Investigations of the Structural, Electrical, and Magnetic Properties for Novel Magnetic Materials

DISSERTATION

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By

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ABSTRACT

In this entire work, we characterize the structural, electrical, and magnetic properties of many novel magnetic polycrystalline materials. Our focus is to investigate these properties to enhance the scientific community and possibly pave the road to explore into other directions, such as growing thin films.

In chapters 2-4, we characterize and study the structural properties from X-ray powder diffraction and neutron powder diffraction, the electrical transport from dc resistivity measurements, and the magnetic properties from the magnetic phase from neutron powder diffraction, magnetization and magnetic susceptibility measurements for AMn$_{0.5}$Ru$_{0.5}$O$_3$ (A = Ca, Ca$_{0.9}$La$_{0.1}$, Ca$_{0.5}$Ca$_{0.5}$, Ba, Ba$_{0.5}$Sr$_{0.5}$, and Ba$_{0.5}$La$_{0.5}$) perovskites. The reason why AMn$_{0.5}$Ru$_{0.5}$O$_3$ perovskites are of interest is because the magnetotransport properties. There is an energetic overlap between the Mn e$_g$ and Ru t$_{2g}$-$\pi^*$ orbitals. This gives rise to delocalized electrons, which favors metallic conductivity. The magnetotransport coupled with varying occupation of the Mn e$_g$ orbitals impacts the magnetism.
In chapter 2, we investigate the effect of charge carrier substitution with chemical disorder for \( \text{Ca}_{1-x}\text{La}_x\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \) \((x = 0.6, 0.5, 0.4, 0.3, 0.2, 0.1, \text{and} \ 0.0)\) double perovskites. X-ray diffraction measurements showed these polycrystalline powders to be phase pure and to exhibit \( Pnma \) symmetry with \( a\overline{b}^+a^- \) octahedral tilting. Neutron powder diffraction (NPD) showed that the crystal structure and magnetic moments do not change significantly across the substitution range. \( \text{Ca}_{0.5}\text{La}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \) exhibits ferrimagnetism with a magnetization of \( 1.26(1) \mu_B \) at 4 K. NPD further concluded the lack of cooperative Jahn Teller distortion. Density functional theory (DFT) calculations confirmed that the extra \( \frac{1}{2} \) electron is responsible for opening the band gap, in that \( 0.295e \) and \( 0.17e \) is being transferred to the Ru and Mn bands, respectively. Thus, the Fermi level is being tuned when \( \text{La}^{3+} \) is substituted into the system. DFT calculations also showed ferrimagnetism to be the most energetically stable magnetic phase. Overall we conclude that despite the chemical disorder, \( \text{Ca}_{0.5}\text{La}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \) is an insulating ferrimagnet with a Curie temperature (\( T_C \)) of 233 K, which is a rare finding to have chemical disorder with magnetic order.

The next chapter, we examine the effects of isovalent substitution in \( \text{Ba}_{1-x}\text{Sr}_x\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \) \((0.9 \geq x \geq 0)\) system. We explore how the larger cation, \( \text{Ba}^{2+} \), impacts the structural, electrical, and magnetic properties. We find that \( \text{BaMn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \) crystallizes in the the 9R polymorph with \( R-3m \) symmetry. \( \text{BaMn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \) is an insulating canted antiferromagnet with a \( T_N \) of 36 K. From neutron diffraction, \( \text{Mn}_1 \) and \( \text{Mn}_2 \) have magnetic moment values of \( 1.60(4) \mu_B/\text{f.u.} \) and \( 2.15(2) \mu_B/\text{f.u.} \), respectively. For simplicity, the Ru moments were not refined. While the refined moments are low for
Mn$^{3+/4+}$, it is assumed that Ru is contributing to the magnetic moments. $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ crystallizes with the 6H crystal structure which has $P6_3/mmc$ symmetry. From low temperature neutron diffraction, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ exhibits glassy behavior since it lacks long-range magnetic order. Resistivity measurements show this compound to be an insulator.

In the following chapter, we continue studying $\text{Ba}_{1-x}\text{A}_x\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ perovskites by substituting in charge carriers. We explore the effects of aliovalent substitution, $\text{La}^{3+}$, by investigating the structural, magnetic, and electrical properties for the phase diagram of $\text{Ba}_{1-x}\text{La}_x\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ ($0.5 \geq x \geq 0$) system. The end members were found to be phase pure solid solutions while the in-between compositions were heterogeneous mixtures. While $\text{BaMn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ exhibits the 9R as noted above, $\text{Ba}_{0.5}\text{La}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ manifests the 3C ($I4/mcm$ space group symmetry) crystal structure and is an insulating ferrimagnet with a $T_C$ of 205 K. From neutron diffraction, both the ferromagnetic and ferrimagnetic structures have similar refinement values. However, the moments obtained from a ferrimagnetic structure (Mn = 3.7 $\mu_B$/f.u. and Ru = -0.88(2) $\mu_B$/f.u.) are more reasonable than for a ferromagnetic structure (Mn = 1.707(7) $\mu_B$/f.u. and Ru = 1.707(7) $\mu_B$/f.u.). Plus the magnetization shows $\text{Ba}_{0.5}\text{La}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ to have 1.54 $\mu_B$/f.u., which is closer in value to the expected spin only ferrimagnetic moment for Mn$^{3+}$ + Ru$^{4+}$ oxidation states. Thus we conclude that $\text{Ba}_{0.5}\text{La}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ is a ferrimagnet based on the refined magnetic moments gathered from neutron diffraction and the magnetization results from SQUID.
Thin films of Sr$_2$CrReO$_6$ have been reported to be metallic (possibly half-metallic) with a high Curie temperature (635K), which makes this material a feasible candidate for spintronic applications. To understand the role of doping, investigations of the structural, electrical, and magnetic properties of on- and off-stoichiometric Sr$_{2+x}$CrReO$_6$ ($x = -0.07, 0.0, 0.05, 0.075,$ and $0.10$), Sr$_2$Cr$_{1+y}$Re$_{1-y}$O$_6$ ($y = -0.1, -0.05, 0.05,$ and $0.1$), and A-site substituted Sr$_{2-z}A_z$CrReO$_6$ ($A = K, Ca,$ and $La; z = 0.10$ and $0.20; z = 1.0$ only for Ca) samples have been achieved. Varying the Cr/Re ratio and aliovalent substitutions on the A-site lead to systematic variations in the magnetization and Curie temperatures. As the Re oxidation state increases, the saturation magnetization increases and the Curie temperature decreases.

In the last chapter, we investigate the structural, magnetic, and electrical properties of phase pure polycrystalline Sr$_2$CrOsO$_6$. From X-ray powder diffraction, Sr$_2$CrOsO$_6$ adopts the $R3$ symmetry and is $73.6(3)$ % ordered. Our magnetic results show Sr$_2$CrOsO$_6$ to be a ferrimagnet with a small net moment of $0.224 \mu_B$/f.u. and the coercivity to be $7.84$ T at $4.5$ K in a field strength of $35$ T, and the Curie temperature is $660$ K. Sr$_2$CrOsO$_6$ is strongly insulating with resistivity of $8.61 \times 10^2 \Omega\cdot$cm at $300$ K and shows activated electron transport.
DEDICATION

This document is dedicated to my loved ones:

Johnny Soliz, Cecilia Soliz, and David Mata.

I love all of you.

Dad, not a day goes by that I do not think about you. I miss you so much. I know you are watching over Mom and me. Te llevaré siempre en mi corazón.
I would like to take this opportunity to acknowledge those who have provided me with support, encouragement, and scientific guidance during the course of my time spent here at The Ohio State University. First of all, I would like to thank my research adviser, Professor Patrick Woodward, who has been a superb adviser and has provided assistance in the completion of this dissertation. Pat has always continued to lend support and guidance to me, whether it be scientifically related or not, and has encouraged me to attend several conferences. I am completely grateful to him for challenging me every step of the way and helping me develop. I have learned a great deal from him, i.e. from a scientific standpoint, from life, and a passion for beer. I will always view him as my “chemistry dad.” Pat has also shown me emotional support, especially during the difficult time from the passing of my father. Because of all this, I am forever indebted to him.

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4. Soliz, J. R.; Mishra, R.; Windl, W.; Woodward, P. M. “Tuning the Fermi Level From Charge Carrier Substitution and Maintaining Ferrimagnetism with Chemical Disorder in Ca$_{1-x}$La$_x$Mn$_{0.5}$Ru$_{0.5}$O$_3$ Perovskites.” *Physical Review B* **2012.** (manuscript in preparation)


**Fields of Study**

Major Field: Chemistry
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Perovskites have a wide span of properties, such as colossal magnetoresistance (CMR), ionic conductivity, superconductivity, piezoelectricity, ferroelectricity, ferromagnetism, and half-metallic transport. Having such properties is needed for technology-based applications, e.g. information data storage, catalysis, multi-ferroics, etc. Because of their vast array of properties and applications, perovskites are undoubtedly an interesting class of materials.

1.1 Ideal Perovskite crystal structure

To begin with, a brief introduction of the perovskite structure will be discussed. As shown in Figure 1, ternary perovskites have the aristotype $ABX_3$ structural formula, with $A$, $B$, and $X$ being the location where the $A$-site cations, $B$-site cations, and anions sit, respectively. The $A$-site cations are located in the body center of the perovskite and are generally low valent, large cations, which are typically rare-earths, alkaline earth, alkali, and other large cations, e.g. $\text{Bi}^{3+}$. The $B$-site cations are located on the corners of the unit cell and are usually high valent, smaller transition metals. The materials discussed in this entire work are oxides, so for all intensive purposes, the anions are oxygens. The oxygens sit on the cell edge. The $A$-site cations and $B$-site cations are 12-coordinate and
6-coordinate, respectively. Surrounding the $B$-site cations are octahedra that are corner-shared. The $B$-site cations and anions are $1/8$ shared and $1/4$ shared, respectively.

**Figure 1:** Aristotype simple cubic perovskites with $ABO_3$ structural formula.

When the unit cell edge is expanded by combining two different $A$-site cations, $B$-site cations, or both substitutions, the structural formula reads $A_2BB'O_6$ or $AA'B'B'O_6$,
which is also referred to as a double perovskite. By expanding the compositional space, this increases the functionality and flexibility in the properties.

1.2 Ordering

Not only do the substitutions on either or both the $A$-sites and $B$-sites change the properties but also the ordering is affected. Perovskites can order in different styles on the $A$-sites and $B$-sites, but the most common type is $B$-site ordering and disorder on the $A$-site. By coupling $B$ and $B'$ cations that are different enough in cation radii and valency, the octahedra can form a rock-salt type ordering; see Figure 2. Planes of $B$ or $B'$ run perpendicular to the [111]. For the premise of this work, other types of ordering such as layered ordering of $A$-site cations will not be discussed.
Figure 2: Rock-salt type ordering of the $B$ and $B'$ cations in a double perovskite.

1.3 Ordered Double Perovskites

$B$-site ordering is important for such materials as half-metals. The ordering affects the magnetic properties in half-metallic materials, i.e. ordering promotes a larger saturated moment ($M_{sat}$). To elaborate on an example, Sr$_2$CrReO$_6$ is predicted to be a fully ordered metallic ferrimagnet (FiM).$^2$ When Cr$^{3+}$ ($d^3$) is neighbors to Re$^{5+}$ ($d^2$
cation), the $M_{sat}$ is approximately 1 $\mu_B$. If a $\text{Cr}^{3+}$ is sitting next to another $\text{Cr}^{3+}$, then through super-exchange interactions the moments cancel each other. Listed in Table 1 are quite a few more interesting double perovskites.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cation Order</th>
<th>Cation Valences</th>
<th>Electrical Transport</th>
<th>Magnetic Behavior</th>
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<tr>
<td>$\text{Sr}_2\text{CrMO}_6$</td>
<td>Yes</td>
<td>3/5</td>
<td>Activated</td>
<td>Ferrimagnetic, $T_C=420$ K</td>
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<tr>
<td>$\text{Sr}_2\text{CrMoO}_6$</td>
<td>Yes</td>
<td>3/5</td>
<td>Metallic</td>
<td>Ferrimagnetic, $T_C=460$ K</td>
</tr>
<tr>
<td>$\text{Sr}_2\text{CrReO}_6$</td>
<td>Yes</td>
<td>3/5</td>
<td>Metallic</td>
<td>Ferrimagnetic, $T_C=620$ K</td>
</tr>
<tr>
<td>$\text{Sr}_2\text{CrRuO}_6$</td>
<td>No</td>
<td>3/5</td>
<td>Activated</td>
<td>Antiferromagnetic, $T_N=400$ K</td>
</tr>
<tr>
<td>$\text{Sr}_2\text{CrOsO}_6$</td>
<td>Yes</td>
<td>3/5</td>
<td>Activated</td>
<td>Ferrimagnetic, $T_C=725$ K</td>
</tr>
<tr>
<td>$\text{Sr}_2\text{MnMoO}_6$</td>
<td>Yes</td>
<td>2/6</td>
<td>Activated</td>
<td>Antiferromagnetic, $T_N=12$ K</td>
</tr>
<tr>
<td>$\text{Sr}_2\text{MnWO}_6$</td>
<td>Yes</td>
<td>2/6</td>
<td>Activated</td>
<td>Antiferromagnetic, $T_N=13$ K</td>
</tr>
<tr>
<td>$\text{Sr}_2\text{MnReO}_6$</td>
<td>Yes</td>
<td>2/6</td>
<td>Activated</td>
<td>Ferrimagnetic, $T_C=120$ K</td>
</tr>
<tr>
<td>$\text{Sr}_2\text{MnRuO}_6$</td>
<td>No</td>
<td>3/5</td>
<td>Activated</td>
<td>Antiferromagnetic, $T_N=200$ K</td>
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<tr>
<td>$\text{Sr}_2\text{FeMO}_6$</td>
<td>Yes</td>
<td>2.5/5.5</td>
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<td>Ferrimagnetic, $T_C=420$ K</td>
</tr>
<tr>
<td>$\text{Sr}_2\text{FeWO}_6$</td>
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<td>2/6</td>
<td>Activated</td>
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<tr>
<td>$\text{Sr}_2\text{FeReO}_6$</td>
<td>Yes</td>
<td>2.5/5.5</td>
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<td>Ferrimagnetic, $T_C=400$ K</td>
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<tr>
<td>$\text{Sr}_2\text{FeRuO}_6$</td>
<td>No</td>
<td>3/5</td>
<td>Activated</td>
<td>Spin Glass, $T_G=50$ K</td>
</tr>
</tbody>
</table>

Table 1: List of some interesting double perovskites that are Cr-, Mn-, and Fe-based.

These $\text{Sr}_2\text{B'B'O}_6$ compounds are Cr-based, Mn-based, and Fe-based. The cation order, valency, electron transport, and magnetic properties are reported for each compound. The compounds highlighted in blue and red have cation order, are metallic or show activated electron transport, are ferrimagnets, and have a $T_C$ above room temperature. These set of
properties are ideal for technological applications. In particular, half-metallic ferromagnets (FM) or FiM with a $T_C$ above room temperature are fundamental for spintronics.

Half-metals, such as $\text{Sr}_2\text{FeMoO}_6$, have the Fermi level ($E_{\text{Fermi}}$) cutting through one metal band. Figure 3 shows a simple band structure calculation for $\text{Sr}_2\text{FeMoO}_6$ as described from Sarma et al. The delocalization of the Mo d\(^1\) spin is responsible for the ferrimagnetism and spin polarization. As previously mentioned, other materials such as $\text{Sr}_2\text{CrReO}_6$ have been predicted to have metallic transport, but this material is not well explored experimentally, which is the basis for studying this compound.
1.4 Disordered Double Perovskites Containing Manganese and Ruthenium

If ordering does not exist, then the double perovskite is completely disordered. In addition, the symmetry is lowered. One system that is of particular interest because of magnetotransport properties is manganese ruthenates, AMn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3}.\textsuperscript{4,5} Having Ca\textsuperscript{2+} or Ba\textsuperscript{2+} sitting on the A-site, the space group symmetry is Pnma and R-3m, respectively. If
these compounds were ordered, the rock-salt type ordering would be $P2_1/n$ for CaMn$_{0.5}$Ru$_{0.5}$O$_3$ and $R-3$ for BaMn$_{0.5}$Ru$_{0.5}$O$_3$, which is calculated from SPuDS software.\textsuperscript{6}

To date, there is no AMn$_{0.5}$Ru$_{0.5}$O$_3$ system found to be experimentally ordered.

### 1.4.1 The Link Between the Tolerance Factor and Different $A$-Site Substitutions in $ABO_3$ ($B$ = Mn, Ru) Ternary Perovskites

Before we begin discussing AMn$_{0.5}$Ru$_{0.5}$O$_3$ double perovskites, let’s first step back and understand why the simple perovskites, AMnO$_3$ and ARuO$_3$, are an interesting class of materials.\textsuperscript{7-10} Table 2 lists the magnetic and electrical properties for AMnO$_3$ and ARuO$_3$ of interest for this work.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Tolerance Factor</th>
<th>Electrical Transport</th>
<th>Magnetic Behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>$AMnO_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BaMnO$_3$</td>
<td>1.1028</td>
<td>insulator</td>
<td>Antiferromagnetic, $T_N$=59 K</td>
</tr>
<tr>
<td>SrMnO$_3$</td>
<td>1.0405</td>
<td>Mott insulator</td>
<td>Antiferromagnetic, $T_N$=235 K</td>
</tr>
<tr>
<td>CaMnO$_3$</td>
<td>1.0039</td>
<td>insulator</td>
<td>Antiferromagnetic, $T_N$=120 K</td>
</tr>
<tr>
<td>LaMnO$_3$</td>
<td>0.9543</td>
<td>insulator</td>
<td>Antiferromagnetic, $T_N$=140 K</td>
</tr>
<tr>
<td>$ARuO_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BaRuO$_3$</td>
<td>1.0537</td>
<td>(9R) Mott insulator; (4H) metallic</td>
<td>(9R) Paramagnetic; (4H) Paramagnetic</td>
</tr>
<tr>
<td>SrRuO$_3$</td>
<td>0.9942</td>
<td>metallic</td>
<td>Ferromagnetic, $T_C$=165 K</td>
</tr>
<tr>
<td>CaRuO$_3$</td>
<td>0.9591</td>
<td>metallic</td>
<td>Paramagnetic</td>
</tr>
<tr>
<td>LaRuO$_3$</td>
<td>0.9383</td>
<td>metallic</td>
<td>Paramagnetic</td>
</tr>
</tbody>
</table>

Table 2: List of AMnO$_3$ and ARuO$_3$ that are of interest to this study.
AMnO₃ are an exciting class of materials mainly due to the possible appearance of CMR and the Jahn Teller (JT) distortion from Mn³⁺. LaMnO₃ is a classic example that exhibits a cooperative JT distortion. Due to the orientation of the half-filled d_z² orbital, LaMnO₃ manifests orbital ordering, which is responsible for the A-type antiferromagnetism (T_N = 140 K). By changing the A-site cation with another cation that is slightly smaller but with a different valency, CaMnO₃ (Ca²⁺ = 1.34 Å) is found to be an insulating G-type antiferromagnet with a T_N of 120 K. Because Mn has the electron count of t²g³ e⁺g⁰, the JT distortion is not a factor and all the neighboring Mn⁴⁺ cations have antiferromagnetic interactions through super-exchange. Replacing Ca with a larger cation and maintaining the same valency for the A-site cation, SrMnO₃ (Sr²⁺ = 1.44 Å) is also a G-type antiferromagnet with a T_N of 235 K. The larger Neel temperature results from the lack of octahedral tilting. Having linear super-exchange pathways allows for the magnetic transition temperature to be higher. In the case with the smaller cation, Ca causes the surrounding octahedra to tilt, and thus, the super-exchange pathways are slightly hindered. Figure 4 compares the bond angles for the two perovskites, CaMnO₃ and SrMnO₃. All these AMnO₃ materials are found to be insulators.
Switching gears to ARuO₃ perovskites, Ru’s 4d orbitals are larger than Mn’s 3d orbitals. Thus Ru has itinerant electrons, which is responsible for its conductivity. Both CaRuO₃ and LaRuO₃ are metallic paramagnets.⁷, ¹³, ¹⁵ SrRuO₃ is also metallic but is a ferromagnet with a $T_C$ of 165 K.¹³, ¹⁶-¹⁷ While the electron configuration is the same between CaRuO₃ and SrRuO₃, the double exchange interactions in SrRuO₃ stabilize the ferromagnetism.¹³, ¹⁶-¹⁷

If we replace the A-site cation with an even larger cation Ba²⁺ (1.61 Å), the substitution can alter the crystal structure. In short when the tolerance factor ($\tau$) is less than 1, the corner-shared octahedra tilt. Notice that we observe this in the CaMnO₃ structure (see Figure 4). However when $\tau$ is substantially greater than 1, face/edge-sharing octahedra can occur and form hexagonal perovskites. This causes the packing to be different. The hexagonal close-packing has the $AB$ sequence; whereas cubic close-packing has the $ABC$ sequence (see Figure 5). Figure 6 shows the relationship between a simple cubic unit cell and the hexagonal unit cell. The unit cell dimensions are:
\( a_{\text{Hexagonal}} = a_p \sqrt{2} \) and \( c_{\text{Hexagonal}} = a_p \sqrt{3} \), where \( a_p \) stands for pseudocubic lattice parameter for \( a \).

