}(1 + (\tau_0/\tau)^{1/zv})\}$ fitting.
The values of fitting parameters ($zv$ and $\tau_0$) for TCMO, TSMO, and TSMO25 (given in Table 5.3) are similar to those obtained for Gd$_{0.5}$Sr$_{0.5}$MnO$_3$ ($\sigma^2 \sim 9 \times 10^{-3}$ Å$^2$, $zv \sim 1.2$, and $\tau_0 \sim 10^{-6}$ s),$^{142}$ Dy$_{0.5}$Sr$_{0.5}$MnO$_3$ ($\sigma^2 \sim 12 \times 10^{-3}$ Å$^2$, $zv \sim 3.6$ and $\tau_0 \sim 10^{-8}$ s),$^{141}$ or Eu$_{0.5}$Ba$_{0.5}$MnO$_3$ ($\sigma^2 \sim 30 \times 10^{-3}$ Å$^2$, $zv \sim 8$ and $\tau_0 \sim 10^{-13}$ s).$^{143}$ It is interesting to note that in these studies as well as in the present samples, faster dynamics (as evidenced by larger $\tau_0$) are generally observed as the ionic-size mismatch at the A-site increases. For large values of $\sigma^2$, the values of $\tau_0$ and $zv$ approach to those of atomic spin glasses.$^{143}$ The present TCMO and TSMO25 samples exhibit slower dynamics that may be related to the collective motion of the Mn$^{3+}$ spins, whereas TSMO behaves similar to a canonical spin glass that is more consistent with dilute interactions. These results are reasonable considering the smaller values of $H_C$ and $M_S$ in TSMO as well as the larger negative value of $\Theta$ observed in the present TSMO sample as compared to TCMO and TSMO25 samples, which also indicate more dilute FM-like interactions in TSMO sample. A large ionic-size mismatch at the A-site is thought to favor spin-glass states in the manganites due to random magnetic anisotropy$^{144}$ that may explain the weaker interactions in the present TSMO sample.

An increment in $T_C$ is generally observed with increasing $<r_A>$ or Mn$^{3+}$/Mn$^{4+}$ ratio,$^{123}$ which is consistent with the three present samples. However, it is important to note that a weaker FM-like ordering is observed in both the TSMO25 and TSMO samples as compared to TCMO, even though TSMO25 has a larger orthorhombic distortion. This indicates that the evolution of the magnetic ordering in these Tb$_{1-x}$A$_x$MnO$_3$ compounds is driven by the ionic-size mismatch at the A-site in addition to the values of $<r_A>$ and the Mn$^{3+}$/Mn$^{4+}$ ratio. The local lattice distortions resulting from a large A-site ionic size mismatch can weaken FM double-exchange interactions and favors frustration between the FM and AFM interactions. In the mixed valence manganites ($R_{1-x}$A$_x$MnO$_3$) as $\sigma^2$ increases, this results in modulation of the magnetic ordering from simple
FM to c-AFM and finally to a spin-glass or to a cluster-glass state at low temperatures. This leads to long-range magnetic ordering in addition to spin-glass-like behavior at low temperatures in the present Ca-doped and Sr-doped TbMnO₃ samples.

5.4. Conclusions

Phase-pure orthorhombic Tb₀.₆₇Ca₀.₃₃MnO₃, Tb₀.₆₇Sr₀.₃₃MnO₃, and Tb₀.₇₅Sr₀.₂₅MnO₃ samples were synthesized via solution route. The DC and AC susceptibility data revealed the presence of long-range canted antiferromagnetic order in all samples. Further, in Tb₀.₆₇Ca₀.₃₃MnO₃ sample, ferrimagnetic behavior due to the anti-alignment of Tb³⁺ to the net Mn³⁺/Mn⁴⁺ moments was observed in the DC susceptibility data. Frequency dependent peak in AC susceptibility data at lower temperatures suggested a transition to a spin-glass-like state. This is believed to be due to the large A-site ionic-size mismatch in the present samples favoring frustration between ferromagnetic and antiferromagnetic interactions.
Chapter 6

Magnetic Structure and Properties of Solid Solution TbMn\(_{1-x}\)Cr\(_x\)O\(_3\)

6.1. Introduction

As mentioned in Chapter 1, the perovskite (ABO\(_3\)) structure allows cations of various sizes at both the A- and B-sites.\(^{19,20}\) Chemical doping of perovskite materials is therefore a fundamental way to tune the physical properties. In general, substitutions at the rare-earth (R) or transition metal (TM) site in R(TM)O\(_3\) materials will alter the crystal field that consequently modifies the TM-TM, R-R, and R-TM interactions.\(^{145}\) The modulation of these interactions is difficult to determine due to competing interactions arising from strong coupling between the lattice, spin, and charge. For example, small Cr substitution (< 5%) in the mixed valence manganites results in a ferromagnetic (FM) metallic ground state in Pr\(_{0.5}\)Ca\(_{0.5}\)MnO\(_3\) but suppresses the ferromagnetism in La\(_{0.7}\)Ca\(_{0.3}\)MnO\(_3\).\(^{146,147}\) The nature of the Mn-Cr interactions (antiferromagnetic \{AFM\} or FM) remains a subject of debate, with conflicting studies supporting both conclusions.\(^{148-151}\) It is generally accepted that the introduction of Cr\(^{3+}\) in RMnO\(_3\) results in a FM component of the magnetization. However, work on solid solutions of RMnO\(_3\) and RCrO\(_3\) is limited, and primarily focuses on manganites exhibiting A-type AFM ordering.\(^{152,153}\) Few studies are available where the RMnO\(_3\) end member is a multiferroic with ferroelectric (FE) and magnetic order. The coexistence of FE and a FM-like ordering has been observed in orthorhombic YMn\(_{1-x}\)Cr\(_x\)O\(_3\)\(^{154}\) and an anomaly in the dielectric constant at high temperatures persisted in YCr\(_{1-x}\)Mn\(_x\)O\(_3\) for up to 30% Mn substitution\(^{155}\). These results suggest that it may be possible to modify the magnetic and hence multiferroic properties of R(TM)O\(_3\) materials through substitution, if both end members are multiferroic.
It has been shown that TbCrO$_3$ exhibits a G-type antiferromagnetic ordering (with all nearest neighbors aligned antiparallel) below $T_N \sim 157$ K with a FM component along the $c$-axis ($G_x F_z$). An anomaly in the dielectric constant and the appearance of a pyroelectric current at high temperatures ($\sim 446$ K) was thought to indicate relaxor ferroelectric behavior in TbCrO$_3$ and other rare-earth chromites (RCrO$_3$). However, the emergence of reversible polar order below $T_N$ was also recently reported by pyroelectric current measurements. Although the mechanism of ferroelectricity in RCrO$_3$ is not yet fully understood, it is expected that TbMn$_{1-x}$Cr$_x$O$_3$ would still be multiferroic in some temperature range throughout the solid solution. Insight into how the magnetic structure is modulated in this solid solution would be essential in understanding the multiferroic properties of this solid solution.

6.2. Sample Synthesis

Bulk ceramic samples were prepared via citrate route. High-purity precursors were mixed in stoichiometric ratios Tb(1)Mn(1-x)Cr(x) for $x = 0, 0.1, 0.33, 0.5, 0.7, \text{ and } 1$ in solvent with citric acid. The resultant solutions were dried to form bulk powders, which were then annealed at 900°C in oxygen for 2 hours.

6.3. Structural Characterizations

The XRD $\theta$-2$\theta$ scans confirm that all the present TbMn$_{1-x}$Cr$_x$O$_3$ compounds are phase pure and orthorhombic with space group $Pbnm$, as shown in Figure 6.1a. The lattice parameters and unit cell volume ($V$) were calculated from the XRD data and are plotted as a function of Cr content in Figure 6.1b.
The lattice parameters $a$ and $b$ generally decrease with increasing Cr content, whereas $c$ remains relatively constant resulting in a decrease in cell volume $V$. The large reduction in $b$ is similar to that observed in $\text{Tb}_{1-x}\text{Ca}_x\text{MnO}_3$, where as $\text{Ca}^{2+}$ content (and therefore $\text{Mn}^{4+}$ content) increased, the value of $b$ decreased with only slight variations in the values of $a$ and $c$ as mentioned in Chapter 5. Although the orthorhombic distortion also decreased by increasing the ionic radius of the rare-earth in $\text{RMnO}_3$, a large increment in $a$ and $c$ is observed, resulting in a larger $V$. It is therefore assumed that the observed structural modulations in the present samples occur primarily through the replacement of JT active $\text{Mn}^{3+}$ with non-JT active $\text{Cr}^{3+}$ ($t_{2g}^3e_g^0$) and not due to an increase in the tolerance factor ($t$) with Cr addition. It should be noted that XPS measurements for a $\text{TbMn}_{0.5}\text{Cr}_{0.5}\text{O}_3$ sample revealed that Mn and Cr ions were in 3+ valence state.
To further probe how Cr substitution affects the structure, room temperature Raman measurements of TbMn$_{1-x}$Cr$_x$O$_3$ were performed as plotted in Figure 6.2. Following the discussion in the previous chapters, 24 Raman active modes for space group $Pbnm$ are $\Gamma = 7A_g + 7B_{1g} + 5B_{2g} + 5B_{3g}$. Comparing Raman spectra of the present samples to previous studies on both $RMnO_3$ and $RCrO_3$ reveals: (i) a $B_{1g}(1)$ symmetric oxygen stretching mode, (ii) $A_g(3)/B_{1g}(2)$ $MO_6$ ($M = Mn, Cr$) O2 bending modes, (iii) an $A_g(1)$ $MO_6$ bending mode, (iv) an $A_g(2)$ out-of-phase rotation of the $MO_6$ octahedra, and (v) an $A_g(6)$ in-phase rotation of the $MO_6$ octahedra as marked by arrows in Figure 6.2a. The shifts in phonon frequencies with varying Cr content (plotted in Figure 6.2b) are generally consistent with previous results comparing Raman spectra of $YMnO_3$ and $YCrO_3$. The crossing of the $B_{1g}$ mode with two separate $A_g$ modes is allowed by symmetry and also allows them to have the same frequency, resulting in a single intense band $\sim 500$ cm$^{-1}$ for the TbMn$_{0.67}$Cr$_{0.33}$O$_3$ (TMCO-33) sample. The $A_g$ modes (related to