**Figure 5:** Stacking patterns for cubic close-packing and hexagonal close-packing.
1.4.2 Different Hexagonal Crystal Structures

As the τ increases, the hexagonal polytypes transform in a general sequence, which is 3C to 6H to 12R to 9R to 2H. Figure 7 shows the general hexagonal crystal structure progression, which steadily increases in the number of layers of face-connecting octahedra. The 3C crystal structure is the usual 3 layers of corner-shared octahedra within the unit cell (see Figure 8). The 6H structure has the \((cch)\)\(_2\) repeating stacking sequence and has 6 layers of octahedra within the hexagonal unit cell. Two-thirds of the 6H structure has cubic close-packing layers and one-third is from the hexagonal layers (see Figure 9). The 12R crystal structure has the \((cchh)\)\(_3\) repeating stacking sequence within the trigonal unit cell (see Figure 10). 50 % of the layers have face-connecting octahedra. The 9R structure contains 6 layers of hexagonal close-packing and 3 layers of cubic close-packing octahedral; thus, an overall 9 layers of octahedra in the trigonal unit cell.
The repeating stacking sequence is \((chh)_3\) (see Figure 11), where two-thirds of the crystal structure has face-connecting octahedra. The 2H crystal structure has columns of face-shared octahedra in the [001] and is the most common hexagonal perovskite. It is also referred to as the ideal hexagonal perovskite. Only 2 layers are needed to complete the unit cell, so if the crystal structure has a repeating \(hh\) stacking, then this is referred to as the 2H structure (see Figure 12).

![Diagram showing crystal structures](image)

**Figure 7:** General progression of increased face-sharing octahedra in hexagonal polytypes.
Figure 8: 3C crystal structure within a unit cell that has the ccc pattern of the corner-shared octahedra.
Figure 9: 6H crystal structure within a unit cell that has the \((hcc)_2\) pattern of the octahedra.
Figure 10: 12R structure that displays (hhcc)$_3$ pattern of the octahedra.
Figure 11: 9R crystal structure within a unit cell that has the \((hhc)_3\) pattern of the octahedra.
Figure 12: 2H crystal structure of BaMnO$_3$ perovskite. The face-shared octahedra are oriented in the [001].

The increased amount of face-connecting octahedra results in an increase in destabilization of the unit cell. $^{18}$ It is well-known that completely corner-connecting octahedra are more stable than its counter-part face-connecting octahedra. $^1$ In order to alleviate destabilization in hexagonal crystal structures, metal-metal bonding occurs, cation ordering occurs, or cation vacancies form. $^1$ Less common hexagonal polytypes can occur, such as 8H, 10H, and 14H, when the number of corner-connecting layers increases. The repeating stacking sequences are (cchc)$_2$, (cchcc)$_2$, and (cchchch)$_2$ for 8H, 10H, and 14H, respectively (see Figure 13, Figure 14, and Figure 15, respectively).
Figure 13: 8H structure that has the $(chec)_2$ pattern of the octahedra.
Figure 14: 10H structure that displays \((cchcc)_2\) pattern of the octahedra.
**Figure 15:** 14H structure that displays \((cchchch)_3\) pattern of the octahedra.

Other more complex trigonal structures are 12R, 15R, 27R, which have the repeating stacking sequences of \((cchh)_3\), \((cchch)_3\), and \((cchchchch)_3\), respectively (see **Figure 10**, **Figure 16**, and **Figure 17**, respectively). For all intensive purposes, these hexagonal
polytypes will not be further discussed since none of these hexagonal polymorphs conversed in this work relate to these structure types. Also these hexagonal and trigonal structures are generally associated with non-stoichiometry.\(^1\)

Having Ba\(^{2+}\) fully substituted on the A-site, BaMnO\(_3\) (Ba\(^{2+}\) = 1.61 Å) is found to be an insulating antiferromagnet with a \(T_N\) of 59 K.\(^19\) Reasons for the decrease in the Neel temperature is due to BaMnO\(_3\) having face-shared octahedra rather than corner-shared octahedra. Depending on the synthesis conditions, BaRuO\(_3\) as a 9R crystal structure is a Mott insulating Pauli paramagnet,\(^20\) and the 4H version is a metallic Pauli paramagnet.\(^20\)-\(^21\) The 4H crystal structure has the \((hc)_2\) repeating stacking sequence and 4 layers of octahedra within the unit cell (see Figure 18).\(^22\) This structure contains equal amounts of cubic- and face-sharing octahedra. The 4H and 9R structures adopt the \(P6_3/mmc\) (space group #194) symmetry and \(R-3m\ H\) (space group #166) symmetry, respectively.\(^20\) BaRuO\(_3\) also exhibits the 3C and 6H crystal structures when synthesized under high pressures.\(^18, 23\)
Figure 16: 15R structure that displays \((hchcc)_3\) pattern of the octahedra.
Figure 17: 27R structure that displays \((cchchchchchch)_3\) pattern of the octahedra.
Figure 18: 4H crystal structure within a unit cell that displays \((hc)_2\) pattern of the octahedra.

One system that shows different hexagonal polymorphs is the \(\text{Ba}_{1-x}\text{Sr}_x\text{RuO}_3\) perovskites. \(\text{SrRuO}_3\), \(\text{Ba}_{0.5}\text{Sr}_{0.5}\text{RuO}_3\), and \(\text{BaRuO}_3\) exhibit the 3C polymorph, mixture of the 6H and 4H polymorphs, and the 9R polymorph, respectively.\(^1\) As the Ba substitution increases, the amount of face-connecting octahedra increases along with the tolerance factor; see Figure 19. The off-white circles in Figure 19 plot the tolerance factor across the substitutions. The progression in the crystal structures is 3C to 6H + 3C to 6H to 6H + 4H to 4H to 9R + 4H to 9R as the Ba substitution increases.\(^1\)
1.5 Overview

Considering this brief review on these Mn- and Ru-based simple perovskites, different A-site substitutions can alter the properties from one cation to another. While these perovskites are definitely interesting, the ones that are FM (or AFM) do not have a $T_C$ (or $T_N$) above room temperature, which is the case for most simple perovskites. For technological applications, the $T_C$ needs to be well above room temperature. Hence, this is the main reason why we seek to double perovskites. By combining $B$ and $B'$ cations from the first row transition metals and the second or third row transition metals, respectively, to form double perovskites, not only do we potentially find an increase in the $T_C$ but also the properties are expanded. These combined $B$-site cations allow for localized and delocalized electrons,\textsuperscript{24} which lead to interesting properties as will be explained later. For this same reason, we also study $\text{Sr}_2\text{Cr}B'O_6$ ($B' = \text{Re}$ and Os) double perovskites.
1.6 References

CHAPTER 2: STUDIES OF THE STRUCTURAL, MAGNETIC AND ELECTRICAL PROPERTIES OF Ca$_{1-x}$La$_x$Mn$_{0.5}$Ru$_{0.5}$O$_3$ PEROVSKITES

2.1 Contribution

This project focuses on characterizing the structural, magnetic, and electrical properties for Ca$_{1-x}$La$_x$Mn$_{0.5}$Ru$_{0.5}$O$_3$ perovskites. Theoretical calculations were also made to answer questions that arose from the empirical results. This chapter will be published with the following authorship in order: Jennifer R. Soliz, Rohan Mishra, Wolfgang Windl, and Patrick M. Woodward. Jennifer R. Soliz synthesized and measured all experimental results, and the theoretical calculations were made by Rohan Mishra in Wolfgang Windl’s lab. Patrick M. Woodward is Jennifer’s adviser and has been informed on all results presented in this work.

2.2 Abstract

Synthesis and characterization of Ca$_{1-x}$La$_x$Mn$_{0.5}$Ru$_{0.5}$O$_3$ ($x = 0.6, 0.5, 0.4, 0.3, 0.2, 0.1, \text{ and } 0.0$) double perovskites was carried out to study the role of aliovalent doping on the properties of the disordered ferrimagnet CaMn$_{0.5}$Ru$_{0.5}$O$_3$. X-ray diffraction measurements showed these polycrystalline powders to be phase pure and to exhibit
Pnma symmetry with $ab^+a^-$ octahedral tilting. Neutron powder diffraction (NPD) showed that the crystal structure and magnetic moments do not change significantly across the substitution range. $\text{Ca}_{0.5}\text{La}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ and $\text{Ca}_{0.9}\text{La}_{0.1}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ compounds exhibit ferro-/ferrimagnetism with a magnetization of 1.26(1) $\mu_B$ at 4 K and 1.25(4) $\mu_B$ at 50 K, respectively. NPD further concluded the lack of cooperative Jahn Teller distortion. Density functional theory (DFT) calculations on $\text{Ca}_{0.5}\text{La}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ confirmed that the extra $1/2$ electron is responsible for opening the band gap, in that 0.295$e$ and 0.17$e$ is being transferred to the Ru and Mn bands, respectively. DFT calculations also showed ferrimagnetism to be the most energetically stable magnetic phase. Overall we conclude that despite the chemical disorder, $\text{Ca}_{0.5}\text{La}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ is an insulating ferrimagnet with a Curie temperature ($T_C$) of 233 K, which is a rare finding to have chemical disorder with ferrimagnetic order.

### 2.3 Introduction

Ternary perovskites, such as $\text{AMnO}_3$ or $\text{ARuO}_3$, have been extensively studied due to their transport and magnetic properties.$^{1-4}$ In particular, $\text{AMnO}_3$ perovskites are popular since a wide variety of these materials exhibit colossal magnetoresistance (MR).$^5$ $\text{CaMnO}_3$ and $\text{LaMnO}_3$ are both antiferromagnetic (AFM) insulators with a $T_N$ of 120K and 140K, respectively.$^6-8$ While $\text{CaMnO}_3$ has type-G spin alignment, $\text{LaMnO}_3$ exhibits the cooperative Jahn Teller (JT) distortion from the $\text{Mn}^{3+}$, and the JT distortion drives the type-A antiferromagnetic order.$^9$ By substituting in $\text{Ca}^{2+}$ for $\text{La}^{3+}$, this introduces carriers into the $\text{Ca}_{1-x}\text{La}_x\text{MnO}_3$ system and causes mixed valency of $\text{Mn}^{3+}$ and $\text{Mn}^{4+}$. For example, $\text{Ca}_{1-x}\text{La}_x\text{MnO}_3$ ($0.2 < x < 0.4$) is a metallic ferromagnet (FM) and is a classic example of
Switching gears to the ruthenates, LaRuO$_3$ and CaRuO$_3$ are metallic paramagnets with low resistivities (range of $10^{-3} \ \Omega \cdot \text{cm}$) at room temperature.$^{1,6}$ When lanthanum replaces calcium in Ca$_{1-x}$La$_x$RuO$_3$ ($x = 0.1$ and $0.5$), the antiferromagnetic semiconducting behavior results, and the $T_N$ decreases as the La substitution increases.$^{14}$ The interesting properties of these simple perovskites suggest that interesting behavior could result when manganese and ruthenium ions are both present in perovskites.$^{15-22}$

It has been predicted by Felser and Seshadri$^{23}$ that by combining a first row transition metal and a second or third row transition metal, this allows there to be a narrow spin polarized band and a broad band partially filled with itinerant electrons to potentially produce materials with large MR. Since the discovery of room temperature large MR in half-metallic Sr$_2$FeMoO$_6$, much work has been made to explore other materials by taking an interest in band filling and bandwidth.$^{24,25}$ By combining manganese and ruthenium ions together to share the same site equally generates AMn$_{0.5}$Ru$_{0.5}$O$_3$ perovskites. This leads to interesting materials because of the energetic overlap between the Mn e$_g$ and Ru t$_{2g}$–O 2p $\pi^*$ orbitals; thus hatching magnetotransport properties.$^{26,27}$ In the study of CaMn$_{1-x}$Ru$_x$O$_3$ ($0.4 \geq x \geq 0.1$) perovskites, the resistivity decreases as the ruthenium content increases, and the $0.4 \geq x \geq 0.1$ compositions exhibit type-G AFM behavior.$^{29}$ Whereas for the LaMn$_x$Ru$_{1-x}$O$_3$ system, the Mn-rich samples ($x \geq 0.05$) are insulating.$^{30}$ The resistivity changes about 7 orders of magnitude across the substitutions in LaMn$_{x}$Ru$_{1-x}$O$_3$ ($0.67 \geq x \geq 0.05$) system. Reason as to why this occurs is not explained. Ferrimagnetism (FiM) is found to exist in the Mn-rich samples ($0.67 \geq x \geq 0.05$).
Gonen et al.\textsuperscript{30} describes that the spins are aligned parallel to each other for Mn\textsuperscript{3+}-O-Mn\textsuperscript{4+} (attributed to double exchange interactions) and anti-parallel for Mn\textsuperscript{3+/4+}-O-Ru\textsuperscript{3+} (attributed to super-exchange interactions). However neutron diffraction data was not gathered, and FiM was only speculated. As for AMn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} (A = Ca, La, and Ca\textsubscript{0.5}La\textsubscript{0.5}) perovskites, these compounds have been well studied. CaMn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} is found to be a metallic FiM with a $T_C$ of 230 K, and LaMn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} (synthesized under Ar gas) is a FM semi-conductor with a $T_C$ of 86 K.\textsuperscript{6,27} The in-between compound, Ca\textsubscript{0.5}La\textsubscript{0.5}Mn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3}, is reported as a FM that shows signs of spin glassiness behavior.\textsuperscript{31}

While the two end members, CaMn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} and LaMn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3}, have been widely studied, substituting in lanthanum for calcium in the Ca\textsubscript{1-x}La\textsubscript{x}Mn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} system raises some questions. How does the charge carrier substitution affect the properties? Is a JT distortion present? How does the chemical disorder affect the magnetic exchange interactions and how do they occur? What is the conductivity? Does the extra electron transfer to manganese or ruthenium? Understanding these questions and how the properties are affected is the motivation for this work. Here we will address these questions by coupling experimental results with first principles calculations.

### 2.4 Experimental Section

Ca\textsubscript{1-x}La\textsubscript{x}Mn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} perovskites with varying compositions ($x = 0.6, 0.5, 0.4, 0.3, 0.2, 0.1$, and $0.0$) were prepared by the conventional solid state ceramic method. Stoichiometric ratio amounts of the starting reagents CaCO\textsubscript{3} (99.95 \%, Mallinckrodt Baker), La\textsubscript{2}O\textsubscript{3} (99.99 \%, Sigma-Aldrich, heated to 900 °C for 8 h prior to usage and then
stored in a desiccator when not in use), Mn$_2$O$_3$ (99.9 %, CERAC), and RuO$_2$ (99.9 %, Sigma-Aldrich) were accurately weighed, mixed, and ground together using an agate mortar and pestle. The samples were individually loaded into high density (99.8 % dense) alumina crucibles to ensure purity of the samples and then heated to 1385 °C in air for 15 h using a high temperature box furnace. The products appeared as dark gray powders. No adjustments were made for oxygen vacancies.

Ca$_{1-x}$La$_x$Mn$_{0.5}$Ru$_{0.5}$O$_3$ samples were cut into dense (~70-81 % dense) rectangular pellets with average dimensions of 0.5×0.5×1 cm. Inconel alloy wires were adhered to the pellet by using conductive silver paint. Using the 4-point probe method, a constant source of current was applied via an ampmeter so that the voltage drop could be measured. Corrections were not adjusted for porosity.

LakeShore vibrating sample magnetometer (VSM) model was used to collect the magnetic measurements for pressed powders (~20 mg) of Ca$_{1-x}$La$_x$Mn$_{0.5}$Ru$_{0.5}$O$_3$ solid solutions. Zero-field cooled (ZFC) and field cooled (FC) magnetic susceptibility curves were gathered with a field strength of 1 kG (all except for $x = 0$, which used 0.5 kG) and were taken in the temperature range of 80-350 K. Hysteresis curves were measured in fields up to ± 1.6 T.

A Bruker D8 diffractometer, which utilizes Cu K$_{\alpha_1}$ radiation ($\lambda = 1.54059$Å) with a Ge 111 incident beam monochromator, was used to collect the X-ray powder diffraction (XRPD) data. This instrument is also equipped with the LynxEye one-dimensional detector. The scans were taken in the 2θ range starting from 10-90 ° with a step size of
0.014286 °. Each XRPD pattern was refined using the Rietveld Method administered through the TOPAS Academic software.\(^\text{32}\)

Neutron powder diffraction (NPD) data was collected on a (HB-2A) neutron powder diffractometer at the Oak Ridge National Laboratory (ORNL). The premonochromator, pre-sample, and sample detector collimations were set to 12’-21’-6’, and the detector bank has 44 \(^3\)He tubes. A Ge (115) monochromator with a take-off angle of 90 ° and a constant wavelength at 1.5385 Å were used. The 2θ scans ranged from 3-155 °. The high-resolution data and order parameter scans were measured at 30 s/point. This instrument is further described from the ORNL website (http://neutrons.ornl.gov/index.shtml). Structure refinements of the NPD data were analyzed using the FullProf Suite refinement analysis\(^\text{33}\), and SARAh Representational Analysis\(^\text{34}\) was used to input the magnetic phase.

While the properties for the CaMn\(_{0.5}\)Ru\(_{0.5}\)O\(_3\) end member have been previously reported,\(^\text{6}\) the magnetic and electrical data is being re-used only as a direct comparison to the rest of the lanthanum-substituted compositions.

2.5 Computational Methods

Density functional theory (DFT) was used to calculate the properties of Ca\(_{0.5}\)La\(_{0.5}\)Mn\(_{0.5}\)Ru\(_{0.5}\)O\(_3\) and compare them with the previously reported results on CaMn\(_{0.5}\)Ru\(_{0.5}\)O\(_3\),\(^\text{35}\) to understand the change in properties with La substitution. We used the projector augmented wave (PAW) method\(^\text{36}\) along with the spin-polarized generalized gradient approximation\(^\text{37}\) (GGA) to DFT as implemented in the Vienna Ab-initio Simulation Package (VASP).\(^\text{38,39}\) To ensure convergence, a plane-wave cutoff energy of
525 eV was employed throughout. We used the PAW-GGA pseudopotentials (La, Ca$_{sv}$, Mn, Ru, and O) from the VASP distribution with valence configurations of 5s$^2$5p$^6$6s$^2$5d$^1$ for La, 3s$^2$3p$^6$4s$^2$ for Ca, 3d$^6$4s$^1$ for Mn, 4d$^7$5s$^1$ for Ru, and 2s$^2$2p$^4$ for O. To sample the Brillouin zone, we used Monkhorst-Pack k-point meshes with mesh divisions $N_i$ such that the product of $N_i$ with the corresponding lattice vectors was as close as possible to 35 Å for structural relaxations and 50 Å for final band-structure calculations. Additionally for the latter the tetrahedron method with Blöchl corrections was used for the Brillouin zone integration. Relaxations were performed, keeping the low temperature experimental lattice constants fixed and allowing the internal coordinates to change until the forces were $<$0.01 eV·Å$^{-1}$.

As the experimental structures have disorder on both Mn/Ru and Ca/La sub-lattices, we use special quasi-random structures (SQS), which are specially designed small unit cell periodic structures that are constructed to reproduce the most important correlation functions of a randomly disordered system. They have been successfully used to simulate random disorder within small periodic supercells convenient for DFT studies. The SQS cells were constructed with the gensqs program of the alloy theoretic automated toolkit. As it was not possible to create a SQS cell which could satisfactorily simulate the random ordering at both the Mn/Ru and Ca/La lattice sites simultaneously, we used two different SQS cells: one being a 20 atom SQS cell with random arrangement of the Ca/La ions but having rock salt ordering of Mn/Ru ions, shown in Figure 20a. We shall refer to this structure as SQS-I. In order to study the effect of Mn/Ru disorder, we used a 40 atom SQS cell of CaMn$_{0.5}$Ru$_{0.5}$O$_3$ with random
ordering of Mn/Ru ions. In order to simulate disordered Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$, we used the low temperature experimental lattice parameters of Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ and since La contains an extra $\frac{1}{2}$ valence electron than Ca, we added $4e$ ($0.5e$ for every La ion) in the calculations to match the electron count of a 40 atom Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ cell. We will call this structure as SQS-II (shown in Figure 20b), for future reference. We have justified the use of such a cell in a later section. The pair-correlation function of the SQS-I and SQS-II cells matched that of a randomly disordered system up to the second and third nearest neighbors, respectively.

Figure 20: (a) SQS-I cell with 2 formula units of Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ having disordered arrangement Ca/La ions and rock salt arrangement of Mn/Ru ions (b) SQS-II cell with 4 formula units of CaMn$_{0.5}$Ru$_{0.5}$O$_3$ having disordered arrangement of Mn/Ru ions. The lattice parameters are that of Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$. 
To treat the strong Coulomb correlations due localized d-electrons in the Mn and Ru ions, we have used the DFT + Hubbard $U$ method,\textsuperscript{45} with the rotationally invariant Dudarev approach, where only one effective Hubbard parameter $U_{\text{eff}} = U - J$ is used, with $U$ and $J$ being Hubbard repulsion and intra-atomic exchange, respectively for the electrons in the localized d states.\textsuperscript{46} We used $U_{\text{eff}}$ values of 3.1 eV and 2.1 eV for Mn and Ru, respectively, similar to what we had used in our previous study on CaMn$_{0.5}$Ru$_{0.5}$O$_3$.\textsuperscript{35}

### 2.6 Experimental Results and Discussion:

#### 2.6.1 Crystal Structure

An overlay of the X-ray powder diffraction patterns for Ca$_{1-x}$La$_x$Mn$_{0.5}$Ru$_{0.5}$O$_3$ ($0.6 \geq x \geq 0$) system is shown in Figure \textit{21} and indicates phase purity. All chemically disordered compounds adopt the orthorhombic $Pnma$ crystal structure and exhibit $a' b' a'$ octahedral tilting. This type of octahedral tilting is directly related to the space group. If these compounds were ordered, then the space group symmetry would change to $P2_1/n$, and there would be a change in the systematic absences for which peaks would be allowed.\textsuperscript{6,47} Table \textit{3} outlines the lattice parameters and Rietveld refinement values, which report good fits. As expected, the lattice parameters change uniformly as lanthanum replaces calcium. Our results are in close agreement with the literature.\textsuperscript{31}
Figure 21: Waterfall of the X-ray powder diffraction patterns for Ca$_{1-x}$La$_x$Mn$_{0.5}$Ru$_{0.5}$O$_3$ compositions.

<table>
<thead>
<tr>
<th>x-Value</th>
<th>0.6</th>
<th>0.5</th>
<th>0.4</th>
<th>0.3</th>
<th>0.2</th>
<th>0.1</th>
<th>0*</th>
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<tr>
<td>space group</td>
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<td>$R_{wp}$</td>
<td>$R_{wp}$</td>
<td>$R_{wp}$</td>
<td>$R_{wp}$</td>
<td>$R_{wp}$</td>
<td>$R_{wp}$</td>
</tr>
<tr>
<td>a (Å)</td>
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<td>5.5212(2)</td>
<td>5.4947(3)</td>
<td>5.4715(3)</td>
<td>5.4492(2)</td>
<td>5.4338(3)</td>
<td>5.4305(1)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>7.7728(2)</td>
<td>7.7462(3)</td>
<td>7.7174(4)</td>
<td>7.6826(3)</td>
<td>7.6468(3)</td>
<td>7.6183(3)</td>
<td>7.5870(2)</td>
</tr>
<tr>
<td>c (Å)</td>
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<td>5.4723(2)</td>
<td>5.4502(3)</td>
<td>5.4228(3)</td>
<td>5.3971(2)</td>
<td>5.3699(2)</td>
<td>5.3403(1)</td>
</tr>
<tr>
<td>Volume (Å$^3$)</td>
<td>236.33(1)</td>
<td>234.04(1)</td>
<td>231.12(2)</td>
<td>234.32(2)</td>
<td>224.95(2)</td>
<td>222.05(2)</td>
<td>220.03(2)</td>
</tr>
</tbody>
</table>

Table 3: Rietveld refinement values and lattice parameters from X-ray powder diffraction for Ca$_{1-x}$La$_x$Mn$_{0.5}$Ru$_{0.5}$O$_3$ compounds. * values taken from Ricciardo et al.$^6$

Because X-rays are not sensitive to oxygen positions, it was not possible to definitively confirm or rule out the presence of JT distortions in Mn-centered octahedra; thus NPD data was gathered for two compounds, Ca$_{0.9}$La$_{0.1}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ and
Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$. Both compounds were refined with Pnma symmetry, which means that there is no long range chemical order of Mn and Ru. The room temperature neutron powder diffraction pattern for Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ is shown in Figure 22.

In order to confirm the magnetic moments, low temperature neutron powder diffraction was also collected. Figure 23a and Figure 23b are refined neutron powder diffraction patterns for Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ at 4 K and Ca$_{0.9}$La$_{0.1}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ at 50 K, respectively. While different magnetic structures were used to refine the magnetic phase for the low temperature neutron powder diffraction, it was found that FM/FiM structures had the best refinement values, which were identical to each other. Thus from low temperature neutron powder diffraction, we cannot confirm whether Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ and Ca$_{0.9}$La$_{0.1}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ compounds exhibit ferromagnetic or ferrimagnetic ordering. We use a ferromagnetic structure, where both the Mn and Ru magnetic moments were constrained to refine equally, in order to avoid arbitrarily choosing the Mn moment. This does not mean that we rule out the ferrimagnetic structure. Table 4 reports the refinement values and obtained magnetic moments for a FM structure. As lanthanum is substituted into the Ca$_{1-x}$La$_x$Mn$_{0.5}$Ru$_{0.5}$O$_3$ system, the crystal structure and magnetic moments do not change significantly across the substitutions. Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ and Ca$_{0.9}$La$_{0.1}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ were found to have moments of 1.26(2) $\mu_B$ at 4 K and 1.25(4) $\mu_B$ at 50 K, respectively, per transition metal site. CaMn$_{0.5}$Ru$_{0.5}$O$_3$ has been reported to have 1.19(7) $\mu_B$.\textsuperscript{6}
Figure 22: Neutron powder diffraction for Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ at room temperature. The black crosses, gray and black lines represent the observed, calculated, and difference patterns, respectively.
Figure 23: Neutron powder diffraction for (a) Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ at 4K and (b) Ca$_{0.9}$La$_{0.1}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ at 50K; the lower Bragg positions refer to the nuclear phase and the upper Bragg positions refer to the magnetic phase. The dark grey dots, light grey and black lines represent the observed, calculated, and difference patterns, respectively.
Despite the sensitivity for atomic positions, the bond lengths in either compound did not suggest that a cooperative JT distortion was present. However, local JT distortions are suspected and thus driving the magnetism. Table 5 reports the room and low temperature crystallographic results for the two compounds. In addition, King et al.\textsuperscript{48} reports that while there is no strong evidence for a cooperative JT distortion from a pair distribution study in either CaMn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} or Ca\textsubscript{0.5}La\textsubscript{0.5}Mn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3}, mixed valence states Mn\textsuperscript{3+} and Mn\textsuperscript{4+} are present for both compounds, and the Mn\textsuperscript{3+} octahedra are JT distorted. CaMn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} is reported to have an average Mn\textsuperscript{3.67+} and Ru\textsuperscript{4.26+} oxidation state while Ca\textsubscript{0.5}La\textsubscript{0.5}Mn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} has an average of Mn\textsuperscript{3.33+} and Ru\textsuperscript{3.92+}.\textsuperscript{48} Ca\textsubscript{0.5}La\textsubscript{0.5}Mn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} is shown to have more elongated Mn-O bonds, meaning that local JT distortions are present.\textsuperscript{48}

\begin{table}
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
\textbf{Moments} & \textbf{CaMn}_{0.5}\textbf{Ru}_{0.5}\textbf{O}_3 & \textbf{Ca}_{0.5}\textbf{La}_{0.5}\textbf{Mn}_{0.5}\textbf{Ru}_{0.5}\textbf{O}_3 & \textbf{Ca}_{0.5}\textbf{La}_{0.5}\textbf{Mn}_{0.5}\textbf{Ru}_{0.5}\textbf{O}_3 \\
\textbf{(10K)} & \textbf{(50K)} & \textbf{(4K)} \\
\hline
\textit{M} (\mu_b) on Mn & 3.33 & 0.63(1) & 0.63(3) \\
\textit{M} (\mu_b) on Ru & -1.14(7) & 0.63(1) & 0.63(3) \\
\textbf{FM Net Moment} & 2.19 & 1.26(1) & 1.26(3) \\
\textbf{R}_{\text{p}} & 5.26 & 6.81 & 6.17 \\
\textbf{R}_{\text{up}} & 6.67 & 8.89 & 7.84 \\
\hline
\end{tabular}
\caption{Refinement values and magnetic moments from low temperature neutron powder diffraction for Ca\textsubscript{1-x}La\textsubscript{x}Mn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} compounds. * values taken from Ricciardo \textit{et al.}\textsuperscript{6}}
\end{table}
Table 5: Neutron powder diffraction refinement values, lattice parameters, bond distances, bond angles and thermal parameters for Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ and Ca$_{0.9}$La$_{0.1}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ at high and low temperatures.
2.6.2 Magnetic Properties

The magnetic susceptibility curves from Figure 24 indicate ferromagnetic/ferrimagnetic behavior for all compounds. While the ZFC and FC susceptibility was collected for each compound, Figure 24a shows the ZFC and FC susceptibilities for CaMn$_{0.5}$Ru$_{0.5}$O$_3$, Ca$_{0.9}$La$_{0.1}$Mn$_{0.5}$Ru$_{0.5}$O$_3$, and Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ for simplicity. Figure 24b plots the FC susceptibility for each compound in the Ca$_{1-x}$La$_x$Mn$_{0.5}$Ru$_{0.5}$O$_3$ (0.6 $\geq x \geq 0$) system. The hysteresis loops are shown in Figure 25 for 0.6 $\geq x \geq 0$, which also support ferromagnetic/ferrimagnetic ordering. The coercivities range from 200-1100 G, increasing drastically from 200 G to 1100 G when lanthanum is first substituted into the system ($x = 0.1$) and then decreasing back down to 230 G for $x = 0.6$ composition. The saturated magnetization ($M_{\text{sat}}$) steadily increases from the calcium-rich end member, CaMn$_{0.5}$Ru$_{0.5}$O$_3$, to Ca$_{0.4}$La$_{0.6}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ with the $T_C$ peaking at about room temperature for the $x = 0.2$ composition. As previously mentioned from the PDF study, CaMn$_{0.5}$Ru$_{0.5}$O$_3$ is reported to have an average Mn$^{3.67+}$ and Ru$^{4.26+}$ oxidation state, and Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ has an average of Mn$^{3.33+}$ and Ru$^{3.92+}$. Considering these oxidation states and that the Mn and Ru cations are being reduced with La substitution, the $M_{\text{sat}}$ values should steadily increase for FiM ordering, which is what we observe (see Figure 26). As the valency changes between the manganese and ruthenium ions when lanthanum is substituted into the system, the covalency of the super-exchange interactions also changes. Figure 26 details the rise and fall of the Curie temperatures and the saturated magnetizations per transition ion for each composition.

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**Figure 24:** (a) Zero-field cooled and field cooled susceptibility for CaMn$_{0.5}$Ru$_{0.5}$O$_3$ (squares), Ca$_{0.9}$La$_{0.1}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ (triangles), and Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ (circles) solid solutions, and (b) is the field cooled susceptibility for the Ca$_{1-x}$La$_x$Mn$_{0.5}$Ru$_{0.5}$O$_3$ solid solutions. All measurements were collected using the vibrating sample magnetometer, starting at 80 K.
Figure 25: Hysteresis loops of the Ca$_{1-x}$La$_x$Mn$_{0.5}$Ru$_{0.5}$O$_3$ solid solutions at 80 K collected from the vibrating sample magnetometer. The inset plot shows the hysteresis loops from 0 to 1.6 T.
Figure 26: Saturated magnetic moments while monitoring the Curie temperatures for the $\text{Ca}_{1-x}\text{La}_x\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ solid solutions.

Furthermore since the $M_{\text{sat}}$ range is from 0.72-1.12 $\mu_B$/f.u. across the compositions, these are too small for true ferromagnetism. If manganese and ruthenium had the oxidation states of 3+ and 5+, respectively, the spin only ferromagnetic moment would be approximately 3.5 $\mu_B$/f.u. If Mn$^{4+}$ and Ru$^{4+}$ were present, the ferromagnetic moment is calculated to be 2.5 $\mu_B$/f.u. For Mn$^{3+}$ and Ru$^{4+}$, the ferromagnetic moment is 3.0 $\mu_B$/f.u. Again, these values are larger than the experimental $M_{\text{sat}}$ values we observe across the substitutions. In the case of ferrimagnetism, the expected moment would be about 0.5 $\mu_B$/f.u. for Mn$^{3+}$ + Ru$^{5+}$ and Mn$^{4+}$ + Ru$^{4+}$ and 1.0 $\mu_B$/f.u. for Mn$^{3+}$ + Ru$^{4+}$. These values are closer to the magnetic moments we experimentally observe than for ferromagnetism.
and are on par to the suggested oxidation states for \(\text{CaMn}_{0.5}\text{Ru}_{0.5}\text{O}_3\) (mostly Mn\(^{4+}\) and Ru\(^{4+}\) character) and \(\text{Ca}_{0.5}\text{La}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3\) (mostly Mn\(^{3+}\) and Ru\(^{4+}\) character).

However as discussed earlier, the low temperature neutron diffraction results could not confirm whether ferri- or ferromagnetic ordering exists for \(\text{Ca}_{0.9}\text{La}_{0.1}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3\) and \(\text{Ca}_{0.5}\text{La}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3\) compounds. While we can make reasonable arguments for ferrimagnetic ordering based on the refined low magnetic moments from the neutron diffraction results and from the magnetic results obtained from SQUID, we need theoretical calculations to support our explanations.

### 2.6.3 Electrical Properties

The conductivities were collected for each sample to gauge the electrical transport as a function of temperature in the \(\text{Ca}_{1-x}\text{La}_x\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3\) \((x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6)\) samples. Figure 27 shows the log of the conductivity ratio \((\sigma_x/\sigma_{298}\text{K}; \ \sigma_x\text{ being the conductivity as temperature varies})\) for each compound. Figure 27 has been normalized because the polycrystalline samples have a fair amount of porosity. Grain boundary resistance is responsible for the variations in conductivity at temperatures above 250 K. The change in resistivity with temperature is a better reflection of the intrinsic conductivity of these samples, which is why the conductivity has been normalized.
Figure 27: The log base 10 was taken of the conductivity ratio for the Ca$_{1-x}$La$_x$Mn$_{0.5}$Ru$_{0.5}$O$_3$ solid solutions.

As more lanthanum is substituted in for calcium, the compounds become substantially more insulating in the low temperature regime. While CaMn$_{0.5}$Ru$_{0.5}$O$_3$ shows metallic behavior with little temperature dependence, Ca$_{0.4}$La$_{0.6}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ is clearly an insulator. At 10 K, the conductivity is 9.93 S/cm and $2.97 \times 10^{-7}$ S/cm for CaMn$_{0.5}$Ru$_{0.5}$O$_3$ and Ca$_{0.4}$La$_{0.6}$Mn$_{0.5}$Ru$_{0.5}$O$_3$, respectively. At 265K, the conductivity is 13.57 S/cm and 4.07 S/cm for CaMn$_{0.5}$Ru$_{0.5}$O$_3$ and Ca$_{0.4}$La$_{0.6}$Mn$_{0.5}$Ru$_{0.5}$O$_3$, respectively. It is possible that grain boundaries could be influencing the conductivity. Thus this leaves us with the questions: (1) why does the conductivity become insulating when charge
carriers are substituted into the system, and (2) why is there such a drastic change in conductivity?

### 2.7 Theoretical Results and Discussion:

Interestingly enough while the conductivity exhibits a significant change in behavior, the crystal structure and magnetic moments observed do not change significantly across the substitutions for Ca$_{1-x}$La$_x$Mn$_{0.5}$Ru$_{0.5}$O$_3$ ($0.5 \geq x \geq 0$) system. We look to DFT calculations to confirm: (1) whether ferrimagnetic ordering is the most energetically stable magnetic structure and compare this with other magnetic structures; and (2) explanations for why the conductivity plummets as the La$^{3+}$ substitution increases.

#### 2.7.1 Computational Results

We begin by studying the effect of disorder in the Ca/La sublattice on the magnetic and electronic properties of Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ with rock salt ordering of Mn/Ru ions. For this purpose we use two different structures: the SQS-I cell as mentioned earlier, and a 20 atom cell of CaMn$_{0.5}$Ru$_{0.5}$O$_3$ having the experimental lattice constants of Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ with an additional $2e$ to compensate the extra $\frac{1}{2}$ valence electron due to the 2 La ions and having rock salt ordering of the Mn/Ru ions. For both the structures, total energies were calculated for four different magnetic configurations: (a) ferrimagnetic, where the spins on Mn ions are aligned parallel to each other and antiparallel to the spins on Ru ions (consequently the spins on Ru ions are aligned parallel to those on other Ru ions); (b) ferromagnetic, where the spins on all the
Mn and Ru ions are aligned parallel to each other; (c) C-type antiferromagnetic, with chains of parallel aligned Mn and Ru ions along the $c$-axis and the neighboring chains being aligned antiparallel to each other; and (d) A-type antiferromagnetic, where the spins on Mn and Ru ions lying on any equatorial plane ($ab$ plane) are parallel to each other whereas the ordering between any two neighboring $ab$ planes is antiparallel. For both the structures we find the ferrimagnetic alignment to be most stable followed by the C-type antiferromagnetic, A-type antiferromagnetic- and ferromagnetic-ordering. The difference in energy of the three unstable configurations with respect to the ferrimagnetic configuration is found to be similar for both the structures, as shown in Table 6, together with the moments on the Mn and Ru ions.
Table 6: Energy calculations of the most stable magnetic phase for each system.

For the ferrimagnetic ordering, we get a saturation magnetization of $2 \mu_B$/f.u. with the value of individual moments on the Mn and Ru ions being $3.7 \mu_B$ and $-1.3 \mu_B$, respectively. We also find a moment of $-0.06 \mu_B$ on the O ions with their sign being equal to that of the Ru ions to which they are connected to, signifying charge sharing between the 4d states of Ru and 2p states of O ions. Henceforth, we consider the moment
of each RuO$_6$ unit, which for the ferrimagnetic configuration carries a moment of $-1.7 \mu_B$. For the SQS-I structure with ferrimagnetic ordering, we get the average Mn–O and Ru–O bond distances to be 1.986 Å and 2.012 Å, respectively. For the simulated Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ structure, having only Ca ions, we find the average Mn–O and Ru–O bond distances to be 2.028 Å and 2.025 Å, respectively, which are 2% and 0.6% larger, respectively, than their values for the SQS-I structure. For both the structures we find the MnO$_6$ and RuO$_6$ to be symmetrical, with the differences between individual bonds being less than 0.1 Å. We plot the total density of states (DOS) of the stable ferrimagnetic configuration in Figure 28 (a), for the SQS-I structure and (b) CaMn$_{0.5}$Ru$_{0.5}$O$_3$ within the experimental structure of Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ with the additional 2$e$. We find that both the structures give an insulating ground state. Leaving aside the region from 2.5 - 4 eV, where the La d-states are present (absent) in Figure 28a (Figure 28b), the overall agreement of their DOS is good. Thus, the good agreement in the magnetic, structural and electronic properties of the two structures, suggests that that the model structure of Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$, with only the Ca ions, is a good substitute to study the properties of Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ with randomly ordered Ca/La ions. In other words, the ordering of Ca/La ions does not affect the properties of Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$, significantly.
Figure 28: Spin-resolved total density of states of (a) Ca_{0.5}La_{0.5}Mn_{0.5}Ru_{0.5}O_{3} in SQS I structure, which has Ca/La ions in a disordered form, while the Mn/Ru ions have rock salt ordering, (b) Rock salt ordered CaMn_{0.5}Ru_{0.5}O_{3} having Ca_{0.5}La_{0.5}Mn_{0.5}Ru_{0.5}O_{3} lattice parameters and extra $\frac{1}{2}$ electrons added to the calculations to compensate for the La ions that have been substituted with Ca, and (c) CaMn_{0.5}Ru_{0.5}O_{3} in SQS-II structure having a random distribution of Mn/Ru ions. The lattice parameters are that of experimentally observed Ca_{0.5}La_{0.5}Mn_{0.5}Ru_{0.5}O_{3}, with extra $\frac{1}{2}$ electrons added to compensate for the substituted La ions.