Figure 6.2. (a) Raman spectroscopic data with phonon modes marked by arrows and (b) shift of phonon frequencies as a function of Cr content.
the MO₆ octahedra) do not vary much with Cr content, which is similar to the effect observed in the chromites with a changing orthorhombic distortion. The O2 bending or stretching modes (B₁g) are determined by the M-O distances and are more affected by the modification of the lattice parameters. In particular, the B₁g mode ~608 cm⁻¹ is activated by JT distortion, and peak position systematically varies with Cr content due to the reduction of JT active B-site cations. However, the intensity of this peak is not diminished with doping, suggesting that this mode may not be solely activated by JT distortion as previously thought. The two modes at lower frequencies (~139 cm⁻¹ and ~157 cm⁻¹) correspond to the vibrations of the Tb³⁺ ions and do not shift substantially with Cr substitution. This indicates that although the lattice volume is decreased, this does not affect the phonon modes of the rare-earth ion.

6.4. Magnetic Measurements

![Temperature dependent coercive field (Hₐ) values for TbMn₁₋ₓCrₓO₃ samples.](image)

**Figure 6.3.** The temperature dependent coercive field (Hₐ) values for TbMn₁₋ₓCrₓO₃ samples.

To evaluate how the magnetic properties changes with Cr substitution, field dependent magnetization data was taken at several different temperatures for each sample. The values of
coercive field \((H_C)\) were extracted and are plotted as a function of temperature in Figure 6.3. As previously discussed in Chapter 4, no hysteresis behavior was observed for pure TbMnO\(_3\) sample prepared via citrate route. However, even for the TbMn\(_{0.9}\)Cr\(_{0.1}\)O\(_3\) (TMCO-10) sample, large values of \(H_C\) are observed that increase with decreasing temperature. A further increment in \(H_C\) occurs in TMCO-33. This suggests a FM component of the magnetization in the Cr-doped samples. A peak in the \(H_C\) vs. \(T\) plot at \(\sim 20\) K and \(\sim 24\) K for \(x = 0.5\) and \(x = 0.7\) (respectively) is similar to that observed in the present TbCrO\(_3\) \((x = 1)\) sample at \(\sim 55\) K. This peak is most likely related to the parallel alignment of the Tb\(^{3+}\) moments to the net Mn\(^{3+}\)/Cr\(^{3+}\) moment that has previously been observed in TbCrO\(_3\)\(^{162}\) with the corresponding reduction in \(H_C\) occurring due to the R-TM interactions that may result in a decrease in magnetocrystalline anisotropy\(^{163}\). This may suggest a G-type AFM alignment of Mn and Cr moments in the present TbMn\(_{0.5}\)Cr\(_{0.5}\)O\(_3\) (TMCO-50) and TbMn\(_{0.3}\)Cr\(_{0.7}\)O\(_3\) (TMCO-70) samples similar to pure TbCrO\(_3\). The discussion of the magnetic structure in these materials will therefore be separated into those materials with (i) low Cr content displaying FM-like ordering at low temperatures and (ii) larger Cr content with behavior similar to pure TbCrO\(_3\).

6.4.1. \(TbMn_{1-x}Cr_xO_3\): \(0 \leq x \leq 0.33\)

As mentioned in Chapter 4, no anomalies due to the ordering of Mn\(^{3+}\) moments is observed in the DC or AC susceptibility data for pure TbMnO\(_3\). However, a bifurcation of the ZFC and FC DC susceptibility \((\chi_{dc})\) data is observed \(\sim 27\) K for TMCO-10 sample (Figure 6.4), corresponding to frequency dependence of the amplitude of the real AC susceptibility \((\chi')\) and a peak in the complex AC susceptibility \((\chi'')\) data.
Together with the large coercivity at low temperatures, these features indicate the onset of FM-like ordering. A weak FM component was observed by neutron diffraction in LaMn\textsubscript{1-x}Cr\textsubscript{x}O\textsubscript{3} and in bulk magnetization measurements in NdMn\textsubscript{1-x}Cr\textsubscript{x}O\textsubscript{3} or orthorhombic YMn\textsubscript{1-x}Cr\textsubscript{x}O\textsubscript{3}.\textsuperscript{56,152,153} Similar features are also observed in present TMCO-33 as shown in Figure 6.5, with two peaks developing in both the ZFC data (~45 K and 26 K as determined by a peak in d\(\chi_{dc}/dT\)) and \(\chi''(T)\) data (~47 K and 29 K as determined by a peak in d\(\chi''/dT\)). Three possibilities for the onset of a FM-like ordering can be identified: (i) Cr\textsuperscript{3+}-Cr\textsuperscript{3+} interactions giving rise to cluster-glass-like behavior, (ii) a ferrimagnetic response due to nonequivalent spins (~4\(\mu_{B}\) for Mn\textsuperscript{3+} and 3\(\mu_{B}\) for Cr\textsuperscript{3+} assuming the orbital contributions are quenched), or (iii) a local canting of the moments is induced by the introduction of Mn\textsuperscript{3+}-Cr\textsuperscript{3+} interactions.
Cation disorder may give rise to small regions with magnetic order similar to that of TbCrO$_3$ (weak FM) or TbMnO$_3$ (AFM). This should result in cluster-glass-like behavior and therefore frequency dependence of the peak positions in $\chi'(T)$ and $\chi''(T)$ would be expected. The relative change of the apparent peak temperature ($T_{\text{peak}}$) with frequency (equation 2.20) was calculated for the peak ~27 K in TMCO-10 and TMCO-33. The average values were lower than what would be expected for a spin glass or cluster glass (ranging from K ~0.005 to 0.007). In addition, a peak due to a weak FM Cr$^{3+}$-Cr$^{3+}$ interaction would be expected at much higher temperatures. It is also interesting to note that the observed transitions are very close to either $T_N$ or $T_{\text{lock}}$ in pure TbMnO$_3$. This suggests that it is not Cr$^{3+}$-rich clusters resulting in this FM-like ordering, but rather a modification of the Mn$^{5+}$ sinusoidal ordering below $T_N$ and the spiral spin ordering below $T_{\text{lock}}$.

The presence of only one peak in the susceptibility data of TMCO-10 sample cannot easily be explained as ferrimagnetism due to nonequivalent spins, since this should result in a
FM-like signal at both transitions. However, either a weak FM or strong AFM Mn$^{3+}$-Cr$^{3+}$ interaction may affect the orientation of neighboring ions resulting in a local distortion of the magnetic ordering and a net magnetic moment as shown in Figure 6.6.

![Diagram](image)

**Figure 6.6.** Projection of the sinusoidal Mn/Cr ordering onto $b$-$c$ plane in (a) TbMn$_{0.9}$Cr$_{0.1}$O$_3$ and (b) TbMn$_{0.67}$Cr$_{0.33}$O$_3$. (c) Local canting of the spiral spin ordering as a result of ferromagnetic Mn-Cr interactions. Nearest neighbors in the projection are located at $b/2$ and $c/2$.

For sinusoidal ordering ($T_N < T < T_{lock}$) it is more probable that the majority of Cr$^{3+}$ nearest neighbors (NN) are already aligned parallel rather than anti-parallel, which would significantly reduce the total canted moment if the interactions are FM (as would follow from Goodenough-Kanamori-Anderson rules). With further addition of Cr, more sites with the majority of anti-parallel NN are expected to be filled, which may explain the discrepancy between the magnetic behavior of TMCO-10 and TMCO-33 samples. A local canting will be induced in the NSS ordering irrespective of where the Cr ion is located in the spiral ordering. This canting due to
Mn-Cr interactions could result in a net magnetic moment that would account for the observed FM-like behavior.

6.4.3. \( \text{TbMn}_{1-x}\text{Cr}_x\text{O}_3 \): \( 0.5 \geq x \geq 1 \)

![Graph showing ZFC and FC DC susceptibility](image)

**Figure 6.7.** The temperature dependent (a) ZFC and FC DC susceptibility and (b) real and complex components of the AC susceptibility data for TbCrO\(_3\).