Next, we study the effect of disorder on the Mn/Ru sublattice. We use the SQS-II structure shown in Figure 20b, where the Mn/Ru ions are present in a disordered form, while at the Ca/La sites, only Ca ions are present with additional $\frac{1}{2}$ electrons added to match the La substitution and valency. Once again, we calculate the energy of the four different magnetic configurations that have been discussed above, and find the ferrimagnetic ordering of the Mn and Ru spins, similar to the previous two cases, which had rock salt ordering of the Mn/Ru ions. The relative stability of the magnetic
configurations is shown in Table 6. For the SQS-II structure, the saturation magnetization is found to be 2.0 $\mu_B$/f.u., with the average moment on the Mn ions and RuO$_6$ octahedra being 3.8 and 1.8 $\mu_B$, respectively. The average Mn–O and Ru–O bond distances for the ferrimagnetic configurations are found to be 2.027 and 2.021 Å, respectively, without any noticeable distortion of the MnO$_6$ and RuO$_6$, octahedra. The DOS of this disordered Mn/Ru structure is shown in Figure 28c.

2.8 Discussion

We compare the calculations on Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ with those on CaMn$_{0.5}$Ru$_{0.5}$O$_3$, as reported from Mishra et al. As we have seen that disorder on either Mn/Ru or Ca/La sublattices do not play any major role, we compare the properties of the simulated Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ structure having rock salt ordering of Mn/Ru ions with rock-salt ordered CaMn$_{0.5}$Ru$_{0.5}$O$_3$ structure. As experimentally observed across the Ca$_{1-x}$La$_x$Mn$_{0.5}$Ru$_{0.5}$O$_3$ (0.6 $\geq x \geq 0$) system, the compositions adopt Pnma symmetry. On moving from CaMn$_{0.5}$Ru$_{0.5}$O$_3$ to Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$, the low temperature lattice parameter along $a$, $b$, and $c$ axes increase by 2.2, 2.4 and 2.8%, respectively. For both the compounds, ferrimagnetic ordering is found to be most stable, with an increase in $M_{\text{sat}}$ from 1.1 $\mu_B$/f.u. in CaMn$_{0.5}$Ru$_{0.5}$O$_3$ to 2.0 $\mu_B$/f.u. in Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$, which are comparable to the experimental magnetic results ($M_{\text{sat}}$ values are 0.72 $\mu_B$/f.u. and 1.0 $\mu_B$/f.u. for CaMn$_{0.5}$Ru$_{0.5}$O$_3$ and Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$, respectively). From the magnetic moments on the Mn and RuO$_6$ ions, we find that the additional $\frac{1}{2}$ electron/f.u. due to the La ion is shared between the Mn and Ru ions, with the Ru ions having a greater fraction (0.3e). The calculated magnetic moments and $M_{\text{sat}}$ for the two compounds are within
reason to the experimental values reported here and in the literature. Based on the neutron diffraction results (0.63(1) $\mu_B$ for Ca$_{0.9}$La$_{0.1}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ and 0.63(3) $\mu_B$ for Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$), the experimental $M_{\text{sat}}$ values (0.72-1.12 $\mu_B$/f.u. across the substitutions), the expected spin only ferrimagnetic moments ($\text{Mn}^{3+} + \text{Ru}^{5+} \approx \text{Mn}^{4+} + \text{Ru}^{4+} \approx 0.5 \mu_B$ and $\text{Mn}^{3+} + \text{Ru}^{4+} \approx 1.0 \mu_B$), and the DFT calculations (1.1 $\mu_B$ and 2.0 $\mu_B$ for CaMn$_{0.5}$Ru$_{0.5}$O$_3$ and Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$, respectively), we conclude that CaMn$_{0.5}$Ru$_{0.5}$O$_3$ and Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ compounds exhibit ferrimagnetic ordering. Despite the chemical disorder, these compounds magnetically order, which is a rare finding.

While the crystal structures and the magnetic moments do not change significantly across the substitutions, the electrical properties drastically change by more than 7 orders of magnitude. The calculated electrical properties of the two compounds however are very different for the two compounds. While CaMn$_{0.5}$Ru$_{0.5}$O$_3$ shows a metallic (half-metallic) ground state as shown in the DOS in Figure 29, Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ shows an insulating state as shown in Figure 28b.
Figure 29: Spin-resolved total and atomic (Mn and Ru) density of states of chemically ordered ferrimagnetic CaMn$_{0.5}$Ru$_{0.5}$O$_3$. (From ref. 35)

The calculated DOS lend support to the significant decrease in conductivities with increase in La doping, as observed experimentally (Figure 27). The atom- and orbital-resolved DOS for Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ indicate that the up-spin states near the Fermi level have predominantly Mn $e_g$ and Ru $t_{2g}$ character as shown in Figure 26. The reason for this observed transition from a metallic to insulating state on doping with La, however is not well understood. It has been proposed previously by Dass et al.\textsuperscript{27} for the case of LaMn$_{0.5}$Ru$_{0.5}$O$_3$ that the increased occupation of the Ru $t_{2g}$ states (compared to CaMn$_{0.5}$Ru$_{0.5}$O$_3$ or Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$) leads to greater overlap with $t_{2g}$ states of the next neighboring Ru atoms, due to the spatially extended nature of these Ru 4d states. This overlap in turn opens up a small gap across the Fermi level. This could be a possible explanation for the opening of band gap on moving from CaMn$_{0.5}$Ru$_{0.5}$O$_3$ to Ca$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ as observed in our calculations.
2.9 Acknowledgement

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2.10 References

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CHAPTER 3: NOVEL HEXAGONAL PEROVSKITES

3.1 Contribution

This project focuses on the characterization of the structural, magnetic, and electrical properties for \( \text{Ba}_{1-x}\text{Sr}_x\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \) (0.9 ≥ x ≥ 0) hexagonal perovskites. This chapter is a manuscript and will be published with the following authors in order: Jennifer R. Soliz and Patrick M. Woodward. Jennifer R. Soliz has synthesized, measured, and analyzed the properties of all these materials. Patrick M. Woodward is Jennifer’s adviser and has been informed about the findings of this work.

3.2 Abstract

The structural, magnetic, and electrical properties for the \( \text{Ba}_{1-x}\text{Sr}_x\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \) (0.9 ≥ x ≥ 0) system have been investigated. Compositions with \( x = 0 \) and 0.5 are phase pure solid solutions while the in-between compositions are two-phase mixtures. \( \text{BaMn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \) adopts \( R\)-3m symmetry, exhibits the 9R crystal structure, and is an insulating, canted antiferromagnet with a \( T_N \) of 36 K. Neutron powder diffraction results reveal an antiferromagnetic structure with spins aligned anti-parallel in the \( z \)-direction and parallel in the \( xy \)-plane. \( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \) adopts the 6H crystal structure \( P6_3/mmc \) symmetry. It is an insulator, and the magnetic susceptibility peaks at 55 K. No
signs of long range magnetic order are evident in the low temperature neutron powder diffraction data, implying that $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ is a spin glass below 55 K.

### 3.3 Introduction

Perovskites are an exciting class of materials and are known to exhibit very diverse properties, such as colossal magnetoresistance, piezoelectricity, ionic or electronic conductivity, ferroelectricity, ferromagnetism, ferroelasticity, multiferroic behavior, etc.\(^1\) Ternary perovskites such as $\text{AMnO}_3$ or $\text{ARuO}_3$ have been widely explored due to their expansive range of properties.\(^2\)\(^-\)\(^5\)

$\text{SrMnO}_3$ (tolerance factor, $\tau_\text{s} = 1.0405$)\(^10\) is a Mott insulating type-G antiferromagnet ($T_N = 235$ K)\(^6\)\(^-\)\(^7\) that crystallizes with the 4H crystal structure.\(^23\)\(^-\)\(^26\) Under high pressures, $\text{SrMnO}_3$ adopts the ideal 3C perovskite crystal form.\(^23\)\(^-\)\(^26\) $\text{CaMnO}_3$ ($\tau = 1.0039$)\(^10\) is an insulating type-G antiferromagnet ($T_N = 120$ K)\(^6\)\(^-\)\(^7\) and consists of corner-shared octahedra.\(^27\) $\text{SrRuO}_3$ ($\tau = 0.9942$)\(^10\), which is isostructural to $\text{CaMnO}_3$, is a metallic ferromagnet ($T_C = 165$ K).\(^6\)\(^,\)\(^8\)\(^-\)\(^9\) When synthesized at ambient pressures, stoichiometric $\text{BaMnO}_3$ ($\tau = 1.1028$)\(^10\) adopts the 2H crystal structure (face-shared octahedra columns are oriented in the [001]; (see Figure 30) and is an antiferromagnet ($T_N = 59$ K).\(^11\)
Figure 30: 2H crystal structure of BaMnO$_3$ perovskite. The face-shared octahedra are oriented in the [001].

Depending on the synthesis conditions, BaRuO$_3$ ($\tau = 1.0537$)$^{10}$ has 4 crystalline forms: 9R, 4H, 6H, and 3C.$^{12-14}$ The latter two crystal structures are formed under high pressures.$^{12}$ The 9-layered rhombohedral (9R) unit cell, the 4-layered hexagonal (4H) unit cell, the 6-layered hexagonal (6H) unit cell, and the unit cell with 3-layered corner-shared octahedra have the hhchchhc pattern, the hchc pattern, the hhchhc pattern, and the ccc pattern, respectively. The h and c stand for face-shared and corner-shared connections linking octahedra, respectively. It can be expected that each polymorph will have
different magnetic and electrical transport properties. The 9R polymorph is a Mott-insulating Pauli paramagnet while the 4H polymorph is a metallic Pauli paramagnet.\(^{14}\)

Having both Mn and Ru cations present in the same compound is of particular interest due to the magnetotransport properties. There is an energetic overlap from the Mn \(t_{2g}\) and Ru \(t_{2g}\) \(\pi^*\) orbitals which can give rise to delocalized electrons and metallic conductivity, coupled with varying occupation of the Mn \(e_g\) orbitals which can impact the magnetism.\(^{16}\) Furthermore since relatively little is known about \(A_{1-x}A_x'Mn_{0.5}Ru_{0.5}O_3\) perovskites that form hexagonal polytypes, we explore the entire phase diagram compositions for the \(Ba_{1-x}Sr_{x}Mn_{0.5}Ru_{0.5}O_3\) \((1 \leq x \leq 0)\) system. This work sheds new light on this system since only the end members have previously been synthesized and characterized.

### 3.4 Experimental Section

\(Ba_{1-x}Sr_{x}Mn_{0.5}Ru_{0.5}O_3\) \((x = 1, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2,\) and \(0.1)\) samples were prepared by the conventional solid state ceramic method. Stoichiometric ratio amounts of the starting reagents \(BaCO_3\) \((99.997\text{ %, Alfa Aesar})\), \(SrCO_3\) \((\geq 99.9\text{ %, Sigma Aldrich})\), \(Mn_2O_3\) \((99.9\text{ %, CERAC})\), and \(RuO_2\) \((99.9\text{ %, Sigma Aldrich})\) were accurately weighed, mixed, and ground together using an agate mortar and pestle. High density \((99.8\text{ % dense})\) alumina crucibles were used to load the individual powders in order to maintain purity. All samples were heated to 1385 °C in air for 15 h using a high temperature box furnace. The products appeared as dark gray powders.
A Bruker D8 Advance diffractometer in Bragg-Brentano geometry equipped with a Ge 111 incident beam monochromator and Cu Kα₁ radiation (λ = 1.54059 Å) was used to collect the X-ray powder diffraction (XRPD) data to determine phase purity. This instrument also has a LynxEye one-dimensional detector. The scans were taken in the 2θ range of 10−90 °. The step size was 0.014286° 2θ, and the count time was 2.0 s/step. Each XRPD pattern was refined using the Rietveld Method administered through the TOPAS Academic software.¹⁷

Ba₁₋ₓSrₓMn₀.₅Ru₀.₅O₃ (x = 0 and 0.5) samples were cut into (~ 56-66 % dense) rectangular pellets with dimensions of approximately 0.25×0.5×1 cm. Copper wires were adhered to the pellet with conductive silver paint. The Quantum Design model 6000 physical property measurement system (PPMS) was used to carry out the 4-point dc resistivity measurements. No field was applied.

Magnetic measurements of Ba₁₋ₓSrₓMn₀.₅Ru₀.₅O₃ (x = 0, 0.5, and 0.6) powders (~ 20 mg) were collected using the superconducting quantum interference device (SQUID). Zero-field cooled (ZFC) and field cooled (FC) magnetic susceptibility curves were measured in 1 kG from 5-400 K temperature range. The hysteresis curves were swept with a field of ± 5 T.

Time of flight (TOF) neutron powder diffraction (NPD) data was collected on a High Intensity Powder Diffractometer (HIPD) instrument at the Lujan Neutron Scattering Center of Los Alamos National Laboratory. The beam source has a 20 Hz pulsed spallation neutron source generated by bombarding a W target with a pulsed proton beam. The samples were loaded individually in vanadium cans, and the collection times
were approximately 4 h. The instrument has 8 detector banks at 4 different angles. Banks 1 and 2 were scanned up to 153°, and the d-range was 0.4-4.0 Å. Banks 3 and 4 were scanned up to 90°, and the d-range was 0.56-5.57 Å. Banks 5 and 6 were scanned up to 40°, and the d-range was 1.13-11.28 Å. Banks 7 and 8 were scanned up to 40°, and the d-range was 3.54-38.0 Å. Because the higher banks have the poorer resolution, banks 7 and 8 were not used. This instrument can be further described from the Los Alamos National Laboratory website (http://lansce.lanl.gov/lujan/). The nuclear and magnetic phases were refined using the GSAS\textsuperscript{18} and SARAh\textsuperscript{19} software.

Since SrMn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} has been extensively studied, we will compare our results for the barium-substituted compounds to the structural, magnetic, and electrical data from Woodward et al.\textsuperscript{16}

### 3.5 Results and Discussion

#### 3.5.1 X-ray Diffraction

Each sample from the Ba\textsubscript{1-x}Sr\textsubscript{x}Mn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} (0.9 ≥ x ≥ 0) system was refined using the Rietveld Method. Table 7 reports the refined lattice parameters and Rietveld refinement values, which indicate good fits across the compositions. When 0.3 ≥ x ≥ 0.1, the refinement values were slightly higher due to large background noise. Figures 31-40 show individual XRPD patterns for each composition, and Figure 41 is a waterfall plot of the different compositions, which clearly shows the peak intensities associated with each phase. Figure 42 is a plot that shows the phase fractions for each phase in the Ba\textsubscript{1-x}Sr\textsubscript{x}Mn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} system.
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<td>9.332(1)</td>
<td>9.3481(8)</td>
<td>9.3702(5)</td>
<td>9.3855(4)</td>
<td>21.3077(5)</td>
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<td><strong>Phase %</strong></td>
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<td>91.44</td>
<td>98.74</td>
<td>100</td>
</tr>
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<td>( P6_3/mmc ) (6H)</td>
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<td>5.682(6)</td>
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<td><strong>c (Å)</strong></td>
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<td>53.56</td>
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<td>1.26</td>
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<td>27.651</td>
<td>30.620</td>
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<td>10.304</td>
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**Table 7:** Rietveld refinement values and unit cell dimensions of Ba\(_{1-x}\)Sr\(_x\)Mn\(_{0.5}\)Ru\(_{0.5}\)O\(_3\) compositions from X-ray powder diffraction.
Figure 31: X-ray powder diffraction pattern of BaMn$_{0.5}$Ru$_{0.5}$O$_3$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The blue vertical marks denote the positions of the Bragg reflections.
Figure 32: X-ray powder diffraction pattern of Ba$_{0.9}$Sr$_{0.1}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The blue vertical marks denote the positions of the Bragg reflections for the 4H (upper) and 6H (lower) phase, respectively.
Figure 33: X-ray powder diffraction pattern of $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The blue vertical marks denote the positions of the Bragg reflections for the 4H (upper) and 6H (lower) phases, respectively.
Figure 34: X-ray powder diffraction pattern of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The blue vertical marks denote the positions of the Bragg reflections for the 4H (upper) and 6H (lower) phases, respectively.
Figure 35: X-ray powder diffraction pattern of $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The blue vertical marks denote the positions of the Bragg reflections for the 4H (upper) and 6H (lower) phases, respectively.
Figure 36: X-ray powder diffraction pattern of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The blue vertical marks denote the positions of the Bragg reflections.
**Figure 37:** X-ray powder diffraction pattern of Ba$_{0.4}$Sr$_{0.6}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The blue vertical marks denote the positions of the Bragg reflections.
Figure 38: X-ray powder diffraction pattern of Ba$_{0.3}$Sr$_{0.7}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The blue vertical marks denote the positions of the Bragg reflections for the 3C (upper) and 6H (lower) phases, respectively.
Figure 39: X-ray powder diffraction pattern of $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The blue vertical marks denote the positions of the Bragg reflections for the 3C (upper) and 6H (lower) phases, respectively.
Figure 40: X-ray powder diffraction pattern of $\text{Ba}_{0.1}\text{Sr}_{0.9}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The blue vertical marks denote the positions of the Bragg reflections for the 3C (upper) and 6H (lower) phases, respectively.
Figure 41: Waterfall plot of the X-ray powder diffraction patterns for $\text{Ba}_{1-x}\text{Sr}_x\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ compositions. The top pattern (red line) and the bottom pattern (black line) correspond to $\text{SrMn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ and $\text{BaMn}_{0.5}\text{Ru}_{0.5}\text{O}_3$, respectively.
Figure 42: The percent of phases present in the $\text{Ba}_{1-x}\text{Sr}_x\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ system.

Our results from the $\text{BaMn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ composition closely match that of Pillai et al. and Yin et al. The structure refinements for $\text{SrMn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ have already been reported in great detail. We will compare our results to the $\text{SrMn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ compound reported in Woodward et al.

Only $\text{BaMn}_{0.5}\text{Ru}_{0.5}\text{O}_3$, $\text{Ba}_{0.4}\text{Sr}_{0.6}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$, and $\text{Ba}_{0.4}\text{Sr}_{0.6}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ samples were found to be homogeneous solid solutions while the other compositions were two-phase mixtures. $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ sample is nearly single phase in that it has
98.74% 4H phase and 1.26% 6H phase. The pure barium composition exhibits the 9R crystal structure, meaning that its rhombohedral unit cell is composed of 9 layers of octahedra connected in the hhchhhchhc fashion. Both $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ and $\text{Ba}_{0.4}\text{Sr}_{0.6}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ samples have the 6H crystal structure, meaning that its hexagonal unit cells have 6 layers of octahedra repeating in the hchchcc pattern. For $0.4 \leq x \leq 0.1$ compositions, the two-phase mixtures were composed of 4H and 6H crystal structures. The Sr-rich samples ($0.9 \geq x \geq 0.7$) were two-phase mixtures of 6H and 3C crystal structures. The 3C crystal structure has 3 layers of corner-shared octahedra, i.e. the ccc pattern in the tetragonal unit cell. For each composition that has a partial 3C component, these all showed $I4/mcm$ symmetry, which is associated with the $a^0d^0c^-$ glazer tilting. The different crystal structures (9R, 4H, 6H, and 3C) are shown in Figures 43-46.
Figure 43: The 9R crystal structure of BaMn$_{0.5}$Ru$_{0.5}$O$_3$ compound.
Figure 44: The 4H crystal structure of Ba$_{0.9}$Sr$_{0.1}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ compound.
Figure 45: The 6H crystal structure of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ compound.
3.5.2 Electrical Properties

The resistance was measured on \( \text{Ba}_{1-x}\text{Sr}_x\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \) (\( x = 0 \) and 0.5) samples as a function of temperature. At 26 K and room temperature, the resistivity for \( \text{BaMn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \) is \( 5.53 \times 10^4 \, \Omega\cdot\text{cm} \) and \( 1.98 \times 10^{-1} \, \Omega\cdot\text{cm} \), respectively. For \( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \), the resistivity is \( 1.68 \times 10^3 \, \Omega\cdot\text{cm} \) and \( 5.77 \times 10^{-2} \, \Omega\cdot\text{cm} \) at 26 K and room temperature, respectively. Figure 47 plots the log of the resistivity versus temperature for both compounds, clearly marking both compounds as insulators. An acceptable fit of the data to a variable range hopping model over the temperature range of...
38-219 K is shown in Figure 48. The $R^2$ values are 0.9997 and 0.9998 for BaMn$_{0.5}$Ru$_{0.5}$O$_3$ and Ba$_{0.5}$Sr$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$, respectively. The linear function supports that both compounds have localized electrons that can hop from one localized atom site to another.

**Figure 47:** Log of the resistivity as a function of temperature for AMn$_{0.5}$Ru$_{0.5}$O$_3$ ($A =$ Ba and Ba$_{0.5}$Sr$_{0.5}$) samples.
3.5.3 Magnetic Properties

The magnetization was carried out using a SQUID magnetometer. Figure 49 shows the ZFC and FC measurements, where 1 kG field was used. The susceptibility ($\chi$) plot supports antiferromagnetic behavior with $T_N$ value of 36 K for $\text{BaMn}_{0.5}\text{Ru}_{0.5}\text{O}_3$. In the paramagnetic temperature regime, the ZFC and FC susceptibility measurements for $\text{BaMn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ do not overlay on each other, which infers some canting. $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ and $\text{Ba}_{0.4}\text{Sr}_{0.6}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ show glassy behavior. The ZFC
magnetization dip below the magnetic susceptibility peaks and the cusps for Ba$_{0.5}$Sr$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ and Ba$_{0.4}$Sr$_{0.6}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ indicate there may be glassy behavior.

![Graph](image)

**Figure 49:** Zero-field cooled and field cooled susceptibility for Ba$_{1-x}$Sr$_x$Mn$_{0.5}$Ru$_{0.5}$O$_3$ ($x = 0$, 0.5, and 0.6) samples.

Curie-Weiss plots from ZFC and FC are shown in Figures 50-52. Table 8 reports the Curie constants, Weiss constants ($\theta$), and effective moments ($\mu_{\text{eff}}$) for BaMn$_{0.5}$Ru$_{0.5}$O$_3$ and Ba$_{0.4}$Sr$_{0.6}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ compounds. The Curie constant gages the amount of unpaired electrons and expresses how the unpaired electrons interact with each other in the paramagnetic region. The Weiss constant signifies the short-range magnetic interactions.
As shown in Figure 51, the inverse susceptibility is not linear in the paramagnetic region for \( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \). Thus the Curie-Weiss information was not extracted for \( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \) since the paramagnetic region that could be measured did not give a linear Curie-Weiss plot. The attainable \( R^2 \) value for \( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \) is lower than for the other two compounds. Higher temperatures would be needed to extrapolate reliable Curie-Weiss information for \( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \). **Table 8** reports the effective moments for \( \text{BaMn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \) and \( \text{Ba}_{0.4}\text{Sr}_{0.6}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \).

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \text{BaMn}<em>{0.5}\text{Ru}</em>{0.5}\text{O}_3 )</th>
<th>( \text{Ba}<em>{0.5}\text{Sr}</em>{0.5}\text{Mn}<em>{0.5}\text{Ru}</em>{0.5}\text{O}_3 )</th>
<th>( \text{Ba}<em>{0.4}\text{Sr}</em>{0.6}\text{Mn}<em>{0.5}\text{Ru}</em>{0.5}\text{O}_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temperature range (K)</strong></td>
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<td>255–328</td>
<td>100–360</td>
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<td><strong>Curie constant</strong></td>
<td>1.29(3)</td>
<td>-</td>
<td>1.020(2)</td>
</tr>
<tr>
<td>( \theta ) (K)</td>
<td>(-869(10))</td>
<td>-</td>
<td>(-23.0(5))</td>
</tr>
<tr>
<td>( \mu_{\text{eff}} ) (( \mu_\text{B} ))</td>
<td>3.212</td>
<td>-</td>
<td>2.856</td>
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<td>( R^2 )</td>
<td>0.9991</td>
<td>0.998</td>
<td>0.99996</td>
</tr>
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</table>

**Table 8**: Field cooled magnetic information gathered from the Curie-Weiss plots.
Figure 50: Zero-field cooled and field cooled Curie-Weiss plot for BaMn$_{0.5}$Ru$_{0.5}$O$_3$. 

BaMn$_{0.5}$Ru$_{0.5}$O$_3$, 1kG
Figure 51: Zero-field cooled and field cooled Curie-Weiss plot for \( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \).
Using the extracted Curie constants gathered from the Curie-Weiss plots, the effective moments are 3.212 $\mu_B$ and 2.856 $\mu_B$ for BaMn$_{0.5}$Ru$_{0.5}$O$_3$ and Ba$_{0.4}$Sr$_{0.6}$Mn$_{0.5}$Ru$_{0.5}$O$_3$, respectively. The expected spin-only effective moment for a compound containing equal amounts of Mn$^{3+}$ (high spin d$^4$) and Ru$^{5+}$ (d$^3$) is 4.416 $\mu_B$. If the cation oxidation states were Mn$^{4+}$ (d$^3$) and Ru$^{4+}$ (low spin d$^4$) instead the effective spin-only moment would drop to 3.391 $\mu_B$. Thus, it appears that the BaMn$_{0.5}$Ru$_{0.5}$O$_3$ favors Mn$^{4+}$ and Ru$^{4+}$ oxidation states. While the effective moment for Ba$_{0.4}$Sr$_{0.6}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ is slightly lower than the
calculated effective moment for Mn$^{4+}$ and Ru$^{4+}$, the value is closer to these oxidation states than Mn$^{3+}$ and Ru$^{5+}$.

Normalized Curie-Weiss plots for BaMn$_{0.5}$Ru$_{0.5}$O$_3$ and Ba$_{0.4}$Sr$_{0.6}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ were also made to verify the involvement of unpaired electrons and help support the presence of AFM or FM behavior; see Figures 53-54. A normalized Curie-Weiss plot was not made for Ba$_{0.5}$Sr$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ because the paramagnetic regime was not linear.

The y-axis and x-axis for these normalized Curie-Weiss plots can be calculated using Equation 1 and 2, respectively.

$$\frac{C}{\chi} \pm 1$$ \quad \text{Equation 1}

$$\frac{T}{\theta}$$ \quad \text{Equation 2}

The Curie constant, Weiss constant, and temperature are defined as $C$, $\theta$, and $T$, respectively. In Equation 1 if the sign of $\theta$ is negative, then 1 will be subtracted. Likewise if the sign of $\theta$ is positive, then the 1 will be added. This is done so that the data will always condense to the ideal Curie-Weiss line (represented as a dashed line in the normalized Curie-Weiss plots; see Figures 53-54) regardless of any sign changes to $\theta$.

By condensing the inverse susceptibility curves to the ideal Curie-Weiss line, the strength of these normalized plots lies in the ability to directly compare different materials in different field strengths. For instance, a positive deviation from the ideal Curie-Weiss line indicates AFM behavior. A negative deviation from the linear line supports FM or FiM behavior.
Figure 53: Normalized Curie-Weiss plot of the zero-field cooled (open gray circles) and field cooled (shaded gray circles) magnetization for BaMn$_{0.5}$Ru$_{0.5}$O$_3$. The dashed line is the ideal Curie-Weiss line.
Figure 54: Normalized Curie-Weiss plot of the zero-field cooled (open red squares) and field cooled (shaded red squares) magnetization for Ba_{0.4}Sr_{0.6}Mn_{0.5}Ru_{0.5}O_{3}. The dashed line is the ideal Curie-Weiss line.

For the pure barium compound, there is a negative deviation followed by the curve moving upwards towards the ideal Curie-Weiss line in the low temperature regime. This could be a reflection of domain wall movement and an indication of spin frustration. The combination of a large negative \( \theta \) with a much smaller \( T_N \) indicates a high degree of frustration. According to Greeden,^22 if the \(|\theta|/T_N\) is > 10, then the material meets the criteria for spin frustration. In the case of BaMn_{0.5}Ru_{0.5}O_{3}, the calculated value from \(|\theta|/T_N\) is approximately 24, well above the minimum.
The Ba$_{0.4}$Sr$_{0.6}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ compound is a less complicated case. The normalized Curie-Weiss plot (see Figure 54) clearly supports the presence of AFM behavior since the curve deviates upward from the ideal Curie-Weiss line. The $\theta$ is $-23.0(5)$ K for Ba$_{0.4}$Sr$_{0.6}$Mn$_{0.5}$Ru$_{0.5}$O$_3$, which indicates AFM interactions since the sign of $\theta$ is negative. The $|\theta|/T_N \approx 0.4$. The separation between the ZFC and FC susceptibility plots at temperatures below the cusp in the susceptibility could be a signature of spin glass state below 55 K.

Figure 55 shows the magnetization verses field plots for BaMn$_{0.5}$Ru$_{0.5}$O$_3$, Ba$_{0.5}$Sr$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$, and Ba$_{0.4}$Sr$_{0.6}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ at 5 K, and the field was swept $\pm$ 5 T. The small opening in the BaMn$_{0.5}$Ru$_{0.5}$O$_3$ curve could infer spin canting.
Figure 55: Magnetization as a function of the applied field for $AMn_{0.5}Ru_{0.5}O_3$ ($A = Ba, Ba_{0.5}Sr_{0.5}$, and $Ba_{0.4}Sr_{0.6}$) compounds.

3.5.4 Neutron Diffraction

Time of flight neutron powder diffraction data was collected at room temperature and 4 K for $BaMn_{0.5}Ru_{0.5}O_3$ and $Ba_{0.5}Sr_{0.5}Mn_{0.5}Ru_{0.5}O_3$; see Figures 56-59. Only histograms 1, 3, and 5 are plotted since histograms 2, 4, and 6 are mirrors of histograms 1, 3, and 5, respectively. Tables 9-11 lists the refinement values and all the refined structural information for these two compounds in the respective temperatures. The refinement values from each compound reported in Table 9 indicate reasonably good fits. The room temperature neutron powder diffraction data matches closely to the XRPD
data. No phase transitions occurred for either compound when the temperature was cooled; thus the space group symmetries were maintained.
Figure 56: Room temperature time of flight neutron powder diffraction patterns from histograms 1, 3, and 5 for BaMn$_{0.5}$Ru$_{0.5}$O$_3$. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The blue vertical marks denote the positions of the Bragg reflections.
Figure 57: Room temperature time of flight neutron powder diffraction patterns from histograms 1, 3, and 5 for Ba\textsubscript{0.5}Sr\textsubscript{0.5}Mn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3}. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The blue vertical marks denote the positions of the Bragg reflections.
Figure 58: Low temperature (4 K) time of flight neutron powder diffraction patterns from histograms 1, 3, and 5 for BaMn$_{0.5}$Ru$_{0.5}$O$_3$. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The blue vertical marks denote the positions of the Bragg reflections.
Figure 59: Low temperature (4 K) time of flight neutron powder diffraction patterns from histograms 1, 3, and 5 for Ba$_{0.5}$Sr$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The blue vertical marks denote the positions of the Bragg reflections.
Table 9: Lattice parameters and refinement results for $A_{0.5}$Ru$_{0.5}$O$_3$ ($A = Ba$, Ba$_{0.5}$Sr$_{0.5}$) from time of flight neutron powder diffraction.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$BaMn_{0.5}Ru_{0.5}O_3$</th>
<th>$Ba_{0.5}Sr_{0.5}Mn_{0.5}Ru_{0.5}O_3$</th>
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<td>$R-3c$</td>
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<td>5.7251(0)</td>
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<tr>
<td>$c$(Å)</td>
<td>21.3900(3)</td>
<td>21.3672(2)</td>
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<td>606.52(1)</td>
</tr>
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</tr>
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<td>0.0200</td>
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<td>0.0208</td>
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<td>$\chi^2$</td>
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<tr>
<td></td>
<td>BaMn$<em>{0.5}$Ru$</em>{0.5}$O$_3$</td>
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</tr>
<tr>
<td>----------</td>
<td>-----------------------------</td>
<td>----------</td>
</tr>
<tr>
<td>T (K):</td>
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<td>4</td>
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<tr>
<td>Ba (1) 3a</td>
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<td>(0, 0, 0)</td>
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<tr>
<td>U$_{iso}$ x 100</td>
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<td>0.26(3)</td>
</tr>
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<td>Occupancy</td>
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<td>1</td>
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<tr>
<td>Ba (2) 6c, (0, 0, z)</td>
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<td>0.21770(4)</td>
</tr>
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<tr>
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<td>(0, 0, ½)</td>
</tr>
<tr>
<td>U$_{iso}$ x 100</td>
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<td>1.2(8)</td>
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<td>Mn Occupancy</td>
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<td>Ru Occupancy</td>
<td>0.357(1)</td>
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</tr>
<tr>
<td>U$_{iso}$ x 100</td>
<td>0.39(3)</td>
<td>0.01(2)</td>
</tr>
<tr>
<td>Mn Occupancy</td>
<td>0.448(1)</td>
<td>0.449(1)</td>
</tr>
<tr>
<td>Ru Occupancy</td>
<td>0.552(1)</td>
<td>0.551(1)</td>
</tr>
<tr>
<td>O(1) 9e</td>
<td>(½, 0, 0)</td>
<td>(½, 0, 0)</td>
</tr>
<tr>
<td>U$<em>{iso}$ or U$</em>{11}$, U$<em>{22}$, U$</em>{33}$, U$<em>{12}$, U$</em>{13}$, U$_{23}$ x 100</td>
<td>0.71(3), 0.06(4), 1.23(3), 0.03(2), 0.32(1), 0.64(3)</td>
<td>0.24(1)</td>
</tr>
<tr>
<td>Occupancy</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>O(2) 18h, x</td>
<td>0.15247(5)</td>
<td>0.15304(4)</td>
</tr>
<tr>
<td>y</td>
<td>-0.15247(5)</td>
<td>0.84696(4)</td>
</tr>
<tr>
<td>z</td>
<td>0.55782(2)</td>
<td>0.55794(1)</td>
</tr>
<tr>
<td>U$_{iso}$ x 100</td>
<td>0.620(9)</td>
<td>0.329(7)</td>
</tr>
<tr>
<td>Occupancy</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 10: Atomic positions for BaMn$_{0.5}$Ru$_{0.5}$O$_3$ from time of flight neutron powder diffraction.
Table 11: Atomic positions for Ba$_{0.5}$Sr$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ from time of flight neutron powder diffraction.

The oxygen occupancies for both BaMn$_{0.5}$Ru$_{0.5}$O$_3$ and Ba$_{0.5}$Sr$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ were set to one since the refined occupancies did not significantly refine away from one. The refinement values did not significantly change either when the occupancies were set.
back to one. Interestingly while there are no findings in the literature of any chemically
ordered $AM_{0.5}Ru_{0.5}O_3$ perovskites, the refined occupancies of Mn/Ru (1) and Mn/Ru (2)
for $BaMn_{0.5}Ru_{0.5}O_3$ showed site preferences at both low and room temperatures. The Ru
and Mn cations preferred to sit on the outer corner-shared octahedra ($M_2$) and the inner
face-shared octahedra ($M_1$), respectively. As for $Ba_{0.5}Sr_{0.5}Mn_{0.5}Ru_{0.5}O_3$, neither $B$-site
cation showed a site preference for the corner- or face-shared octahedra.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$BaMn_{0.5}Ru_{0.5}O_3$</th>
<th>$Ba_{0.5}Sr_{0.5}Mn_{0.5}Ru_{0.5}O_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ba &amp; Mn/Ru</td>
<td>Ba &amp; Mn/Ru</td>
</tr>
<tr>
<td></td>
<td>$O_2$-Mn/Ru$_2$ ($^\circ$)</td>
<td>$O_2$-Mn/Ru$_2$ ($^\circ$)</td>
</tr>
<tr>
<td></td>
<td>78.40(3)</td>
<td>77.90(3)</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>180</td>
</tr>
<tr>
<td>Mn/Ru$_1$-$O_2$-Mn/Ru$_2$ ($^\circ$)</td>
<td>6$\times$ 1.9603(3)</td>
<td>6$\times$ 1.9552(3)</td>
</tr>
<tr>
<td></td>
<td>3$\times$ 1.9621(1)</td>
<td>3$\times$ 1.9411(1)</td>
</tr>
<tr>
<td>Mn/Ru$_2$-$O_3$ ($\bar{A}$)</td>
<td>3$\times$ 1.9800(8)</td>
<td>3$\times$ 1.9920(8)</td>
</tr>
<tr>
<td></td>
<td>2$\times$ 2.4790(2)</td>
<td>2$\times$ 2.4510(2)</td>
</tr>
<tr>
<td>Mn/Ru$_3$-$Mn/Ru$_2$ ($\bar{A}$)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mn$_1$ magnetic moment ($\mu_B$)</td>
<td>-</td>
<td>1.60(4)</td>
</tr>
<tr>
<td>Mn$_2$ magnetic moment ($\mu_B$)</td>
<td>-</td>
<td>2.15(2)</td>
</tr>
</tbody>
</table>

**Table 12:** Bond angles, bond lengths, and magnetic moments for $AMn_{0.5}Ru_{0.5}O_3$ ($A =$
$Ba$ and $Ba_{0.5}Sr_{0.5}$) from time of flight neutron powder diffraction.
Figure 60: Metal-metal bonding within a trimer from BaMn$_{0.5}$Ru$_{0.5}$O$_3$. The red and white lines refer to the metal-metal bonding and B-O bond distances, respectively, at 4 K.

Figure 61: Metal-metal bonding within a dimer from Ba$_{0.5}$Sr$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$. The red and white lines refer to the metal-metal bonding and B-O bond distances, respectively, at 4 K.
Table 12 reports the bond angles, bond distances, metal-metal bonding, and refined magnetic moments for BaMn$_{0.5}$Ru$_{0.5}$O$_3$ and Ba$_{0.5}$Sr$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$. Considering that Mn has a site preference for the middle face-shared octahedra in the 9R crystal structure for BaMn$_{0.5}$Ru$_{0.5}$O$_3$, the bond lengths for this particular octahedron is 1.9552(3) Å. Taking into account that Mn$^{3+}$-O and Mn$^{4+}$-O bond lengths are 2.045 Å and 1.93 Å, respectively, the B-O bond lengths gathered from neutron powder diffraction infer mixed valency of Mn with slightly more Mn$^{4+}$ character and by default more Ru$^{4+}$ character. If we look at the symmetrical octahedron that does not have metal-metal bonding interfering, the Mn/Ru(1)-O bond length is 1.9842(6) Å for Ba$_{0.5}$Sr$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$. Since Mn and Ru do not have a site preference, this infers mixed valency for the Mn and Ru cations with slightly more Mn$^{3+}$ character. Considering that Mn and Ru share the same site, these are purely estimates of the oxidation states for Mn and Ru for both compounds. XANES is one method that would be more intuitive about the oxidation states. Figure 60 shows the metal-metal bonding found within the trimers of BaMn$_{0.5}$Ru$_{0.5}$O$_3$. As noted in Figure 60, the metal sites on the outer corner-connecting octahedra (M$_2$) shift towards the metal site found in the middle face-shared octahedron (M$_1$), which supports metal-metal bonding. Likewise, metal-metal bonding exists on the dimers for Ba$_{0.5}$Sr$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$, in that the metal sites are shifted towards each other; see Figure 61. These metal-metal bond lengths from both compounds match well with the metal-metal bonding found in SrMnO$_3$, which is 2.500(6) Å from the dimers in its 4H hexagonal crystal structure. Metal-metal bonding helps stabilize the hexagonal crystal structures.
At low temperature, new magnetic peaks appeared in the diffraction pattern for the \( \text{BaMn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \) sample. **Figure 62** shows an overlay of the 4 K and 300 K neutron diffraction patterns, and the magnetic peaks are marked with a green asterisk. The propagation vector \((0, 0, 0.5)\) was found to be the best model to fit the new magnetic peaks. As **Figure 63** depicts, the layered spin direction is aligned parallel in the \( ab \)-plane with anti-parallel spins along the \( c \)-axis. In the magnetic structure, ions in octahedra that are connected either by face-sharing or by corner-sharing are antiferromagnetically coupled to their nearest neighbors.
Figure 62: Low temperature (top) and room temperature (bottom) time of flight neutron powder diffraction patterns from histogram 3 for BaMn$_{0.5}$Ru$_{0.5}$O$_3$. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The blue vertical marks relating to the 300 K neutron powder diffraction pattern denote the Bragg reflections of just the nuclear phase. In the 4 K neutron powder diffraction pattern, the upper and lower blue vertical marks denote the Bragg reflections of the nuclear phase and the magnetic phase, respectively. The green asterisks point to the magnetic peaks that arise at low temperatures.
**Figure 63:** The $1\times1\times2$ magnetic structure for BaMn$_{0.5}$Ru$_{0.5}$O$_3$. The grey spheres correspond to both the Mn and Ru magnetic ions. The red arrows have the spins oriented in the up direction, and the gray arrows have the spins positioned downward. The numbers off to the side indicate the magnetic ion sites from the magnetic phase.
Based on assumptions that little magnetic contribution is coming from the Ru cations, the Mn magnetic moments were only refined. This is purely an assumption to focus on the magnitude of the moments. Magnetic moments along different directions were also tried but these led to inferior fits and did not model the intensities of the magnetic peaks well, see Table 13. Thus we can conclude with confidence that the magnetic moment is favored along the z-axis. Considering the different structural environments for the magnetic ions, the Mn cations exhibited different moments for the middle face-shared octahedra (M₁) versus the outer corner-shared octahedra (M₂). The Mn cations on the M₁ and M₂ sites had a moment of 1.60(4) and 2.15(2) \( \mu_B \), respectively. These moments are fairly low from expected traditional moments of Mn\(^{3+} \) or Mn\(^{4+} \). The low refined moments can be attributed to the Ru magnetic moments contributing to the total magnetic moments on these sites, which should reduce the overall moment if Mn and Ru are antiferromagnetically coupled.