A sharp increase in the FC data of pure TbCrO\(_3\) as determined by the \( d\chi_{dc}/dT \) plot (Figure 6.7) and the bifurcation of the ZFC and FC data is observed ~155 K. In addition, the onset of peaks in the ZFC data and both \( \chi'(T) \) and \( \chi''(T) \) also suggest a FM-like transition. The transition temperature \( T_N \) is ~155 K in the present sample is close to previous reports of \( T_N = 157 \) K and therefore the magnetic structure in the present sample is expected to be G-type AFM with moments pointed along the \( c \)-axis with a canted component along \( a \)-axis (\( \Gamma_2 \) following the notation from symmetry analysis developed by Bertaut), accounting for the observed FM-like signal in the susceptibility data.\(^{156,157}\)
Features in the DC and AC susceptibility similar to TbCrO₃ sample are also observed for TMCO-50 sample as shown in Figure 6.8. An anomaly in the ZFC data ~80 K, clearly observed as a local minimum in the $d\chi_{dc}/dT$ plot, confirms the onset of long-range magnetic ordering at $T_N = 84$ K. A slight anomaly ~ 44 K may indicate a second magnetic transition in this sample. This does not appear to be a spin-glass transition as there is no corresponding peak in the AC susceptibility data. It should be noted that $T_N$ in the present TMCO-50 sample is between that of TbMnO₃ and TbCrO₃ (41 K and 157 K, respectively), suggesting that for higher Cr content, the Néel temperature in this solid solution can be tuned by adjusting the Mn/Cr ratio.

**Figure 6.8.** The temperature dependent (a) ZFC and FC DC susceptibility with $d\chi_{dc}/dT$ plot and (b) real and complex components of the AC susceptibility data for TbMn₀.₅Cr₀.₅O₃.
For TMCO-70, behavior similar to TMCO-50 and TbCrO$_3$ is observed in the DC and AC susceptibility (Figure 6.9) at temperatures $T_N \sim 122$ K (as determined by a peak in the ZFC $\chi_{dc}$ data). However, as the temperature is decreased below 90 K, the FC $\chi_{dc}(T)$ values sharply decrease and pass through zero value (go negative) at the compensation temperature ($T_{comp}$) $\sim 37$ K. At $\sim 25$ K, a negative maximum in the susceptibility occurs and eventually results in a second compensation temperature, $T_{comp2} \sim 14$ K. This ferrimagnetic behavior is similar to that shown for Tb$_{0.67}$Ca$_{0.33}$MnO$_3$ in Chapter 5 and is also observed in other rare-earth manganites or chromites when the FM component of the moments at the $B$-site imposes an internal magnetic field that rotates the paramagnetic rare-earth moments antiparallel to the net $B$-site moment.$^{127,164,165}$ The application of a 1000 Oe magnetic field results in positive FC susceptibility values down to low temperatures, demonstrating that the internal field seen at the A-site is comparable to that in similar systems.$^{166}$ In addition, the appearance of an upturn in the magnetization values at low
temperatures in GdCrO$_3$/TmCrO$_3$ has been shown to correspond to a spin reorientation transition$^{164,165}$ In these rare-earth chromites, the rare-earth and net Cr$^{3+}$ moments are also aligned antiparallel before the Cr moments rotate in the $a$-$c$ plane as the magnetic structure changes from $\Gamma_4$ ($G_xF_z$) to $\Gamma_2$ ($G_zF_x$). The continuous rotation of the moments could result in a point with zero net magnetization at $T_{\text{comp}}$. Similar behavior has also been observed in the rare-earth orthoferrites (RFeO$_3$), where it was proposed that the energetic preference of the Fe$^{3+}$ spins is the $\Gamma_4$ configuration, whereas the energetic preference of the magnetic rare-earth ions is for the $\Gamma_2$ state and this second term dominates at low temperatures, resulting in the spin reorientation.$^{167}$ Therefore, it is expected that in the present TMCO-70 sample, the Mn$^{3+}$/Cr$^{3+}$ moments undergo a similar spin reorientation from parallel to the $a$-axis at high temperatures to parallel to the $c$-axis below ~25 K.

6.5. Neutron Diffraction of TbMn$_{0.5}$Cr$_{0.5}$O$_3$

To further examine the magnetic properties of the present TMCO-50 sample, neutron powder diffraction data was taken at temperatures between 100 K and 3.4 K. Rietveld refinement of the diffraction data at 100 K (above the magnetic ordering temperature) confirms that TbMn$_{0.5}$Cr$_{0.5}$O$_3$ is an orthorhombically distorted perovskite with space group $Pbnm$. Two peaks develop at $Q = 1.40$ Å$^{-1}$ and 1.45 Å$^{-1}$ in diffraction patterns taken below 70 K as shown in Figure 6.10a, indicating the onset of long range AFM ordering. An increase in intensity is also observed for the (110), (121), and (211) reflections at 3.4 K as compared to 100 K data, which suggests a FM component to the magnetic structure. The AFM peaks can be indexed to a magnetic propagation vector $k_M = (0, 0, 0)$. The Rietveld refinement of the diffraction pattern measured at 3.4 K (Figure 6.10b) reveals that a G-type AFM alignment of both Mn$^{3+}$ and Cr$^{3+}$ moments with
spins oriented along the $a$-axis best fits the data, with a goodness of fit $\chi^2 \sim 4.89$. In modeling the low temperature magnetic phase, the Mn$^{3+}$ and Cr$^{3+}$ moments were not reliable if they were refined independently. The magnetic moment is therefore assumed to be equal at each B-site, and this value was found to saturate to $0.77 \mu_B \pm 0.05$ per Mn$^{3+}$/Cr$^{3+}$ ion at 3.4 K.

Figure 6.10. The (a) neutron diffraction data at low-Q at temperatures between 3.4 K and 100 K, with magnetic reflections marked with subscript M, and (b) Rietveld refinement of the diffraction pattern at 3.4 K. The magnetic phase is best fit with a collinear G-type AFM ordering of the Mn and Cr spins along the $a$-axis.

The temperature dependence of the intensity at $Q = 1.4$ Å$^{-1}$ that corresponds to the (011)$_M$ reflection of the magnetic structure (Figure 6.11) reveals an onset of the long-range AFM ordering at $T_N \sim 84$ K. This agrees with $T_N$ as determined from both the DC and AC susceptibility data. The precision of this refinement in the moment along the $b$-axis and $c$-axis (determined as the value before a significant change in $\chi^2$) was $\sim 0.01 \mu_B$, indicating that the spins lie almost completely along the $a$-axis and therefore any canting due to the FM component cannot be accurately determined. The relative intensity of (011)$_M$ and (101)$_M$ is similar for all temperatures below $T_N$, indicating the magnetic structure does not vary except for the saturation of the static ordered moment at the B-site.
In Figure 6.10a, an increase in intensity at low Q is also observed \( \sim 1.15 \text{ Å}^{-1} \) in the diffraction patterns below 40 K. This broad peak indicates the presence of short-range ordering that closely related to the (010)\textsubscript{M} and (100)\textsubscript{M} reflections of the magnetic structure. This broad peak can be modeled by the introduction of a FM correlation along the \( c \)-axis. This suggests that the G-type AFM order is canted towards the \( c \)-axis at low temperatures. The in-plane correlation length can be calculated from the full width at half maximum of the peak, and is \( \sim 11.3 \text{ Å} \) for the short range FM correlation in the present TMCO-50 sample. The temperature dependence of the intensity at \( Q_{SR} = 1.15 \text{ Å}^{-1} \), shown in Figure 6.12, reveals the onset of this short-range magnetic order at \( T_{SR} \sim 40 \text{ K} \). This may correspond with the second peak observed in the \( d\chi/dT \) data, which would suggest that this anomaly develops as a result of a short range FM component.

**Figure 6.11.** Temperature dependence of the intensity of the (011)\textsubscript{M} magnetic reflection normalized to the saturated moment at 3.4 K of 0.77 \( \mu_B \pm 0.05 \) per Mn/Cr.
In order to examine the most stable spin ordering in TMCO, energy optimization was performed by Dr. Vinit Sharma and Dr. Ramprasad at the University of Connecticut as described in Chapter 4. Calculations were performed for ionic configurations (that are consistent with symmetry analysis) with non-magnetic, FM, A-type AFM, and G-type AFM configurations with spins oriented along the $a$ as well as $c$-axis imposed on the Mn and Cr ions. The results of the energy minimization calculations are consistent with the magnetic structure revealed by the neutron diffraction measurements. For this collinear G-type AFM spin structure imposed along the $a$-axis, the favored ionic order is such that Mn$^{3+}$ and Cr$^{3+}$ ions form alternating planes along the $c$-axis resulting in an ordered double-perovskite-like structure for the present TbMn$_{0.5}$Cr$_{0.5}$O$_3$ sample.

In single crystals of TbMnO$_3$, neutron diffraction has revealed a magnetic configuration described with an incommensurate wave vector $k_M = (0, q, 0)$, where $q \sim 0.28$ below the ferroelectric transition temperature, $T_{lock}$. As mentioned previously, the magnetic structure of TbCrO$_3$ is described by a canted collinear G-type AFM with the moments along the $c$-axis.