<table>
<thead>
<tr>
<th>Moment along x-axis</th>
<th>Histogram 3 R_p</th>
<th>Histogram 3 R_wp</th>
<th>( \chi^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moment along y-axis</td>
<td>0.0206</td>
<td>0.0280</td>
<td>8.570</td>
</tr>
<tr>
<td>Moment along z-axis</td>
<td>0.0206</td>
<td>0.0280</td>
<td>8.589</td>
</tr>
<tr>
<td>Moments along xy</td>
<td>0.0202</td>
<td>0.0267</td>
<td>6.942</td>
</tr>
<tr>
<td>Moments along xz</td>
<td>0.0202</td>
<td>0.0267</td>
<td>6.971</td>
</tr>
<tr>
<td>Moments along yz</td>
<td>0.0202</td>
<td>0.0267</td>
<td>6.971</td>
</tr>
<tr>
<td>Moments along xyz</td>
<td>0.0207</td>
<td>0.0284</td>
<td>9.072</td>
</tr>
</tbody>
</table>
Table 13: Comparison of histogram 3 refinement values from time of flight neutron powder diffraction at 4 K obtained from the magnetic moments along different directions for BaMn$_{0.5}$Ru$_{0.5}$O$_3$.

As for the Ba$_{0.5}$Sr$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ compound, no new peaks occurred in the low temperature neutron powder diffraction patterns nor did the peak intensities increase, except one peak with a d-spacing of $\approx 2.8$ Å had a slightly higher peak intensity; see Figure 64. Because of this uncertainty in whether a magnetic structure exists at low temperatures, the neutron powder diffractions patterns were refined with and without a magnetic phase. Since no new magnetic reflections occurred at 4 K, the propagation vector (0, 0, 0) was used. A similar layered spin arrangement to the pure barium compound was also used; i.e. the spins were ferromagnetically aligned in the xy-plane, and antiferromagnetically aligned along the z-axis; see Figure 65. In either case of face- or corner-connecting octahedra, the spins are antiferromagnetically coupled to their nearest neighbors.
Figure 64: Low temperature (top) and room temperature (bottom) time of flight neutron powder diffraction patterns from histogram 3 for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The blue vertical marks denote the Bragg reflections of just the nuclear phase.
Figure 65: The 1×1×1 magnetic structure for Ba$_{0.5}$Sr$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$. The grey spheres correspond to both the Mn and Ru magnetic ions. The red arrows have the spins oriented in the up direction, and the gray arrows have the spins positioned downward. The numbers off to the side indicate the magnetic ion sites from the magnetic phase.

For the magnetic phase, only the Mn moments were refined, and like the pure barium sample, the Mn magnetic moments were different depending on the structural environment. In the 6H structure, the face-shared octahedra that form a dimer between
the magnetic ions and the completely cornered-shared octahedra will be represented as M₁ and M₂, respectively. The Mn moments for M₁ (atoms 1 and 2; see Figure 65) and M₂ (atoms 3-6; see Figure 65) are 0.81(9) μB and 0.3(1) μB, respectively. Because these moments are unusually small for Mn⁵⁺/⁴⁺, Ba₀.₅Sr₀.₅Mn₀.₅Ru₀.₅O₃ was refined without a magnetic phase. Figure 64 shows the refinements of the time of flight neutron powder diffraction patterns from histogram 3 at room temperature and at 4 K without a magnetic phase. Table 14 reports the comparison of Ba₀.₅Sr₀.₅Mn₀.₅Ru₀.₅O₃ with and without a magnetic structure at 4 K. The results taken in combination with the susceptibility measurements strongly suggest that the spins in Ba₀.₅Sr₀.₅Mn₀.₅Ru₀.₅O₃ freeze into a spin glass.

<table>
<thead>
<tr>
<th>Ba₀.₅Sr₀.₅Mn₀.₅Ru₀.₅O₃ at 4K</th>
<th>R_p</th>
<th>R_wp</th>
<th>χ²</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM phase</td>
<td>0.0330</td>
<td>0.0262</td>
<td>9.290</td>
</tr>
<tr>
<td>No magnetic phase</td>
<td>0.0222</td>
<td>0.0276</td>
<td>6.882</td>
</tr>
</tbody>
</table>

Table 14: Comparing the refinement values of time of flight neutron powder diffraction for Ba₀.₅Sr₀.₅Mn₀.₅Ru₀.₅O₃ with and without a magnetic phase at 4 K.

3.6 Discussion

We have successfully synthesized and characterized the structural, magnetic, and electrical properties for Ba₁₋ₓSrₓMn₀.₅Ru₀.₅O₃ (0.9 ≥ x ≥ 0) system. Phase-pure BaMn₀.₅Ru₀.₅O₃ and Ba₀.₅Sr₀.₅Mn₀.₅Ru₀.₅O₃ compounds exhibit the 9R and 6H structures, respectively. For BaMn₀.₅Ru₀.₅O₃, the Mn cations were found to have site preferences for
the center octahedron in the trimer of face-sharing octahedra in the 9R structure. Whereas, the $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ sample did not show any site preferences for either $B$-site cation. Both $\text{BaMn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ compounds showed evidence of metal-metal bonding across the trimers and dimers, respectively. The metal-metal bonding from these two structures is on par with the metal-metal bonding observed from the 4H crystal structure of $\text{SrMnO}_3$.\textsuperscript{27}

From the magnetic measurements gathered from SQUID, $\text{BaMn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ is a canted antiferromagnet while $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ and $\text{Ba}_{0.4}\text{Sr}_{0.6}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ compounds show glassy behavior. The structural and magnetic properties for $\text{Ba}_{0.4}\text{Sr}_{0.6}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ resemble $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ in that both compounds adopt the same symmetry, manifest the 6H crystal structure, and appear to form spin glass states below roughly 50 K. For $0.9 \geq x \geq 0.7$ compositions, these are two-phase mixtures of 3C and 6H. The $0.4 \geq x \geq 0.1$ compositions are two-phase mixtures of 6H and 4H. As the tolerance factor increases, the amount of face-connecting octahedra increases, and the crystal structures change from 3C to 6H to 4H to 9R.

From neutron powder diffraction, $\text{BaMn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ is an antiferromagnet with spins ferromagnetically coupled in the $xy$-plane and spins antiferromagnetically coupled along the $z$-axis. The $M_1$ and $M_2$ moments for Mn are 1.60(4) $\mu_B$ and 2.15(2) $\mu_B$, respectively. These refined magnetic moments are different because the surrounding environments for $M_1$ and $M_2$ are different in the 9R crystal structure. While these moments are low for Mn$^{3+}$/$^{4+}$ cations, it is expected that the magnetic moments from Ru are contributing to the total magnetic moment. As for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$, neutron
powder diffraction confirms that a magnetic structure does not exist at 4 K based on the comparison of the refinements with and without a magnetic phase. Instead glassy behavior resulting from the chemical disorder is responsible for the magnetic behavior observed.

Future studies from Ru Mossbauer spectroscopy or XANES would be ways to detect the mixed valence states of the Ru or both the Mn and Ru cations, respectively. These measurements could remove any ambiguity of charge transfer between the two cations.

3.7 Acknowledgement

Financial support from the NSF through a Materials World Network grant (MWN-0603128) is gratefully acknowledged. We would also like to acknowledge Dr. Graham King for assistance with the TOF neutron diffraction experiments. This work has benefited from the use of HIPD at the Lujan Center at Los Alamos Neutron Science Center, funded by DOE Office of Basic Energy Sciences. Los Alamos National Laboratory is operated by Los Alamos National Security LLC under DOE Contract No. DE-AC52 06NA25396.
3.8 References

CHAPTER 4: SYNTHESIS AND CHARACTERIZATION OF 
\[ \text{Ba}_{1-x}\text{La}_x\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \] PEROVSKITES

4.1 Contribution

The focus of this project is to continue characterizing barium-based manganese ruthenates. Chapter 3 studies the effect of chemical pressure with isovalent substitution of Sr\(^{2+}\) in the Ba\(_{1-x}\)Sr\(_x\)Mn\(_{0.5}\)Ru\(_{0.5}\)O\(_3\) system. Now the story continues of how the properties are affected with aliovalent substitution of La\(^{3+}\). This chapter will be submitted for publishing, and the order of authors is as followed: Jennifer R. Soliz and Patrick M. Woodward. Jennifer R. Soliz has synthesized and characterized the structural, magnetic, and electrical properties for Ba\(_{1-x}\)La\(_x\)Mn\(_{0.5}\)Ru\(_{0.5}\)O\(_3\). Patrick M. Woodward is Jennifer’s adviser and has been informed about the details of this project.

4.2 Abstract

The structural, magnetic, and electrical properties for the phase diagram of Ba\(_{1-x}\)La\(_x\)Mn\(_{0.5}\)Ru\(_{0.5}\)O\(_3\) \((0.5 \geq x \geq 0)\) system were investigated. The end members were found to be phase pure solid solutions while the in-between compositions were heterogeneous mixtures. While BaMn\(_{0.5}\)Ru\(_{0.5}\)O\(_3\) exhibits the 9R \((R\text{-}3m\) space group symmetry) crystal structure and is an insulating, canted antiferromagnet with a \(T_N\) of 36
K, \( \text{Ba}_{0.5}\text{La}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \) manifests the 3C (\( I4/mcm \) space group symmetry) crystal structure and is an insulating ferri- or ferromagnet with a \( T_C \) of 205 K. Low temperature neutron powder diffraction results show \( \text{BaMn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \) to exhibit magnetic moments of 1.60(4) \( \mu_B \) and 2.15(2) \( \mu_B \) for face-shared octahedra and corner-shared octahedra, respectively. As for \( \text{Ba}_{0.5}\text{La}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \), the magnetic moments from a ferrimagnetic structure are more reasonable than the moments obtained from a ferromagnetic structure, so we report the moments of a ferrimagnetic structure to be 3.7 \( \mu_B \) and -0.88(2) \( \mu_B \) for Mn and Ru cations, respectively.

### 4.3 Introduction

Perovskites without a doubt are a fascinating class of materials that exhibit a vast breath of properties.\(^1\) By fully or partially substituting in another cation for either the \( A \)-site or \( B \)-site in perovskites, the properties can change significantly. The widely studied \( \text{LaMnO}_3 \) (tolerance factor, \( \tau = 0.9543 \))\(^{10}\) exhibits insulating behavior and A-type AFM (\( T_N = 140 \) K). This perovskite has a cooperative JT distortion due to the Mn\(^{3+} \). From the orientation of the half-filled \( d_{z^2} \) orbitals, also referred to as orbital ordering, the super-exchange magnetic interactions stabilize this type of magnetism. Replacing Mn\(^{3+} \) with Ru\(^{3+} \), \( \text{LaRuO}_3 \) (\( \tau = 0.9383 \))\(^{10}\) is a metallic paramagnet.\(^6\)\(^8\)\(^-\)\(^9\)

Perovskites that have Ba\(^{2+} \) (atomic radii = 1.61 Å) instead of the smaller cation La\(^{3+} \) (atomic radii = 1.36 Å) sitting on the \( A \)-site are known to adopt different structural modifications. As previously mentioned, the large size of the atomic radii from Ba\(^{2+} \) causes the tolerance factor to increase above one, which often leads to face-sharing octahedra. Depending on the conditions of how the synthesis was carried out and the
oxygen vacancies, stoichiometric BaMnO$_3$ ($\tau = 1.1028$) has face-sharing octahedra columns along the [001], which is commonly referred to as the 2H crystal structure. BaMnO$_3$ is also an antiferromagnet with a $T_N$ of 59 K. Also dependent upon the synthesis conditions is BaRuO$_3$ ($\tau = 1.0537$), where this complex oxide has 4 crystalline forms: 9R, 4H, 6H, and 3C. All but the 3C crystal structure have layered face-sharing octahedra in the unit cell. The 9R structure is a Mott-insulating Pauli paramagnet, and the 4H structure is a metallic Pauli paramagnet. In the case of La$_{1-x}$Ba$_x$MnO$_3$ ($1 \leq x \leq 0$) system, the $x \leq 0.35$ compositions are phase-pure semi-conducting ferromagnets$^{25-26}$. The $T_C$ and saturated moments decrease as the Ba content increases for this range$^{25}$. When $x > 0.35$, there is a two-phase mixture where a fraction of BaMnO$_3$ is present, and these compositions show signs for super-paramagnetism$^{25}$.

The structural, magnetic, and electrical properties of the Ba$_{1-x}$La$_x$Mn$_{0.5}$Ru$_{0.5}$O$_3$ ($0.5 \leq x \leq 0$) perovskite system were explored. To the best of our knowledge, the in-between compositions ($0.4 \leq x \leq 0.1$) have not been investigated; hence this study sheds new light. As mentioned previously, the structural properties from X-ray powder diffraction (XRPD) and magnetic properties for the end member BaMn$_{0.5}$Ru$_{0.5}$O$_3$ have been reported, and our results match closely to the literature$^{20}$. The structural properties from XRPD for Ba$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ have also been reported$^{20}$, but there have been mixed reports of which crystal symmetry Ba$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ adopts. Horikubi and Kamegashira$^{23}$ report Ba$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ to have cubic symmetry ($Pm-3m$) while Pillai $et$ $al.$$^{20}$ reports orthorhombic symmetry ($Pbnm$). In a collaborative study with King $et$ $al.$$^{24}$, we find Ba$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ to manifest tetragonal symmetry ($I4/mcm$). Thus
this work will elaborate on the investigation of the true crystal symmetry for \( \text{Ba}_{0.5}\text{La}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \). We will also analyze the structural properties for the in-between compositions and study the magnetic and electrical properties for any solid solutions.

### 4.4 Experimental Section

The \( \text{Ba}_{1-x}\text{La}_x\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \) system with varying compositions of \( x = 0.5, 0.4, 0.3, 0.2, 0.15, 0.125, \) and 0.1 were synthesized by the conventional solid state ceramic method. Stoichiometric ratio amounts of the starting reagents \( \text{BaCO}_3 \) (99.997 %, Alfa Aesar), \( \text{La}_2\text{O}_3 \) (99.99 %, Sigma-Aldrich; heated to 900 °C for 8 h prior to usage and then stored in a desiccator when not in use), \( \text{Mn}_2\text{O}_3 \) (99.9 %, CERAC), and \( \text{RuO}_2 \) (99.9 %, Sigma Aldrich) were accurately weighed, mixed, and ground together using an agate mortar and pestle. High density (99.8 % dense) alumina crucibles were used to load the individual powders in order to maintain purity. All samples were heated to 1385 °C in air for 15 h using a high temperature box furnace. The products appeared as dark gray powders.

A Bruker D8 Advance diffractometer in Bragg-Brentano geometry equipped with a Ge 111 incident beam monochromator and Cu K\( \alpha_1 \) radiation (\( \lambda = 1.54059 \text{ Å} \)) was used to collect the X-ray powder diffraction (XRPD) data to determine phase purity. This instrument also has a LynxEye one-dimensional detector. The scans were taken in the 2\( \theta \) range of 10-90 °. The step size was 0.014286 ° 2\( \theta \), and the count time was 2.0 s/step. Each XRPD pattern was refined using the Rietveld Method administered through the TOPAS Academic software.\(^{17}\)
Ba_{1-x}La_xMn_{0.5}Ru_{0.5}O_3 (x = 0 and 0.5) samples were cut into (~ 66-74 % dense) rectangular pellets with dimensions of approximately 0.25×0.5×1.1 cm. Copper wires were adhered to the pellet with conductive silver paint. The Quantum Design model 6000 physical property measurement system (PPMS) was used to carry out the dc resistivity measurements. No field was applied. Due to the versatility and suitability for conductive materials, the 4-point electrical probe method was used over the 2-point probe method because of the elimination of contact resistance.

Magnetic measurements of Ba_{1-x}La_xMn_{0.5}Ru_{0.5}O_3 (x = 0 and 0.5) powders (~ 20 mg) were collected using the superconducting quantum interference device (SQUID). Zero-field cooled (ZFC) and field cooled (FC) magnetic susceptibility curves were measured in 1 kG from 5-400 K temperature range. The hysteresis curves were swept with a field of ± 5 T.

Time of flight (TOF) neutron powder diffraction (NPD) data was collected on a High Intensity Powder Diffractometer (HIPD) instrument at the Lujan Neutron Scattering Center of Los Alamos National Laboratory. The beam source has a 20 Hz pulsed spallation neutron source generated by bombarding a W target with a pulsed proton beam. The samples were loaded individually in vanadium cans, and the collection times were approximately 4 h. The instrument has 8 detector banks at 4 different angles. Banks 1 and 2 were scanned up to 153 °, and the d-range was 0.4-4 Å. Banks 3 and 4 were scanned up to 90 °, and the d-range was 0.56-5.57 Å. Banks 5 and 6 were scanned up to 40 °, and the d-range was 1.13-11.28 Å. Banks 7 and 8 were scanned up to 14 °, and the d-range was 3.54-38.0 Å. Because the higher banks have the poorer resolution, banks 7
and 8 were not used. This instrument can be further described from the Los Alamos National Laboratory website (http://lansce.lanl.gov/lujan/). The nuclear and magnetic phases were refined using the GSAS\textsuperscript{18} and SARA\textsuperscript{19} software.