Figure 6.12. The temperature dependent intensity of the short-range ordering peak centered at $Q = 1.15 \, \text{Å}^{-1}$. 

![Temperature vs. Intensity Graph](image-url)
These structures are not consistent with the neutron diffraction patterns of TMCO-50. Thus, phase coexistence between Mn-rich and Cr-rich regions is not expected in the present TMCO-50 sample and the G-type AFM order along the \(a\)-axis should describe both \(\text{Mn}^{3+}\) and \(\text{Cr}^{3+}\) moments. This magnetic structure (unlike either parent compound) suggests a modulation of the superexchange interactions either through the changes in the lattice or through the introduction of Mn-Cr interactions. These results suggest that the present TMCO-50 sample may also exhibit unique multiferroic properties as well.

### 6.6. Proposed Magnetic Phase Diagram

*Figure 6.13.* The proposed multiferroic phase diagram for the solid solution \(\text{TbMn}_{1-x}\text{Cr}_x\text{O}_3\). Paramagnetic (PM) and antiferromagnetic (AFM) are noted. Dotted lines indicate approximately where the transitions between AFM configurations are expected to occur. Transition temperatures for \(\text{TbMnO}_3\) are taken from [3]. The value of \(T_N\) for \(x = 0.1\) (open symbol) is assumed from the trend.
A magnetic phase diagram of the TbMn$_{1-x}$Cr$_x$O$_3$ solid solution is proposed based on these results as shown in Figure 6.13. With low Cr content, the magnetic and therefore the expected ferroelectric behavior is similar to pure TbMnO$_3$, but with a FM component that may be due to a local canting induced by Mn-Cr interactions. In TbMn$_{0.5}$Cr$_{0.5}$O$_3$, neutron diffraction revealed a canted G-type AFM with moments parallel to the $a$-axis with a canted component along the $c$-axis developing at low temperatures. In TbMn$_{0.3}$Cr$_{0.7}$O$_3$, the magnetic structure is assumed to also be a canted G-type AFM, but with a spin reorientation $(G_yF_x) \rightarrow (G_zF_x)$ occurring ~25 K. This composition is therefore expected to lie near the phase boundary between the G-type ordering with the spins along the $a$-axis (like in TMCO-50) and along the $c$-axis (similar to TbCrO$_3$), with the competition between the two magnetic structures driving the spin reorientation. Both the TMCO-50 and TMCO-70 samples are also expected to be multiferroic, with a ferroelectric polarization developing through a similar mechanism as in pure TbCrO$_3$. This phase diagram demonstrates that both Néel temperature and the spin configuration in TbMn$_{1-x}$Cr$_x$O$_3$ can be tuned by adjusting the Mn$^{3+}$/Cr$^{3+}$ ratio.

6.6. Conclusions

Phase pure orthorhombic TbMn$_{1-x}$Cr$_x$O$_3$ ($0 \leq x \leq 1$) bulk samples were prepared via solution route. The lattice parameters and Raman modes shift due to the introduction of non-Jahn-Teller Cr$^{3+}$ ion. For low Cr content, anomalies most likely corresponding to $T_N$ and $T_{lock}$ were observed, suggesting that the magnetic ordering in the material is similar to pure TMO but with a FM component. This FM signal may be due to a local canting induced by the Mn-Cr interactions. For higher Cr content, a collinear G-type antiferromagnetic (AFM) order was revealed by neutron diffraction and bulk magnetic measurements. The AFM-aligned spins were
found to align parallel to the $a$-axis for lower Cr content and parallel to the $c$-axis in pure TbCrO$_3$. This resulted in a spin reorientation transition at low temperatures for TbMn$_{0.3}$Cr$_{0.7}$O$_3$ sample.
Chapter 7

La$_{0.67}$Sr$_{0.33}$MnO$_3$-insulator Nanocomposite Films with Low-field Magnetoresistance

7.1. Introduction

The low-field magnetoresistance (LFMR) in polycrystalline La$_{0.67}$Sr$_{0.33}$MnO$_3$ (LSMO) or LSMO:insulator nanocomposites, as discussed in Chapter 1, has potential for several applications including in bolometric detectors, magnetic read heads, and magnetic field sensors or position sensors.$^{17,170,171}$ Although several studies in literature have focused on the MR properties of bulk ceramic composites, there are currently limited investigations on the MR response of manganite:insulator composite films that would be necessary for device integration. As can be seen from the results presented in Table 1.2, addition of an insulating secondary phase such as ZnO, CeO$_2$, Mn$_3$O$_4$, SrTiO$_3$, or MgO have both been shown to enhance the MR response of composites.$^{70–72,74,76,172}$ In addition, most studies focused on PLD grown films with insulating phase (or manganite phase) as columnar microstructure that was shown to improve LFMR as compared to pure manganite phase. The columnar structure cannot be maintained above a critical thickness and composite films cannot be deposited in large area by this technique. Thus, new studies on solution synthesis of columnar composites are necessary that would allow for this morphology to be maintained in thicker films over large areas, as well as examining different composite microstructures. Further, to realize sensors based on this phenomenon, both large LFMR values and a facile and low-cost fabrication technique are necessary. The results of two separate studies will therefore be discussed to address these challenges.
In this chapter, section 7.2 will focus on a LSMO:ZnO nanocomposite fabricated by solution deposition of LSMO onto ZnO nanorod array synthesized by a hydrothermal route, and section 7.3 will concentrate on solution-grown LSMO + Mg(O) composite films grown by mixed solution method that yields a 0-3 type particulate composite structure.

7.2. LSMO:ZnO Nanocomposite Films on (0001) Al₂O₃ Substrate

7.2.1. Sample preparation

First, a ZnO nanorod array was grown on (0001) Al₂O₃ substrate (1 cm x 1 cm) utilizing hydrothermal synthesis method by Dr. Haiyong Gao and Dr. Pu-Xian Gao at the University of Connecticut. For this, an aqueous solution of zinc acetate and hexamethylenetetramine was spin-coated onto the substrate and annealed at 600°C to form a ZnO seed layer. The substrate with the seed layer was then immersed in solution in a sealed container, in a water bath set to 90°C. After a growth time of 15 minutes, the samples were taken out, rinsed with DI water several times and dried overnight. To avoid the pH of the LSMO solution affecting the nanorods, high-purity precursors were mixed in La(0.67)Sr(0.33)Mn(1) molar ratio in water and ethylene glycol. To prepare pure LSMO and LSMO:ZnO composite films, the solution was spin-coated onto: (i) a (0001) Al₂O₃ substrate and (ii) ZnO nanorod array coated (0001) Al₂O₃ substrate several times until desired thickness was achieved. After each coating, the films were pyrolyzed at 600°C for 5 minutes in oxygen atmosphere and after the final coating, the two films were annealed at 850°C in oxygen for 2 hours.
7.2.2. XRD of films

The $\theta$-2$\theta$ patterns of the LSMO film reveals the presence of (110), (202)/(006), (111), (024) and (211) diffraction peaks of LSMO phase as shown in Figure 7.1a. The stronger relative intensity of the (110) peak suggests that the LSMO phase is preferentially oriented along (110) direction. This may be due to a relatively large mismatch with the hexagonal substrate.

![XRD scans of LSMO and LSMO:ZnO thin films](image)

Figure 7.1. The XRD $\theta$-2$\theta$ scans of (a) LSMO and (b) LSMO:ZnO thin films on (0001) Al$_2$O$_3$.

The peaks of LSMO phase (as mentioned above) are also observed in the LSMO:ZnO film as plotted in Figure 7.1b. In addition, the presence of only the (0002) and (0004) reflections of ZnO confirms that the nanorods are highly $c$-axis oriented. Pseudo-cubic lattice parameters can be calculated for LSMO assuming $a \approx b = \sqrt{2}a_{\text{cubic}}$. In the pure LSMO and LSMO:ZnO nanocomposite films, these values are 3.857 Å and 3.871 Å, respectively. These values are similar to the bulk lattice parameter of LSMO (3.873 Å$^{173}$) indicating that the films are relaxed (i.e. without strain). An increase in the lattice parameter has previously been observed in similar mixed-valence manganites with an introduction of oxygen vacancies, which are known to
strongly affect the properties of the material. Therefore, lower values of the lattice parameter in the present films may indicate the absence of oxygen vacancies in the present sample. The out-of-plane lattice parameter of ZnO is calculated to be 5.194 Å, which is close to the previously reported value of 5.207 Å. The average crystallite size (size of the polycrystalline LSMO grains) can be calculated by Scherrer’s equation,

\[ D = \frac{0.9\lambda}{\beta \cos\theta} \]  

(7.1)

where \( \lambda \) is the wavelength of the x-ray source (1.54 Å for Cu K\( \alpha \)), \( \beta \) is the full width at half maximum of the XRD peaks, and \( \theta \) is the Bragg angle. The average values of \( D \) were found to be 29.3 nm and 20.5 nm for the LSMO and LSMO:ZnO films, respectively.