4.5 Results and Discussion

4.5.1 X-ray Diffraction

Each composition of the $\text{Ba}_{1-x}\text{La}_x\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ ($0.5 \leq x \leq 0$) system was refined using the Rietveld method. Table 15 and Table 16 report the lattice parameters and refinement values, and Figures 66-72 are the associated XRPD patterns for each composition.
<table>
<thead>
<tr>
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<th>0.125</th>
<th>0.15</th>
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<td>5.7128(1)</td>
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<td>c (Å)</td>
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<td>21.3542(6)</td>
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<td>9R Phase %</td>
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**Table 15:** Rietveld refinement values and unit cell dimensions of Ba$_{1-x}$La$_x$Mn$_{0.5}$Ru$_{0.5}$O$_3$ (x = 0, 0.1, 0.125, and 0.15) compositions from X-ray powder diffraction.
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<td><strong>a (Å)</strong></td>
<td>5.6950(2)</td>
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</tr>
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<td>(I4/mcm)</td>
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<td><strong>a (Å)</strong></td>
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<td>5.5904(1)</td>
<td>5.5954(2)</td>
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<td><strong>3C Phase %</strong></td>
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<td><strong>R_p</strong></td>
<td>9.173</td>
<td>8.917</td>
<td>10.984</td>
<td>8.747</td>
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**Table 16:** Rietveld refinement values and unit cell dimensions of \(\text{Ba}_{1-x}\text{La}_x\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3\) (\(x = 0.2, 0.3, 0.4, \text{and} 0.5\)) compositions gathered from X-ray powder diffraction.
Figure 66: X-ray powder diffraction pattern of Ba$_{0.9}$La$_{0.1}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The upper and lower blue vertical marks denote the positions of the Bragg reflections for the 9R and 3C phases, respectively.
Figure 67: X-ray powder diffraction pattern of $\text{Ba}_{0.875}\text{La}_{0.125}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. Starting from the top and moving down, the blue vertical marks denote the positions of the Bragg reflections for the 9R, 4H, 6H, and 3C phases, respectively.
Figure 68: X-ray powder diffraction pattern of $\text{Ba}_{0.85}\text{La}_{0.15}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The upper, middle, and lower blue vertical marks denote the positions of the Bragg reflections for the 4H, 6H, and 3C phases, respectively.
Figure 69: X-ray powder diffraction pattern of $\text{Ba}_{0.8}\text{La}_{0.2}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The upper, middle, and lower blue vertical marks denote the positions of the Bragg reflections for the 4H, 6H, and 3C phases, respectively.
Figure 70: X-ray powder diffraction pattern of $\text{Ba}_{0.7}\text{La}_{0.3}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The upper, middle, and lower blue vertical marks denote the positions of the Bragg reflections for the 4H, 6H, and 3C phases, respectively.
Figure 71: X-ray powder diffraction pattern of Ba$_{0.6}$La$_{0.4}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The upper, middle, and lower blue vertical marks denote the positions of the Bragg reflections for the 4H, 6H, and 3C phases, respectively.
Figure 72: X-ray powder diffraction pattern of $\text{Ba}_{0.5}\text{La}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The blue vertical marks denote the positions of the Bragg reflections for the 3C ($I4/mcm$ symmetry) phase. The inset figure to the left is the 3C crystal structure, and the inset figure to the right is a doublet peak (004 and 220 peaks) showing that tetragonal symmetry is the correct system for this compound.
Figure 73: Waterfall plot of the X-ray powder diffraction patterns for $\text{Ba}_{1-x}\text{La}_x\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ compositions. The top pattern (red line) and the bottom pattern (black line) correspond to $\text{Ba}_{0.5}\text{La}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ and $\text{BaMn}_{0.5}\text{Ru}_{0.5}\text{O}_3$, respectively. The peaks that arise from a different phase are marked with a box. The red box, black box, blue box, and the gold box represent the 9R phase, 4H phase, combination of the 4H and 6H phases, and 6H phase, respectively.
Figure 74: The percent of phases present in the Ba$_{1-x}$La$_x$Mn$_{0.5}$Ru$_{0.5}$O$_3$ system.

Only the end members, BaMn$_{0.5}$Ru$_{0.5}$O$_3$ and Ba$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$, are homogenous solid solutions. The in-between compositions are of mixed phases. Figure 73 is a waterfall plot of all the compositions and the different phases are marked appropriately. Figure 74 shows the rise and fall of the presence of the different phases in the compositions. Ba$_{0.9}$La$_{0.1}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ is a two-phase mixture of the 9R and 3C phases. Ba$_{1-x}$La$_x$Mn$_{0.5}$Ru$_{0.5}$O$_3$ ($x = 0.125, 0.15, 0.2, 0.3$, and $0.4$) are composed are 3 different phases, 3C, 4H, and 6H. A three-phase mixture is unusual for perovskites; thus crystal equilibrium must not have been achieved. Perhaps higher synthesis temperatures may be
required. The 3C component in Ba$_{0.9}$La$_{0.1}$Mn$_{0.5}$Ru$_{0.5}$O$_3$, Ba$_{0.875}$La$_{0.125}$Mn$_{0.5}$Ru$_{0.5}$O$_3$, Ba$_{0.85}$La$_{0.15}$Mn$_{0.5}$Ru$_{0.5}$O$_3$, and Ba$_{0.8}$La$_{0.2}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ samples adopt the cubic $Pm-3m$ symmetry; whereas the Ba$_{0.7}$La$_{0.3}$Mn$_{0.5}$Ru$_{0.5}$O$_3$, Ba$_{0.6}$La$_{0.4}$Mn$_{0.5}$Ru$_{0.5}$O$_3$, and Ba$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ samples adopt the tetragonal $I4/mcm$ symmetry. If we look at the higher angled peaks in the XRPD patterns, Ba$_{0.9}$La$_{0.1}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ and Ba$_{0.8}$La$_{0.2}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ samples have symmetric peaks versus Ba$_{0.7}$La$_{0.3}$Mn$_{0.5}$Ru$_{0.5}$O$_3$, Ba$_{0.6}$La$_{0.4}$Mn$_{0.5}$Ru$_{0.5}$O$_3$, and Ba$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ samples have asymmetric doublet peaks. The top XRPD pattern in the 2$\theta$ range from 45.6-46.4 degrees in Figure 75 shows one of the asymmetric doublet peaks, 004 and 220 in this case. The bottom XRPD pattern in Figure 75 shows this same 2$\theta$ range, but here the peak is a singlet. In addition to the asymmetric peaks for Ba$_{0.7}$La$_{0.3}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ and Ba$_{0.6}$La$_{0.4}$Mn$_{0.5}$Ru$_{0.5}$O$_3$, octahedral tilting ($a^0 a^0 c^-$ in Glazer notation) is present (see Figure 76).
Figure 75: X-ray powder diffraction pattern of Ba$_{0.6}$La$_{0.4}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ (top) and Ba$_{0.7}$La$_{0.3}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ (bottom) compounds. The peak from Ba$_{0.7}$La$_{0.3}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ is symmetrical, and the peak splitting becomes more pronounced in the more La-rich compound, Ba$_{0.6}$La$_{0.4}$Mn$_{0.5}$Ru$_{0.5}$O$_3$; thus, indicating a change in the crystal symmetry.
Figure 76: The 3C crystal structure of $\text{Ba}_{0.5}\text{La}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ compound. The right side shows the octahedral tilting occurring down the $c$-axis.

The Rietveld refinements values are lower, indicating a better overall fit than $Pm\text{-}3m$ symmetry. Table 17 reports this comparison along with $Pnma$ symmetry. For $\text{Ba}_{0.5}\text{La}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$, there have been mixed reports of the space group symmetry. Horikubi and Kamegashira\textsuperscript{23} report this compound to be $Pm\text{-}3m$ whereas Pillai et al.\textsuperscript{20} reports orthorhombic symmetry ($Pbnm$). While these reports are contradicting in each other, neither literature attempted tetragonal symmetry nor did a comparison of the possible space groups. King et al.\textsuperscript{24} finds that $\text{Ba}_{0.5}\text{La}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ adopts the space group $I4/mcm$, and our results match well with this study.
Table 17: Comparing the X-ray powder diffraction Rietveld refinements from different crystal systems for Ba\textsubscript{0.5}La\textsubscript{0.5}Mn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3}.

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<th>Pnma</th>
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<td>(a' b^+ a^-)</td>
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<td>b (Å)</td>
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<td>GOF</td>
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<td>1.137</td>
<td>1.176</td>
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The entire Ba\textsubscript{1-x}La\textsubscript{x}Mn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} system shows complete chemical disorder. For space groups such as Pm-3m and I4/mcm to exist in this system, means that this system is chemically disordered. If the Ba\textsubscript{1-x}La\textsubscript{x}Mn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} compositions showed chemical order, then the space groups Fm-3m and I4/m would then be allowed. The XRPD patterns would also have certain peaks present but are instead absent, further indicating that chemical order is not present. In addition, there has yet to be any reports in the literature of chemical order for bulk AMn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} systems.

There are also no obvious signs for a cooperative Jahn Teller (JT) distortion in any of the Ba\textsubscript{1-x}La\textsubscript{x}Mn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} compositions. For instance, the bond lengths from the B-O\textsubscript{6} octahedra, which are 1.9866(1) Å and 1.98(3) Å, in Ba\textsubscript{0.5}La\textsubscript{0.5}Mn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} do not differ much from each other as in the bond lengths from LaMnO\textsubscript{3}. While a cooperative JT distortion may not be present, there may be local JT distortions. Since all the compositions are completely disordered, the bond lengths result from the average of the Ru-O and Mn-O bonds.
4.5.2 Electrical Properties

The resistivity was measured for $AMn_{0.5}Ru_{0.5}O_3$ ($A = Ba, Ba_{0.5}La_{0.5}$) compounds. Both compounds exhibit insulating behavior (see Figure 77). At 30 K and 300 K, the resistivities are $4.85 \times 10^4 \ \Omega \cdot cm$ and $1.39 \ \Omega \cdot cm$, respectively, for $BaMn_{0.5}Ru_{0.5}O_3$. For $Ba_{0.5}La_{0.5}Mn_{0.5}Ru_{0.5}O_3$, the resistivities are $6.61 \times 10^5 \ \Omega \cdot cm$ and $5.52 \times 10^{-2} \ \Omega \cdot cm$ at 30 K and 300 K, respectively. The $Ba_{0.5}La_{0.5}Mn_{0.5}Ru_{0.5}O_3$ compound is more insulating than the pure barium compound by at least an order of magnitude at low temperatures, but at higher temperatures ($T \geq 115 \ K$), the pure barium compound is more insulating. Between the two compounds, the resistivity differs by a couple of orders of magnitude at room temperature. Figure 78 plots the variable range hopping model over the temperature range of 38-219 K. The $R^2$ values are 0.9997 and 0.9987 for $BaMn_{0.5}Ru_{0.5}O_3$ and $Ba_{0.5}La_{0.5}Mn_{0.5}Ru_{0.5}O_3$, respectively. While $BaMn_{0.5}Ru_{0.5}O_3$ shows a linear function for the variable range hopping model, $Ba_{0.5}La_{0.5}Mn_{0.5}Ru_{0.5}O_3$ does not show a good fit. Therefore we can conclude that $Ba_{0.5}La_{0.5}Mn_{0.5}Ru_{0.5}O_3$ does not support localized electrons that can hop from one localized atom site to another.
Figure 77: Log of the resistivity as a function of temperature for $AMn_{0.5}Ru_{0.5}O_3$ ($A =$ Ba and $Ba_{0.5}La_{0.5}$) samples.
4.5.3 Magnetic Properties

The magnetization was collected for $A\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ ($A = \text{Ba}$ and $\text{Ba}_{0.5}\text{La}_{0.5}$) compounds using the SQUID. Since the details of the $\text{BaMn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ compound have already been discussed in the previous chapter, the findings will be mentioned for reasons of comparison and not be elaborated here. The shape of the ZFC and FC susceptibilities (see Figure 79) shows FM-/FiM-like behavior and AFM behavior with some canting for
$\text{Ba}_{0.5}\text{La}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ and $\text{BaMn}_{0.5}\text{Ru}_{0.5}\text{O}_3$, respectively. The $T_N$ is 36 K and $T_C$ is 205 K for $\text{BaMn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ and $\text{Ba}_{0.5}\text{La}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$, respectively.

**Figure 79:** Zero-field cooled and field cooled susceptibility for $\text{Ba}_{0.5}\text{La}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$. The inset plot shows the zero-field cooled and field cooled susceptibility for the pure barium compound.
Figure 80: Zero-field cooled and field cooled Curie Weiss plot for Ba$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ compound.

The ZFC and FC inverse susceptibility plot for Ba$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ is shown in Figure 80. Table 18 reports the Curie constants, Weiss constants, and the effective moments ($\mu_{\text{eff}}$) calculated from the Curie constants. The positive $\theta$ matches closely to the $T_C$ for Ba$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$, which suggests a well-behaved FM/FiM. The calculated effective moments for Mn$^{3+}$ (high spin d$^5$) + Ru$^{5+}$ (d$^3$), Mn$^{4+}$ (d$^3$) + Ru$^{4+}$ (low spin d$^4$), and Mn$^{3+}$ + Ru$^{4+}$ are 4.416 $\mu_B$, 3.391 $\mu_B$, and 4.000 $\mu_B$, respectively. Considering these calculated values, the effective moment calculated from the Curie constant for Ba$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ does not agree because of charge balancing. Acknowledging that
the $R^2$ value is 0.997 for the measurable paramagnetic region in the Curie-Weiss plot, the extracted Curie constant has some uncertainty. In order to alleviate this ambiguity, higher temperatures are needed. Thus, no claims can be confirmed about the oxidation states for Mn and Ru from this Curie-Weiss information alone.

<table>
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<th>BaMn$<em>{0.5}$Ru$</em>{0.5}$O$_3$</th>
<th>Ba$<em>{0.5}$La$</em>{0.5}$Mn$<em>{0.5}$Ru$</em>{0.5}$O$_3$</th>
</tr>
</thead>
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<td>250–375</td>
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<td><strong>Curie constant (emu·K/mol)</strong></td>
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<td>1.23(3)</td>
</tr>
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<tr>
<td><strong>$\mu_{\text{eff}}$ (μB)</strong></td>
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<tr>
<td><strong>$R^2$</strong></td>
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</table>

**Table 18:** Field cooled magnetic information gathered from the normalized Curie-Weiss plots.

While BaMn$_{0.5}$Ru$_{0.5}$O$_3$ shows AFM behavior with some canting, Ba$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ exhibits FM-/FiM-like behavior from the hysteresis loop shown in **Figure 81**. The $M$ is 1.54 μB/f.u. at 5 K for Ba$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$. The spin-only ferromagnetic moments are 3.5 μB/f.u., 2.5 μB/f.u., and 3.0 μB/f.u. for the oxidation states of Mn$^{3+}$ (high spin d$^4$) + Ru$^{5+}$ (d$^3$), Mn$^{4+}$ (d$^3$) + Ru$^{4+}$ (low spin d$^4$), and Mn$^{3+}$ + Ru$^{4+}$, respectively. The spin-only ferrimagnetic moments are 0.5 μB/f.u., 0.5 μB/f.u., and 1.0 μB/f.u. for the oxidation states of Mn$^{3+}$ + Ru$^{5+}$, Mn$^{4+}$ + Ru$^{4+}$, and Mn$^{3+}$ + Ru$^{4+}$, respectively. Considering these values and charge balancing, the $M$ for Ba$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ agrees with the spin only ferrimagnetic moment for Mn$^{3+}$ + Ru$^{4+}$. Thus we can make reasonable assumptions that Ba$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ has a
ferrimagnetic structure and favors Mn$^{3+}$ + Ru$^{4+}$ oxidation states based on the magnetization gathered from the hysteresis loop.

**Figure 81:** Magnetization as a function of applied field for $A$Mn$_{0.5}$Ru$_{0.5}$O$_3$ ($A$ = Ba and Ba$_{0.5}$La$_{0.5}$) compounds.
4.5.4 Neutron Diffraction

Time of flight neutron powder diffraction data was collected at room temperature and 4 K for BaMn$_{0.5}$Ru$_{0.5}$O$_3$ and Ba$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$. Figure 82 and Figure 83 show the room and low temperature time of flight neutron powder diffraction patterns, respectively, for histograms 1, 3, and 5 for the Ba$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ compound. Histograms 2, 4, and 6 are not shown since these histograms are mirrors of histograms 1, 3, and 5, respectively. Table 19 reports the refinement values from each histogram and the refined structural information of the 4 K and room temperature time of flight neutron powder diffraction results for both BaMn$_{0.5}$Ru$_{0.5}$O$_3$ and Ba$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ compounds.
Figure 82: Room temperature time of flight neutron powder diffraction patterns from histograms 1, 3, and 5 for Ba$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The blue vertical marks denote the Bragg reflections.
**Figure 83:** Low temperature (4 K) time of flight neutron powder diffractions from histograms 1, 3, and 5 for $\text{Ba}_{0.5}\text{La}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The upper and lower blue vertical marks denote the Bragg reflections of the nuclear phase and magnetic phase, respectively.
Table 19: Structural refinement results for $AMn_{0.5}Ru_{0.5}O_3$ ($A = Ba$ and $Ba_{0.5}La_{0.5}$) from time of flight neutron powder diffraction.

The low refinement values from both compounds indicate an overall good fit for each histogram. The space group symmetries were maintained for both compounds at room and low temperatures. Table 20 reports the atomic positions, U values, and occupancies at low and room temperatures from both compounds. Unlike in the 9R crystal structure for $BaMn_{0.5}Ru_{0.5}O_3$, there are no preferentially site occupancies for the Mn or Ru cations in $Ba_{0.5}La_{0.5}Mn_{0.5}Ru_{0.5}O_3$. The oxygen occupancies were refined and noted that there are minute levels of vacancies present in $Ba_{0.5}La_{0.5}Mn_{0.5}Ru_{0.5}O_3$. As for $BaMn_{0.5}Ru_{0.5}O_3$, the
Oxygen occupancies were set to one since the refined occupancies did not significantly deviate from one, and the refinement values did not significantly change either.

<table>
<thead>
<tr>
<th>T (K):</th>
<th>BaMn$<em>{0.5}$Ru$</em>{0.5}$O$_3$</th>
<th>Ba$<em>{0.5}$La$</em>{0.5}$Mn$<em>{0.5}$Ru$</em>{0.5}$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>space group</td>
<td>R-3c</td>
<td>R-3c</td>
</tr>
<tr>
<td>Ba / Ba$<em>{0.5}$La$</em>{0.5}$ (1)</td>
<td>(0, 0, 0)</td>
<td>(0, 0, 0)</td>
</tr>
<tr>
<td>U$_{iso}$ x 100</td>
<td>0.65(4)</td>
<td>0.26(3)</td>
</tr>
<tr>
<td>Occupancy</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Mn / Ru (1)</td>
<td>(0, 0, 0)</td>
<td>(0, 0, 0)</td>
</tr>
<tr>
<td>U$_{iso}$ x 100</td>
<td>0.06(9)</td>
<td>1.2(8)</td>
</tr>
<tr>
<td>Mn Occupancy</td>
<td>0.64(3)</td>
<td>0.63(9)</td>
</tr>
<tr>
<td>Ru Occupancy</td>
<td>0.357(1)</td>
<td>0.361(5)</td>
</tr>
<tr>
<td>Mn / Ru (2), (0, 0, 0)</td>
<td>0.38428(9)</td>
<td>0.38447(8)</td>
</tr>
<tr>
<td>U$_{iso}$ x 100</td>
<td>0.39(3)</td>
<td>0.01(2)</td>
</tr>
<tr>
<td>Mn Occupancy</td>
<td>0.448(1)</td>
<td>0.449(1)</td>
</tr>
<tr>
<td>Ru Occupancy</td>
<td>0.552(1)</td>
<td>0.551(1)</td>
</tr>
<tr>
<td>O (1)</td>
<td>(1/5, 0, 0)</td>
<td>(1/5, 0, 0)</td>
</tr>
<tr>
<td>U$<em>{iso}$ or U$</em>{11}$, U$<em>{22}$, U$</em>{33}$, U$<em>{12}$, U$</em>{13}$, U$_{23}$ x 100</td>
<td>0.71(3), 0.064(4), 1.23(3), 0.03(2), 0.32(1), 0.64(3)</td>
<td>0.24(1), 2.07(4), 2.07(4), 1.34(8), 0, 0, 1.30(3), 1.30(3), 0.36(7), 0, 0, 0</td>
</tr>
<tr>
<td>Occupancy</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>O (2), x</td>
<td>0.15247(5)</td>
<td>0.15304(4)</td>
</tr>
<tr>
<td>y</td>
<td>-0.15247(5)</td>
<td>0.84696(4)</td>
</tr>
<tr>
<td>z</td>
<td>0.55782(2)</td>
<td>0.55794(1)</td>
</tr>
<tr>
<td>U$<em>{iso}$ or U$</em>{11}$, U$<em>{22}$, U$</em>{33}$, U$<em>{12}$, U$</em>{13}$, U$_{23}$ x 100</td>
<td>0.620(9)</td>
<td>0.329(7)</td>
</tr>
<tr>
<td>Occupancy</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 20: Structural atomic positions for AMn$_{0.5}$Ru$_{0.5}$O$_3$ (A = Ba, Ba$_{0.5}$La$_{0.5}$) from time of flight neutron powder diffraction.