7.2.3. Scanning electron microscopy

Figure 7.2. (a) Cross-sectional scanning electron microscopy (SEM) images of ZnO nanorod array, (b) top-view of partially-coated nanorods, and (c) cross-sectional SEM image of the LSMO:ZnO composite film on Al\(_2\)O\(_3\).

The cross-sectional SEM images of the ZnO nanorod array in Figure 7.2a show that the nanorods are \(~400\) nm in length. The ZnO nanorods have a diameter of 60 – 80 nm with an average spacing of 30 – 50 nm. A top-view image of the nanorods after several LSMO coatings (partially coated) on a ZnO nanorod coated (0001) Al\(_2\)O\(_3\) substrate is shown in Figure 7.2b. The LSMO solution coats the nanorods but some material is also filling the space between them. The appropriate number of coatings to completely coat ZnO nanorods was determined and the cross-
sectional image presented in Figure 7.2c confirms that the volume between the nanorods is completely filled and no pores are left. The LSMO phase is expected to fill about 1/3 the total film volume in the composite film. The small spacing between ZnO rods is believed to be a limiting factor in defining the grain size of LSMO in the present nanocomposite film that may explain the difference in grain size as found by Scherrer’s equation. It should also be noted that a small amount of Zn substitution at the Mn site has previously been observed at the interfaces in LSMO:ZnO ceramic composites,175,176 and therefore a modification of the composition at the interfaces may also modify grain boundaries in the present nanocomposite film as compared to pure LSMO film.

7.2.4. Magnetic characterizations

![Figure 7.3](image)

**Figure 7.3.** (a) The temperature dependent ZFC and FC DC magnetization data, and (b) the temperature coefficient of magnetization versus temperature data for LSMO and LSMO:ZnO films.

The temperature dependent ZFC and FC DC magnetization (M) values (measured with 100 Oe applied magnetic field) for both pure LSMO and LSMO:ZnO composite films are shown in Figure 7.3a. The magnetization values of the composite film are smaller than for pure composite film. This may simply result from the fractional percentage of LSMO in the sample
volume. The ferromagnetic Curie temperature \((T_C)\) is decreased in the composite film as compared to pure LSMO. To further examine this, the temperature coefficient of magnetization (TCM) for the FC data, defined as:

\[
TCM = \frac{1}{M} \frac{dM}{dT}
\]

is plotted in Figure 7.3b. In FM materials, a peak in TCM versus temperature plot is observed at \(T_C\).\(^{177,178}\) The sharpness of the peak observed in pure LSMO \(\sim 360\) K is expected for a first-order FM transition. The value of \(T_C\) in the present LSMO film is similar to that reported in single crystals with same composition.\(^{58}\) A broader peak centered \(\sim 315\) K is observed for the LSMO:ZnO composite film, which is consistent with the decrease in \(T_C\) and a smoother (second order) transition as observed in both the ZFC and FC data. Similar lowering of \(T_C\) values and broadening of TCM is reported for other manganite:insulator composites.\(^{177}\)

![Figure 7.4](image-url)

**Figure 7.4.** The DC magnetization data normalized to the saturation magnetization at 10 K (a) at different temperatures and (b) with field applied parallel and perpendicular to the plane of the film at 10 K for LSMO:ZnO composite film.

The field-dependent DC magnetization data (M vs. H) at several temperatures for the LSMO:ZnO composite film, normalized to the value of saturation magnetization at 10 K, is
presented in Figure 7.4a with corrections for the diamagnetic background due to the substrate. Both samples show well-defined FM hysteresis loops with coercivity and remanence observed below $T_C$. The coercive field ($H_C$) in the LSMO:ZnO composite film is ~240 Oe at 10 K, which is slightly higher than $H_C$ ~235 Oe observed in the present pure LSMO film. Balcells et al. observed an increment in $H_C$ as the particle size was decreased. Thus, larger $H_C$ in the present LSMO:ZnO nanocomposite film as compared to that in pure LSMO film could be the result of smaller grain size. M vs. H loops with the field applied parallel and perpendicular to the plane of the film (as shown in Figure 7.4b) reveal the presence of an easy plane anisotropy, indicating demagnetizing effects similar to (001) oriented LSMO films.

The ferromagnetic coupling among Mn$^{3+}$/Mn$^{4+}$ ions in the grain boundary region is assumed to be weaker than in a particular grain due to the disorder inherent in this region. Consequently, as the composite film is expected to have a larger volume fraction of grain boundaries (GBs) in the overall film as compared to the pure LSMO film, the overall FM coupling could be weaker. The broadening of the TCM peak may also be due to the presence of compositional disorder in the GB region. Below $T_C$, the compositional disorder may result in the GBs still being paramagnetically ordered as compared to the FM ordering in the core of the grain that would result in a broader transition. In addition, the presence of a non-magnetic secondary phase is thought to further dilute double exchange near the GBs, which could also explain the reduction of $T_C$ in the composite film.

### 7.2.5. Resistivity versus temperature behavior

The temperature dependent resistivity $\rho(T)$ values of the LSMO and LSMO:ZnO nanocomposite film are shown in Figure 7.5. In epitaxial films and single crystals of LSMO, a
metal-insulator transition ($T_{M-I}$) occurs at a temperature close to $T_C$.\textsuperscript{5,58} However, $T_{M-I}$ (as determined by the peak in $\rho(T)$ data) is ~285 K and ~170 K for the pure LSMO and composite films, respectively, and is lower than $T_C$ in both cases.

![Temperature dependent resistivity and MR values](image)

**Figure 7.5.** The temperature dependent resistivity ($\rho$) for LSMO and LSMO:ZnO films, and the temperature dependent MR values with 0.5 T applied field for LSMO:ZnO film.

This is as expected, as both films exhibit preferential orientation and are not single-crystal-like and therefore exhibit grain-size effects. It should also be noted that in the LSMO:ZnO nanocomposite film, $T_{M-I}$ is shifted to lower temperatures as compared to $T_{M-I}$ of the pure LSMO film, and that the peak resistivity is much higher than in the pure LSMO film. Smaller grain size (and therefore a larger volume fraction of grain boundaries), increased disorder, as well as the addition of the insulating ZnO phase (that may increase the energy barrier for electrical transport) can explain higher resistivity as well as lower $T_{M-I}$ as compared to pure LSMO film.\textsuperscript{5,68,185}

The resistivity values for both samples are found to decrease with applied magnetic fields (hence MR was observed). As shown in Figure 7.5, the MR values at 0.5 T applied magnetic
field are negligible at temperatures higher than $T_{M-I}$, but at temperatures below $T_{M-I}$ a significant negative MR is observed that decreases as the temperature is lowered to 10 K. In polycrystalline La$_{1-x}$Ca$_x$MnO$_3$ or La$_{1-x}$Sr$_x$MnO$_3$ films, two distinct contributions to the temperature-dependent MR values were observed corresponding to the contribution from CMR near $T_C$ and due to spin-polarized scattering and tunneling at GBs at low temperatures. However, in the present composite film, absence of a peak near $T_C$ or $T_{M-I}$ indicates that the spin-dependent scattering is the dominant MR mechanism in the present nanocomposite film.

More details about the transport properties of these films can be determined by modeling the resistivity data above and below $T_{M-I}$. In the metallic regime, the zero-field resistivity data can be fitted with the equation:

$$\rho = \rho_0 + \rho_0 T^y$$

where $\rho_0$ is the temperature-independent contributions from scattering at domain walls, grain boundaries and defects, and $y = 2$ indicates primarily electron-electron scattering contributions to the temperature dependence whereas $y = 2.5$ indicates a combination of electron-electron, electron-phonon, and electron-magnon scattering. By looking at the $T^2$ and $T^{2.5}$ dependence of the low-temperature resistivity data of the pure LSMO film in Figure 7.6, the equation shows a better fit with $y = 2$ and the fitting parameters for both the films are given in Table 7.1. The value of $\rho_0$ is an order of magnitude larger in the LSMO:ZnO composite film, suggesting an enhanced scattering at the grain boundaries in this composite film as compared to pure LSMO.
The low temperature ρ(T) data of pure LSMO film on Al$_2$O$_3$ fit with the polynomial expansion ρ = ρ$_0$ + ρ$_2$T$^2$ for (a) y = 2 and (b) y = 2.5.

![Graph showing ρ(T) for different y values](image)

**Table 7.1.** The fitting parameters for the resistivity below $T_{M-I}$ ($\rho = \rho_0 + \rho_2T^2$) and above $T_{M-I}$ ($\rho = \rho_A\exp(E_A/k_BT)$) for LSMO and LSMO:ZnO films on Al$_2$O$_3$ substrate.

<table>
<thead>
<tr>
<th></th>
<th>$\rho_0$ (Ωm)</th>
<th>$\rho_2$ (Ωm)</th>
<th>$\rho_A$ (Ωm)</th>
<th>$E_A$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSMO on Al$_2$O$_3$</td>
<td>7.4x10$^{-4}$</td>
<td>2.3x10$^{-8}$</td>
<td>2.9x10$^{-8}$</td>
<td>0.142</td>
</tr>
<tr>
<td>LSMO:ZnO on Al$_2$O$_3$</td>
<td>6.7x10$^{-3}$</td>
<td>7.6x10$^{-7}$</td>
<td>1.4x10$^{-8}$</td>
<td>0.180</td>
</tr>
</tbody>
</table>

The ρ(T) data in the insulating regime (above $T_{M-I}$) for mixed-valence manganites in general is fitted with the adiabatic small polaron hopping model:

$$\rho = \rho_A \exp \left( \frac{E_A}{k_BT} \right)$$

(7.4)

where $\rho_A$ is a constant, $k_B$ is the Boltzmann constant, and $E_A$ is the activation energy for electron hopping, and the fitting parameters are presented in Table 7.1. From the fitting parameters, it is clear that the activation energy is larger in LSMO:ZnO than in pure LSMO film. Similar
increase in barrier height has been reported in other manganite:insulator composites, which corresponds to a disordered region at the grain boundaries. This confirms that the energy barrier for the spin-dependent conduction in the present LSMO:ZnO film is in fact increased by the addition of an insulating second phase in the GB region.

7.2.6. Resistivity versus magnetic field behavior

Figure 7.7. The field dependent MR values (a) at 10 K for LSMO and LSMO:ZnO with field applied perpendicular to the current and for LSMO:ZnO with field applied parallel to the current, and (b) for LSMO:ZnO with field applied parallel to the current at 10 K, 80 K, and 170 K.

The field-dependent resistivity values \{\rho(H)\} were measured at 10 K, 80 K, and 170 K with the magnetic field applied perpendicular and then parallel to the current (and the film). This data was used to calculate MR and the values at 10 K are show in Figure 7.7a. The MR values display hysteretic behavior (not shown here), with peak resistivity values observed at \(H_C\) for both LSMO and LSMO:ZnO films. This indicates that the field associated with the increase in MR is correlated with domain rotation, which is a characteristic of the spin-dependent tunneling and scattering (extrinsic MR effect). An increment in the MR values with increasing magnetic field is followed by a region where the MR varies almost linearly with field that has been shown to
indicate the presence of a magnetically disrupted layer at the grain boundaries.\textsuperscript{179} The out-of-plane MR of the LSMO:ZnO composite film shows larger MR values at all applied fields and a sharper increase at low fields (\(\leq 0.5\) T) as compared to the pure LSMO film. This is due to enhanced spin-polarized tunneling and scattering through modified grain boundaries and the introduction of an insulating ZnO phase. A clear difference is observed when the field is applied parallel to the current (along the easy axis). Similar anisotropic MR has previously been observed in LSMO:CeO\(_2\) composites and is thought to be due to reduced coupling between LSMO grains.\textsuperscript{193} Sharp LFMR is observed even up to 170 K when the field is applied parallel to the film as shown in Figure 7.7b. The maximum LFMR value is -23.9\% at 0.5 T applied field and 10 K for LSMO:ZnO film, with a maximum magnetic field sensitivity of 631 \%/T. It should be noted that this is considerably higher than previously reported La\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\):ZnO composites grown by PLD (values given in Table 1.2).\textsuperscript{70,71} Thus, the LSMO:ZnO composite film synthesized by solution routes shows promise for applications in magnetic field sensors due to a significant change in MR with a small change in the applied magnetic field.

7.3. LSMO + Mg(O) Nanocomposite Films on (001) LaAlO\(_3\) Substrates by Mixed Solution Method

7.3.1. Sample preparation

High purity precursors were mixed in stoichiometric ratio La(0.67)Sr(0.33)Mn(1) in solvent. A separate solution of Mg ethoxide was prepared and the two solutions were mixed in various ratios as listed in Table 7.2. The La(0.67)Sr(0.33)Mn(1) and La(0.67)Sr(0.33)Mn(1)Mg(x) solutions were spin-coated onto (001) LaAlO\(_3\) (LAO) substrates.
After each coating, the films were pyrolyzed at 600°C for 5 minutes and after the final coating, the films were annealed at 850°C for 2 hours in oxygen.

<table>
<thead>
<tr>
<th>La(0.67)Sr(0.33)Mn(1):Mg</th>
<th>Sample Name</th>
<th>(c_{\text{LSMO}}) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0</td>
<td>LSMO</td>
<td>3.867</td>
</tr>
<tr>
<td>1:0.005</td>
<td>LM0.5</td>
<td>3.864</td>
</tr>
<tr>
<td>1:0.04</td>
<td>LM4</td>
<td>3.864</td>
</tr>
<tr>
<td>1:0.065</td>
<td>LM6.5</td>
<td>3.866</td>
</tr>
<tr>
<td>1:0.09</td>
<td>LM9</td>
<td>3.863</td>
</tr>
<tr>
<td>1:0.14</td>
<td>LM14</td>
<td>3.861</td>
</tr>
<tr>
<td>1:0.16</td>
<td>LM16</td>
<td>3.861</td>
</tr>
</tbody>
</table>

Table 7.2. The LSM:Mg molar ratios, corresponding sample names and the out-of-plane pseudo-cubic lattice parameter of LSMO \(c_{\text{LSMO}}\) for the LSMO + Mg(O) films on LaAlO\(_3\).

7.3.2. XRD of films

The XRD \(\theta\)-2\(\theta\) scan of the pure LSMO film on LAO is shown in Figure 7.8a. High intensity (00\(l\)) peaks as well as a lower intensity (110) peak of LSMO were observed indicating that LSMO phase is preferentially c-axis oriented. Similar peaks for the LSMO phase were observed in all the present composite films as shown in Figure 7.8b – d. The pseudo-cubic lattice parameters of LSMO phase \(c_{\text{LSMO}}\) were calculated from the (00\(l\)) peaks and are given for all films in Table 7.2. The value of \(c_{\text{LSMO}}\) in the pure LSMO film is slightly lower than the bulk value, indicating that the film is relaxed and there are no significant oxygen vacancies present.\(^{98,173}\) With the addition of Mg, the lattice parameter decrease slightly up to the higher concentrations (LM14 and LM16 films).
No peaks due to MgO phase were observed in films with lower Mg concentrations, i.e. up to LM9. However, the (002) peak of MgO was observed in the XRD scans of the LM14 and LM16 composite films (shown with the fitted peak in 7.8c and d) and the intensity of this peak increased with Mg addition. The lattice parameter of MgO phase was ~4.155 Å in both LM14 and LM16 films as compared to 4.2 Å for bulk MgO. A similar trend was observed for the lattice parameters of La$_{0.67}$Ca$_{0.33}$MnO$_3$:ZnO bulk composites and it was demonstrated that the ZnO phase formed near the manganite grain boundaries above the solubility limit of Zn$^{2+}$ in the lattice. Similar behavior has also been observed in La$_{0.8}$Sr$_{0.2}$MnO$_3$:CeO$_2$ composites. Limited solubility of Mg$^{2+}$ at both the A-site and B-site of LSMO lattice is anticipated based on Mg doping in related perovskite systems. It is therefore expected that doping of Mg into LSMO in the present case occurs up to the solubility limit (~0.9% Mg) and above this value, Mg separates to form MgO grains. The shift in $c_{\text{LSMO}}$ (as presented in Table 7.2) is likely due initially to effects of Mg doping on the LSMO lattice and for higher concentrations, the MgO grains may impose strain on the LSMO lattice that could also explain the decreased lattice parameter.
7.3.3. Transmission electron microscopy

Transmission electron microscopy (TEM) in collaboration with Dr. Claudia Cantoni at Oak Ridge National Laboratory was used to examine the microstructure of the films as well as to perform elemental mapping to investigate the distribution of Mg within the bulk of the LSMO film. It was observed that the LSMO grains at the film-substrate interface were epitaxial but some misoriented grains were observed away from the interface. This may be a result of the large thickness (~300 nm) and lattice mismatch (-2.2%) of the films,\textsuperscript{197,198} which can result in additional unfavorable nucleation events in addition to interfacial nucleation as discussed in section 2.1.2.

Elemental analysis of LM9 and LM16 films was performed by focusing the electron beam to form a probe with resolution of ~1 nm and scanning over a selected cross section with a step size of 3 nm. At each step, the EDX spectrum is acquired and analyzed to produce a map showing the distribution of elements in the region as shown in Figure 7.9. For the LM9 film in 7.9a, the La, Sr, and Mn signal is observed throughout the bulk, but the Mg signal is comparable to the noise.

![Figure 7.9](image_url)

**Figure 7.9.** The Z-contrast STEM images and elemental mapping of selected area using EDX for (a) LM9 and (b) LM16 composite films.
level, indicating that the Mg content is close to the experimental limit of a few atomic %. This result combined with the observation by XRD indicate that in LM9 film, Mg is doped at the La/Sr site into the LSMO lattice and no separate MgO grains are formed. However, in LM16 film (Figure 7.9b), regions with high Mg concentration are observed that most likely represent separate MgO grains that have formed in this sample, as detected by XRD as well. Similar behavior is expected in LM14 film. Thus, TEM and EDX confirm the segregation of a separate MgO phase in addition to small Mg doping for composite films with larger Mg concentration.

7.3.4. Magnetic characterizations

Figure 7.10. The temperature dependent ZFC (open symbols) and FC (closed symbols) magnetization data for LSMO and LSMO + Mg(O) films, normalized to the magnetization values at 10 K.

The temperature dependent ZFC and FC magnetization data (measured with 100 Oe applied magnetic field) for all films are shown in Figure 7.10. The $T_C$ of the pure LSMO was 370 K that is consistent with previously reported values for single crystals and other thin films. However, it is clearly observed that $T_C$ is shifted to lower temperatures even with the lowest
amount of Mg addition (in LM0.5 film). This reduction of $T_C$ has also been reported for related composite films, and may be due to the proposed Mg doping at the La/Sr site of LSMO lattice.\textsuperscript{74,177} The substitution of Mg$^{2+}$ may not only affect the lattice (as observed in the decreased $c_{\text{LSMO}}$ values), but could also result in a modification of the Mn$^{3+}$/Mn$^{4+}$ ratio in the films that would affect the double-exchange interaction and thereby lower the $T_C$.\textsuperscript{58,199} However, this doping effect appears to saturate for higher Mg concentration ($x \geq 0.09$) as $T_C$ does not significantly change for LM9, LM14, and LM16 films. Above $x = 0.09$, the Mg solubility limit in LSMO may be reached leading to a separate MgO phase and biphasic composite films formed as indicated by XRD and TEM as well.

7.3.5. Resistivity versus temperature behavior

![Figure 7.11](image_url)

Figure 7.11. The temperature dependent resistivity ($\rho$) normalized to the resistivity value at corresponding $T_{M-I}$ and (b) MR values at 0.5 T applied magnetic field for LSMO and LSMO + Mg(O) films.

The $\rho(T)$ data for all LSMO and LSMO + Mg(O) films, normalized to the peak resistivity at $T_{M-I}$, is shown in Figure 7.11a. $T_{M-I}$ for the pure LSMO is ~365 K, which is similar to $T_C$ and thus confirms intrinsic behavior of LSMO phase in this film. The values of $\rho$ at $T_{M-I}$ were
$2.76 \times 10^{-4} \, \Omega \text{cm}, 0.0025 \, \Omega \text{cm}, 0.047 \, \Omega \text{cm}, 0.117 \, \Omega \text{cm}, 0.488 \, \Omega \text{cm}, 2.21 \, \Omega \text{cm},$ and $6.52 \, \Omega \text{cm}$ for LSMO, LM0.5, LM4, LM6.5, LM9, LM14, and LM16 films, respectively. The value of $T_{MI}$ decreases and $\rho$ increases with small addition of Mg, i.e. in LM0.5 film, and these parameters systematically change with increasing Mg addition. Similar behavior has been observed previously in $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3:\text{Al}_2\text{O}_3$, $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3:\text{CeO}_2$, and $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3:\text{ZrO}_2$ (ref. 177) bulk composites and could be due to increased scattering at the LSMO grain boundaries as a result of the disorder due initially to Mg$^{2+}$ doping in the grain boundary region and, with further Mg addition, to the presence of insulating MgO phase in the grain boundary region. The $\rho(T)$ data of all samples was also fitted with equation 7.4 and 7.3 above and below $T_{MI}$, respectively, and the fitting parameters are given in Table 7.3.

\[
\rho = \rho_A T \exp\left(\frac{E_A}{k_B T}\right)
\]

<table>
<thead>
<tr>
<th></th>
<th>$\rho_A$ ((\Omega\text{cm}))</th>
<th>$E_A$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSMO</td>
<td>$2.28 \times 10^{-8}$</td>
<td>0.090</td>
</tr>
<tr>
<td>LM9</td>
<td>$7.38 \times 10^{-7}$</td>
<td>0.110</td>
</tr>
<tr>
<td>LM14</td>
<td>$8.37 \times 10^{-7}$</td>
<td>0.116</td>
</tr>
<tr>
<td>LM16</td>
<td>$3.52 \times 10^{-6}$</td>
<td>0.116</td>
</tr>
</tbody>
</table>

**Table 7.3.** Fitting parameters of the adiabatic small-polaron hopping model (equation 7.4) for LSMO, LM9, LM14, and LM16 films.

For the LSMO +Mg(O) films, a similar trend with an increase in the activation energy $E_A$ derived from the fit of small polaron hopping model (equation 7.4) was found to increase with the addition of Mg. In the metallic region, equation 7.3 fit the data well for $y = 2.5$ indicating the enhanced contribution of electron-phonon and electron-magnon scattering in the present films.
grown on LAO possibly due to more single-crystal-like nature of the film (as observed by the epitaxial relationship at the film-substrate interface and $T_C \sim T_{M-I}$ in pure LSMO film).

The $\rho(T)$ data was also measured at 0.5 T and this was used to calculate the temperature dependent MR values as shown in Figure 7.11b. As expected, the MR behavior in the pure LSMO film is consistent with CMR behavior, i.e. with a peak near $T_C$ and decreasing MR values as the temperature is lowered below $T_C$. The MR behavior in the pure LSMO film is therefore confirmed to be completely intrinsic. Similar MR behavior is also observed for the present composite films with low Mg addition ($x \leq 0.065$), although small non-zero values of MR appear at low temperatures indicating a small extrinsic MR contribution in addition to mostly intrinsic behavior. However, for nanocomposite films with LSMO:Mg molar ratios of 1:0.09 and higher, the MR behavior does not show any peak near $T_C$ but instead increases dramatically as the temperature is decreased below $T_C$ that is consistent with purely extrinsic MR behavior in the LM9, LM14, and LM16 films. Significant values of MR in LM16 film are also observed at low temperatures with large applied fields, with MR values of over -80% below 100 K with 3 T applied field.

To compare the magnetic and transport properties of these films, the values of $T_C$, $T_{M-I}$, and the temperatures of the peak MR values ($T_{peak,MR}$) are plotted together for LSMO and LSMO + Mg(O) nanocomposite films in Figure 7.12. From this plot, it is clear that the pure LSMO film exhibits purely intrinsic behavior. For nanocomposite films with $x \leq 0.065$, $T_C \sim T_{M-I}$ but the peak values of MR are slightly below $T_C$ indicating both intrinsic and extrinsic MR behavior. For films with $x \geq 0.09$, a significant difference between $T_C$ and $T_{M-I}$ values as well as large values of MR below $T_{peak,MR}$ is consistent with purely extrinsic behavior in the present LM9, LM14, and LM16 films.
7.3.6. Resistivity versus magnetic field behavior

The field dependent MR values \{MR(H)\} were calculated from the \(\rho(H)\) data at 10 K and are shown in Figure 7.13a. At 10 K, low MR values even at high fields are observed for the pure LMSO film, which is consistent with the intrinsic behavior as previously discussed. Similar MR(H) data was obtained for the LM0.5, LM4, and LM6.5 films at 10 K and this data is therefore omitted from the plot. However, the films with higher Mg addition show significantly enhanced MR values at all applied fields as compared to pure LSMO, with a sharp increase in MR at low fields and linear increase at higher applied fields. The linear behavior at high fields may indicate that the addition of Mg results in a modification of the double exchange in these nanocomposite films and therefore gives rise to a magnetically disrupted grain boundary region.\(^{179}\)
To further investigate the LFMR effect, the MR(H) data at 10 K for LM9 is plotted with the field-dependent magnetization in Figure 7.13b. Hysteretic behavior in MR values (measured with increasing and decreasing applied fields) reveals two peaks at a magnetic field equal to the coercive field \( (H_C) \). Similar to the effects observed in polycrystalline LSMO and LSMO:ZnO films (section 7.2), the large LFMR effect in these LSMO + Mg(O) films with larger LSMO:Mg ratios is due to the alignment of LSMO grains that allows for enhanced spin-dependent tunneling at the grain boundaries that is a characteristic of an extrinsic MR.

For all the present films, the MR values at 10 K and 100 K with several applied fields are given in Table 7.4. At both temperatures, a significant enhancement in MR values is observed in the biphasic composite films with a maximum LFMR of -35.5% at 0.5 T and 10 K for LM16 film as compared to -3.5% for the pure LSMO film measured in the same conditions. It should be noted that this is one of the highest values of LFMR reported for manganite:insulator
composite films to date as compared to -25% at 0.5 T and 4.2 K and -32% at 0.5 T and 10 K for LSMO:MgO films\textsuperscript{74,75} or -15% at 0.3 T and 86 K for LSMO:Al\textsubscript{2}O\textsubscript{3} film\textsuperscript{73} and -15% at 0.5 T and 20 K for LSMO:CeO\textsubscript{2} film\textsuperscript{72}.

These enhanced values of MR in both low and high applied fields in the LSMO + Mg(O) composite films could result from the introduction of disorder in the grain boundary region due to the modification of GBs with doping and the presence of MgO phase due to increased spin-dependent tunneling and scattering at the interfaces.\textsuperscript{68,186} As such, these films display potential for tailoring the magnetic and electric properties of manganites by controlling interactions at the interfaces.

<table>
<thead>
<tr>
<th></th>
<th>MR (%) at 10 K and:</th>
<th>MR (%) at 100 K and:</th>
<th>Magnetic field sensitivity at 10 K (%/T)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1 T, 0.5 T, 1 T, 3 T</td>
<td>0.1 T, 0.5 T, 1 T, 3 T</td>
<td></td>
</tr>
<tr>
<td>LSMO on Al\textsubscript{2}O\textsubscript{3}</td>
<td>-0.7, -8.4, -20.8, -29.1</td>
<td>-</td>
<td>42</td>
</tr>
<tr>
<td>LSMO:ZnO</td>
<td>-17.4, -23.9, -27.6, -38.0</td>
<td>-</td>
<td>631</td>
</tr>
<tr>
<td>LSMO on LaAlO\textsubscript{3}</td>
<td>-2.2, -3.5, -4.1, -5.46</td>
<td>-2.3, -3.2, -3.7, -5.39</td>
<td>53</td>
</tr>
<tr>
<td>LM0.5</td>
<td>-2.0, -3.3, -4.1, -5.56</td>
<td>-1.8, -2.5, -3.2, -5.16</td>
<td>53</td>
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<tr>
<td>LM4</td>
<td>-1.8, -2.9, -4.1, -6.3</td>
<td>-1.5, -2.6, -3.7, -7.5</td>
<td>40</td>
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<tr>
<td>LM6.5</td>
<td>-1.4, -2.4, -4.1, -8.2</td>
<td>-1.2, -3.9, -4.3, -12.0</td>
<td>58</td>
</tr>
<tr>
<td>LM9</td>
<td>-4.8, -9.9, -14.5, -25.2</td>
<td>-8.2, -20.7, -32.0, -56.2</td>
<td>74</td>
</tr>
<tr>
<td>LM14</td>
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<td>-11.8, -30.0, -45.8, -75.1</td>
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<tr>
<td>LM16</td>
<td>-20.5, -35.5, -45.3, -83.2</td>
<td>-11.1, -29.8, -46.1, -76.2</td>
<td>252</td>
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</table>

Table 7.4. MR values at 10 K and 100 K with several applied magnetic fields and the field sensitivity (dMR/dH) at 10 K for both the LSMO:ZnO and LSMO + Mg(O) nanocomposite films.
grain boundaries through varying the LSMO:Mg molar ratio, resulting in significant values of MR over a wide range of temperatures.

7.4. Conclusions

In conclusion, two sets of samples were synthesized by solution deposition routes: (i) La$_{0.67}$Sr$_{0.33}$MnO$_3$ (LSMO) and LSMO:ZnO films on (0001) Al$_2$O$_3$, and (ii) pure LSMO and LSMO + Mg(O) composite films on (001) LaAlO$_3$ substrates. X-ray diffraction data showed that the pure LSMO and LSMO:ZnO films were relaxed, with lattice parameters close to bulk LSMO. A decrease in grain size in LSMO:ZnO film as calculated by Scherrer’s equation was also observed in SEM images. The decrease in grain size as well as possible structural or chemical disorder at the LSMO/ZnO interfaces resulted in decreased $T_C$ and $T_{M-I}$. The modification of the electronic transport in the composite film resulted in enhanced values of MR at all applied magnetic fields. In LSMO + Mg(O) nanocomposite films, the change in lattice parameter of LSMO with Mg addition suggested Mg$^{2+}$ doping in the lattice (possibly at the grain boundaries) until the solubility limit, after which separate MgO phase was formed as observed in the bulk of the films by TEM and EDX. The magnetic and transport behavior was modified by Mg$^{2+}$ doping at the La/Sr site in LSMO phase resulting in a decrease in $T_C$ and $T_{M-I}$ values. The MR behavior was modulated in the biphasic composite films {LSMO:ZnO and LSMO + Mg(O)} with significant values of MR at low fields observed in a wide range of temperatures.
Chapter 8

Summary and Future Work

8.1. A-site and B-site Doped TbMnO₃

8.1.1. Summary

In Chapter 3, it was revealed that the magnetic properties of TbMnO₃ (TMO) are sensitive to the synthesis route. This allowed for the observation of anomalies at the Neel temperature \( T_N \) and the noncollinear spiral spin (NSS) ordering at \( T_{lock} \) never reported before in bulk samples.

In Chapter 4, the magnetic moment of the rare-earth substituted at the A-site was found to play a role in the magnetic and the ferroelectric properties of doped TMO. The 33% Ho-doped TMO sample showed anomalies in the DC and AC susceptibility data that suggested the presence of a weak ferromagnetic (FM) ordering. In addition, an anomaly due to a Ho-Mn exchange striction was observed in the ferroelectric polarization measurements.

In Chapter 5, long-range magnetic order was observed in \( \text{Tb}_{0.67}\text{Ca}_{0.33}\text{MnO}_3 \), \( \text{Tb}_{0.67}\text{Sr}_{0.33}\text{MnO}_3 \), and \( \text{Tb}_{0.75}\text{Sr}_{0.25}\text{MnO}_3 \) samples for the first time. In addition, a transition to a spin-glass-like state at lower temperatures is also observed in the AC susceptibility data.

In Chapter 6, the first report of \( \text{TbMn}_{1-x}\text{Cr}_x\text{O}_3 \) samples showed that the structural and magnetic properties could be tuned by adjusting the Mn/Cr ratio. For samples with low Cr\(^{3+}\) content, the introduction of weak ferromagnetic interactions resulted in magnetic properties similar to pure TbMnO₃ but with a net moment and large coercivity. For samples with higher Cr content, a G-type antiferromagnetic ordering of Mn\(^{3+}\)/Cr\(^{3+}\) moments was observed with direction of moments shifting from parallel to a-axis to parallel to c-axis with increasing Cr content.
8.1.2. Future Work

Neutron powder diffraction is currently planned for the Tb$_{0.67}$Ho$_{0.33}$MnO$_3$ sample as well to compare with the theoretical calculations. This should clarify if there is a coexistence between the NSS and E-type AFM ordering and/or if there is any FM component to the magnetic structure. A complete study of Tb$_{1-x}$Sr$_x$MnO$_3$ can be performed in the future. This will not only clarify if a similar ferrimagnetic order (with the anti-alignment of Tb$^{3+}$ moments to the net Mn$^{3+}$/Mn$^{4+}$ moment) is observed as revealed for Tb$_{0.67}$Ca$_{0.33}$MnO$_3$ sample but also identify the maximum Sr doping for which long-range ordering is favored before resulting in a spin-glass state. In the future, the magnetic structure of the samples with low Cr content should be examined by neutron diffraction with complimentary calculations performed to understand the effects of the Mn-Cr interactions on the spin configuration. In addition, as the entire solid solution is expected to be multiferroic, polarization measurements can be performed to examine how the ferroelectric properties are modified by the substitution of Cr$^{3+}$. Those results would most likely reveal that both the magnetic and ferroelectric properties can be tuned by adjusting the Mn/Cr ratio. Further, solid solutions of TbMnO$_3$ with TbNiO$_3$ or TbCoO$_3$ can be planned to examine the possibility of multiferroicity in these materials that has been previously observed in double perovskites.

8.2. LSMO:insulator Nanocomposite Films

8.2.1. Summary

In Chapter 7, the addition of a secondary phase in La$_{0.67}$Sr$_{0.33}$MnO$_3$ (LSMO):ZnO and LSMO + Mg(O) nanocomposite films, as well of doping of Mg$^{2+}$ at the La/Sr site in LSMO lattice in LSMO + Mg(O) films, were both found to significantly impact both the magnetic and
electric properties of the composites. In both studies, significant enhancements of the low-field magnetoresistance (LFMR) with applied magnetic fields $< 0.5$ T were observed for biphasic composite films as compared to pure LSMO. This is thought to be due to an increase in spin-dependent tunneling and scattering at the interfaces. The values of LFMR obtained in this dissertation work are some of the highest values currently reported for similar composite films.

8.2.2. Future Work

Looking forward, high resolution transmission electron microscopy studies similar to the one performed in the LSMO + Mg(0) series could be done for the LSMO:ZnO composite film to examine compositional or structural disorder due to doping of $\text{Zn}^{2+}$ at the interfaces that could also lead to the enhancement in MR values. Further, the grain size of LSMO phase in composite films could be modulated by varying the annealing temperature which may reveal the effects of increased grain boundary volume fraction (grain-size effects) versus effects structural or magnetic disorder induced at the grain boundary by the secondary phase. Lastly, different insulating materials that do not form solid solution with LSMO or whose elements do not get substituted in LSMO could be incorporated using the mixed solution route in order to study the effects on MR behavior of the composite films.
Chapter 9

References


21 V.M. Goldschmidt, Die Naturwissenschaften 14, 477 (1926).


88 *PPMS Hardware and Options Manual* (Quantum Design, n.d.).


Appendix A

Publications Resulting from Dissertation Work

1. **M. Staruch** and M. Jain, “Evidence of Antiferromagnetic and Ferromagnetic Superexchange Interactions in Bulk TbMn$_{1-x}$Cr$_x$O$_3$”, under review.

2. **M. Staruch**, V. Sharma, C. dela Cruz, R. Ramprasad, and M. Jain, “Magnetic Ordering in TbMn$_{0.5}$Cr$_{0.5}$O$_3$”, under review.

3. **M. Staruch**, L. Kuna, and M. Jain, “Magnetocaloric Effect in Bulk Tb$_{0.67}$R$_{0.33}$MnO$_3$ (R = Dy, Y, and Ho)”, under review.