At 4 K, the time of flight neutron powder diffraction pattern for Ba$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ did not show any new peaks, but some of the peaks did increase in intensity. Thus, the propagation vector (k = 0, 0, 0) was used. Figure 84 overlays the 4 K
and 300 K time of flight neutron powder diffraction patterns from histogram 3 to capture the magnetic peaks increasing in intensity at low temperature. The change in peak intensities for the d-spacings of ~ 2.4, 2.8, and 4.0 Å have been labeled with a green asterisk. Ferromagnetic and ferrimagnetic structures were used to refine the low temperature time of flight neutron powder diffraction patterns. Antiferromagnetic structures were not used since unwanted magnetic peak reflections occurred. In the ferromagnetic model, both the Mn and Ru magnetic moments were refined equally, yielding a total magnetic moment of 3.414 μB. Whereas in the ferrimagnetic model, the Mn magnetic moment was set to 3.7 μB and left unrefined while the Ru magnetic moment was refined to -0.88(2) μB. In the last model, only the Mn magnetic moment was refined with 100% occupancy of Mn on the magnetic sites; the previous models had 50% occupancies for Mn and Ru. With 100% occupancy of Mn, the magnetic moment refined to 1.577(6) μB. **Table 21** reports the comparison of the refinement values from histogram 3 at 4 K and the moments from each magnetic structure. Based on the refinement values from each model, we cannot confirm whether Ba0.5La0.5Mn0.5Ru0.5O3 is a ferri- or ferromagnetic structure. However, the moments obtained from the ferrimagnetic model are more reasonable than the other models. The moments from the ferrimagnetic model are reported in **Table 22**. The results for BaMn0.5Ru0.5O3 have already been discussed in the previous chapter but will be recapitulated here to compare these results to that of Ba0.5La0.5Mn0.5Ru0.5O3.
Figure 84: Overlay of the neutron powder diffraction patterns from 4 K and 300 K in the d-spacing range of 2.25-4.5 Å for Ba_{0.5}La_{0.5}Mn_{0.5}Ru_{0.5}O_{3}. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. In the 4 K neutron powder diffraction pattern, the upper and lower blue vertical marks denote the Bragg reflections of the nuclear phase and magnetic phase, respectively. For the room temperature neutron powder diffraction pattern, the blue vertical marks denote the Bragg reflections of just the nuclear phase. The green asterisks refer to the magnetic peaks.
<table>
<thead>
<tr>
<th></th>
<th>Ba_{0.5}La_{0.5}Mn_{0.5}Ru_{0.5}O_3 (4K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M(\mu_0)$ on Mn</td>
<td>3.7</td>
</tr>
<tr>
<td>$M(\mu_0)$ on Ru</td>
<td>-0.88(2)</td>
</tr>
<tr>
<td><strong>FiM Net Moment</strong></td>
<td>2.82</td>
</tr>
<tr>
<td>$R_p$</td>
<td>0.0198</td>
</tr>
<tr>
<td>$R_{vp}$</td>
<td>0.0256</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>5.701</td>
</tr>
<tr>
<td>$M(\mu_0)$ on Mn, Occ. = 1.0</td>
<td>1.707(7)</td>
</tr>
<tr>
<td>$M(\mu_0)$ on Ru, Occ. = 0</td>
<td>1.707(7)</td>
</tr>
<tr>
<td><strong>FM Net Moment</strong></td>
<td>3.414</td>
</tr>
<tr>
<td>$R_p$</td>
<td>0.0200</td>
</tr>
<tr>
<td>$R_{vp}$</td>
<td>0.0257</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>5.694</td>
</tr>
<tr>
<td>$M(\mu_0)$ on Mn, Occ. = 1.0</td>
<td>1.577(6)</td>
</tr>
<tr>
<td>$M(\mu_0)$ on Ru, Occ. = 0</td>
<td>0</td>
</tr>
<tr>
<td><strong>Total Moment</strong></td>
<td>1.577(6)</td>
</tr>
<tr>
<td>$R_p$</td>
<td>0.199</td>
</tr>
<tr>
<td>$R_{vp}$</td>
<td>0.257</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>5.697</td>
</tr>
</tbody>
</table>

**Table 21**: Comparison of the 4 K time of flight neutron powder diffraction refinement results from histogram 3 for the ferrimagnetic structure, ferromagnetic structure, and Mn moment with 100% occupancy for Ba_{0.5}La_{0.5}Mn_{0.5}Ru_{0.5}O_3.
Table 22: Bond angles, bond lengths, and magnetic moments of AMn$_{0.5}$Ru$_{0.5}$O$_3$ (A = Ba and Ba$_{0.5}$La$_{0.5}$) compounds from time of flight neutron powder diffraction.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Mn,Ru$_2$O$_6$-Mn/Ru$_6$ (°)</th>
<th>Mn,Ru$_2$O$_6$-Mn/Ru$_6$ (Å)</th>
<th>Mn$_1$ magnetic moment ($\mu_0$)</th>
<th>Mn$_2$ magnetic moment ($\mu_0$)</th>
<th>Ru magnetic moment ($\mu_0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>280</td>
<td>78.40(3)</td>
<td>3×1.9603(3)</td>
<td>1.60(4)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>298</td>
<td>77.90(3)</td>
<td>3×1.9552(3)</td>
<td>1.99940(1)</td>
<td>2×1.9929(1)</td>
<td>-</td>
</tr>
</tbody>
</table>

The bond lengths did not vary widely in B-O$_6$ octahedra; thus suggesting that a cooperative JT distortion is not present in Ba$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ (see Table 22). However, the B-O bond lengths suggest that Ba$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ supports the oxidation states of Mn$^{3+}$ and Ru$^{4+}$ because Mn$^{3+}$-O and Ru$^{4+}$-O have bond lengths of 2.045 Å and 2.02 Å, respectively. This matches well with the magnetization results obtained from SQUID. Thus, it is likely that local JT distortions are present considering the valency of Mn and is driving the magnetism. A pair distribution function (PDF) study from King et al.$^{24}$ reported that local JT distortions are indeed present in this compound, and the reported bond valence sum calculations closely match the suggested oxidations states that we gather from the bond lengths for Ba$_{0.5}$La$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$.

4.6 Discussion

The structural, magnetic, and electrical properties for the Ba$_{1-x}$La$_x$Mn$_{0.5}$Ru$_{0.5}$O$_3$ (0.5 ≥ x ≥ 0) system have been investigated. The end members are found to be...
homogenous solid solutions while the in-between compositions were of mixed phases. This can be attributed to that equilibrium was never achieved. BaMn_{0.5}Ru_{0.5}O_{3} is a strong insulator and a canted antiferromagnet with a T_{N} of 36 K. The neutron powder diffraction results confirms that the crystal structure is 9R, and the magnetic structure has antiferromagetically coupled spins oriented in the z-axis with ferromagnetically coupled spins aligned in the \( xy \)-plane. The Mn magnetic moments from M_{1} and M_{2} sites are refined to 1.60(4) \( \mu_{B} \) and 2.15(2) \( \mu_{B} \), respectively. Since these moments for Mn\(^{3+/4+}\) are fairly low, Mn and Ru cations share the same sites, and the Ru magnetic moment was not refined, we can assume that the magnetic moment from Ru is contributing to the total magnetic moment observed. This would account for why we see lower than expected moments for these sites. As for the 50% La\(^{3+}\) substitution, this compound has a completely different set of properties compared to the pure barium compound. Ba_{0.5}La_{0.5}Mn_{0.5}Ru_{0.5}O_{3} adopts \( I4/mcm \) symmetry, has the 3C crystal structure, and is an insulating ferri-/ferromagnet with a \( T_{C} \) of 205 K. The \( M \) at 5 K, which is 1.54 \( \mu_{B} \)/f.u. from the hysteresis loop, is closer in value to the spin only ferrimagnetic moment for the oxidation states of Mn\(^{3+}\) and Ru\(^{4+}\). The calculated bond lengths for Mn\(^{3+}\)-O and Ru\(^{4+}\)-O also closely match the bond lengths gathered from the time of flight neutron powder diffraction results. From the low temperature neutron powder diffraction refinement values for ferromagnetic and ferrimagnetic structures, we cannot confirm that Ba_{0.5}La_{0.5}Mn_{0.5}Ru_{0.5}O_{3} is a ferri- or ferromagnetic structure. However, comparing the moments obtained from the ferromagnetic and ferrimagnetic models, the ferrimagnetic moments are more reasonable than the ferromagnetic moments. Thus we can make
sensible conclusions that $\text{Ba}_{0.5}\text{La}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ exhibits the ferrimagnetic structure based on the logical ferrimagnetic moments obtained for Mn and Ru cations.

4.7 Acknowledgement

Financial support from the NSF through a Materials World Network grant (MWN-0603128) is gratefully acknowledged. We would also like to acknowledge Dr. Graham King for assistance with the TOF neutron diffraction experiments. This work has benefited from the use of HIPD at the Lujan Center at Los Alamos Neutron Science Center, funded by DOE Office of Basic Energy Sciences. Los Alamos National Laboratory is operated by Los Alamos National Security LLC under DOE Contract No. DE-AC52 06NA25396.
4.8 References

CHAPTER 5: UNDERSTANDING THE BULK PROPERTIES OF ON-STOICHIOMETRIC, OFF-STOICHIOMETRIC, AND A-SITE SUBSTITUTED Sr$_2$CrReO$_6$ PEROVSKITES

5.1 Contribution

The thrusts of this work is to (1) help understand how the properties are affected when deviating from on-stoichiometry of Sr$_2$CrReO$_6$ and (2) how isovalent and aliovalent A-site substitutions influence the properties compared to Sr$_2$CrReO$_6$. This chapter will be published, and the authors in order are: Jennifer R. Soliz, Adam J. Hauser, Jeremy Lucy, Fengyuan Yang, and Patrick M. Woodward. Jennifer R. Soliz has synthesized all materials noted in this chapter and has collected the structural results from XRPD, magnetic results from SQUID, and electrical results using the PPMS. Adam J. Hauser and Jeremy Lucy have measured the magnetic susceptibilities using the VSM in Fengyuan Yang’s lab. Adam and Fengyuan have also measured the magnetization from the VSM at the National High Magnetic Field Laboratory. Patrick M. Woodward is Jennifer’s adviser and has been informed about the details of this project.
5.2 Abstract

Thin films of Sr$_2$CrReO$_6$ have been reported to be metallic (possibly half-metallic) with a high Curie temperature (635K), which makes this material a feasible candidate for spintronic applications. To understand the role of doping, investigations of the structural, electrical, and magnetic properties of on- and off-stoichiometric Sr$_{2+x}$CrReO$_6$ (x = -0.07, 0.0, 0.05, 0.075, and 0.10), Sr$_2$Cr$_{1+y}$Re$_{1-y}$O$_6$ (y = -0.1, -0.05, 0.05, and 0.1), and A-site substituted Sr$_{2-x}$A$_x$CrReO$_6$ (A = K, Ca, and La; z = 0.10 and 0.20; z = 1.0 only for Ca) samples have been achieved. All studied compounds exhibit a near linear trend in the pseudocubic lattice parameters and are more than 58 % ordered. Sr$_{2+x}$CrReO$_6$ (x = -0.07, 0.0, 0.05, 0.075, and 0.10) and Sr$_2$Cr$_{1+y}$Re$_{1-y}$O$_6$ (y = -0.1, -0.05, 0.05, and 0.1) are more metallic than the A-site substituted Sr$_{2-x}$A$_x$CrReO$_6$ (A = K, Ca, and La; z = 0.10 and 0.20; z = 1.0 only for Ca) compounds. This is attributed to sintering effects considering that these polycrystalline samples had a fair amount of porosity. Cr- and aliovalent substitutions showed expected trends in the magnetization and Curie temperatures. As the Re becomes oxidized, the magnetization increases and the Curie temperatures decrease, which was observed for Sr$_2$Cr$_{1+y}$Re$_{1-y}$O$_6$ (y = -0.1, -0.05, 0, and 0.05) and Sr$_{1.5}$K$_{0.1}$CrReO$_6$ compounds. With La$^{3+}$-substitution, the opposite occurs in that the magnetization decreases and the Curie temperatures increase because Re is reduced. As for isovalent substitutions, octahedral tilting resulting from steric effects is responsible for decreasing the Curie temperature and somehow influencing the magnetization.
5.3 Introduction

The quest to find a suitable half-metallic ferromagnetic material that is 100% spin polarized with a high $T_C$ is a kind of “holy grail” of spintronic materials. $\text{Sr}_2\text{CrReO}_6$ has theoretically been predicted to be half-metallic with $M_{\text{sat}}$ of 1 \(\mu_B/f.u.\),\textsuperscript{1-4} and spin-orbit coupling calculations predict $M_{\text{sat}}$ of 1.28 \(\mu_B/f.u.\).\textsuperscript{5} The experimental bulk properties for $\text{Sr}_2\text{CrReO}_6$ have been reported as a metallic (possibly half-metallic) FiM with a high $T_C$ of 635K, and the highest reported $M_{\text{sat}}$ in $\text{Sr}_2\text{CrReO}_6$ powders is 1.01 \(\mu_B/f.u.\).\textsuperscript{6} Recently Hauser et al.\textsuperscript{7} has reported highly ordered smooth $\text{Sr}_2\text{CrReO}_6$ thin films grown epitaxially upon $\text{SrTiO}_3$ (STO) substrates, and these high quality $\text{Sr}_2\text{CrReO}_6$ films have a $M_{\text{sat}}$ of 1.29 \(\mu_B/f.u.\) and a $T_C$ of 508 K. Unexpectedly the electrical properties show semi-conducting behavior. In efforts to understand this intrinsic semi-conducting n-type behavior observed in these films, bulk materials were synthesized. Off-stoichiometric samples were prepared to help understand the effects of deviating away from on-stoichiometry. By intentionally making the materials Sr-deficient and Sr-rich, this can cause Cr/Re cation vacancies and possibly lead to p-type behavior. Slightly adjusting the Cr:Re ratio in $\text{Sr}_2\text{CrReO}_6$ could also lead to the cross-over from p-type to n-type conductivity. Isovalent and aliovalent A-site substitutions were also made to examine how the properties can change. With electron-hole substitution, it is expected that the B-site ordering would increase since the charge differences become greater in the B-site cations; thereby, charge carrier substitution should decrease the B-site ordering. Whereas, the B-site ordering should be approximately the same for isovalent substitution as observed in $\text{Sr}_2\text{CrReO}_6$. From these expectations, we can anticipate that the
magnetization will be directly affected. Considering that the $B$-site cations are antiferromagnetically coupled, the magnetization should increase with electron-hole substitution because this type of substitution promotes ordering and rhenium is becoming oxidized. The opposite should occur with charge carrier substitution in that the magnetization should decrease since rhenium should be reduced. The magnetization from isovalent substitution should be nearly equal to the magnetization observed in $\text{Sr}_2\text{CrReO}_6$.

By investigating all these substitutions, we will be able to study the effects on the properties. Furthermore studying these substitutions in $\text{Sr}_2\text{CrReO}_6$ has never been explored except for Cr-rich substitutions in conjunction with $Ln$ ($Ln = \text{La, Nd, Sm}$) substitution in $\text{Sr}_{2-x}Ln_x\text{Cr}_{1+x/2}\text{Re}_{1-x/2}\text{O}_6$ ($x \leq 0.5$) system.\(^8\) Phase-pure $\text{Sr}_{2-x}\text{La}_x\text{CrReO}_6$ compounds were attempted but unsuccessful.\(^8\) Thus, this project will shed new light and deepen our knowledge in this field.

### 5.4 Experimental Section

Different stoichiometric $\text{Sr}_{2+x}\text{CrReO}_6$ ($x = -0.07, 0.0, 0.05, 0.075,$ and $0.10$), $\text{Sr}_2\text{Cr}_{1+y}\text{Re}_{1-y}\text{O}_6$ ($y = 0.1, -0.05, 0.05,$ and $0.1$), and $A$-site substituted $\text{Sr}_{2-y}A_y\text{CrReO}_6$ ($A = \text{K, Ca, and La}; z = 0.10$ and $0.20$; $z = 1.0$ only for Ca) systems were synthesized via the solid state method. Stoichiometric ratio amounts of the starting reagents $\text{SrO}$ (99.9 %, Sigma Aldrich), $\text{CaCO}_3$ (99.95 %, Mallinckrodt Baker), $\text{La}_2\text{O}_3$ (99.99 %, Sigma-Aldrich; heated to 900 °C for 8 h prior to usage and then stored in a desiccator when not in use), $\text{K}_2\text{CrO}_4$ (99.5 %, JT Baker Chemical Company), $\text{Cr}_2\text{O}_3$ (99 %, Fisher Scientific), $\text{ReO}_3$ (99.9 %, Fisher Scientific), and $\text{Re}$ (99.99 %, Fisher Scientific) were accurately weighed and ground together using an agate mortar and pestle inside a glove box with O$_2$ and H$_2$O.
at part-per-million levels. High density (99.8 % dense) alumina tubes were used to load the individual powders in order to maintain purity. These tubes were then individually sealed in an evacuated quartz tube. All samples were heated to 1100 °C for 48 h using a box furnace. Each product appeared as black powders.

A Bruker D8 Advance diffractometer in Bragg-Brentano geometry equipped with a Ge 111 incident beam monochromator and Cu Kα1 radiation (λ = 1.54059 Å) was used to collect the X-ray powder diffraction (XRPD) data to determine phase purity. This instrument also has a LynxEye one-dimensional detector. The scans were taken in the 2θ range of 10-90 °. The step size was 0.014286 ° 2θ, and the count time was 2.0 s/step. Each XRPD pattern was refined using the Rietveld Method administered through the TOPAS Academic software.17

\[ \text{Sr}_{2+x}\text{CrReO}_6 \ (x = -0.07, 0, \text{ and } 0.075), \ \text{Sr}_2\text{Cr}_{1+y}\text{Re}_{1-y}\text{O}_6 \ (y = -0.1, -0.05, 0.05, \text{ and } 0.1), \ \text{and } \text{Sr}_{2-z}\text{A}_z\text{CrReO}_6 \ (A = K \text{ when } z = 0.1; A = \text{La when } z = 0.2; A = \text{Ca when } z = 1) \]
samples were cut into dense (~ 51-66 % dense) rectangular pellets with dimensions of approximately 0.25×0.5×0.8 cm. Using conductive silver paint, copper wires were adhered to the pellet. The Quantum Design model 6000 physical property measurement system (PPMS) was used to carry out the dc resistivity measurements. No field was applied. Due to the versatility and suitability for conductive materials, the 4-point electrical probe method was used over the 2-point probe method because of the elimination of contact resistance. No corrections were made for porosity.

Magnetic measurements of \( \text{Sr}_{2+x}\text{CrReO}_6 \ (x = -0.07, 0, \text{ and } 0.075), \text{Sr}_2\text{Cr}_{1+y}\text{Re}_{1-y}\text{O}_6 \ (y = -0.1, -0.05, 0.05, \text{ and } 0.1), \text{and } \text{Sr}_{2-z}\text{A}_z\text{CrReO}_6 \ (A = K \text{ when } z = 0.1; A = \text{La when } z = 0.2; A = \text{Ca when } z = 1) \)
$A = \text{La when } z = 0.2; A = \text{Ca when } z = 1$) powders (~ 20 mg) were collected using the superconducting quantum interference device (SQUID) for the hysteresis loops and the Lakeshore vibrating sample magnetometer (VSM) for the susceptibility curves. The room temperature hysteresis curves were swept with a field of ± 5 T. The high temperature zero-field cooled (ZFC) and field cooled (FC) magnetic susceptibility measurements were measured in a field strength of 8 kG in the temperature range of 300-700 K.

5.5 **Results and Discussion**

5.5.1 **X-ray Diffraction**

Each composition from $\text{Sr}_{2+x}\text{CrReO}_6$ ($x = -0.07, 0.0, 0.05, 0.075, \text{ and } 0.10$), $\text{Sr}_2\text{Cr}_{1+y}\text{Re}_{1-y}\text{O}_6$ ($y = -0.1, -0.05, 0.0, 0.05, \text{ and } 0.1$), and $\text{Sr}_{2-z}A_z\text{CrReO}_6$ ($A = \text{K, Ca, and La; } z = 0.0, 0.1, 0.2; z = 1 \text{ only for Ca}$) systems were refined using the Rietveld method. All samples were found to adopt the $I4/m$ symmetry. **Figures 85-100** show the respective XRPD patterns for each composition. **Figure 101**, **Figure 102**, and **Figure 103** illustrate the waterfall plots for each $\text{Sr}_{2+x}\text{CrReO}_6$ ($x = -0.07, 0.0, 0.05, 0.075, \text{ and } 0.10$), $\text{Sr}_2\text{Cr}_{1+y}\text{Re}_{1-y}\text{O}_6$ ($y = -0.1, -0.05, 0.0, 0.05, \text{ and } 0.1$), and $\text{Sr}_{2-z}A_z\text{CrReO}_6$ ($A = \text{K, Ca, and La; } z = 0, 0.1, 0.2; z = 1 \text{ only for Ca}$) system, respectively. **Tables 23-25** report the refinement values, lattice parameters, phase purity, and $B$-site ordering ($\xi$) for each system. The $B$-site ordering reported from each composition in **Tables 23-25** is the highest ordering that can be achieved from either Wyckoff position: 2a site (0, 0, 0) and 2b site ($\frac{1}{2}, \frac{1}{2}, 0$).
Figure 85: X-ray powder diffraction pattern of Sr$_{1.93}$CrReO$_6$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The upper and lower blue vertical marks denote the Bragg reflections for $I4/m$ symmetry and the Re metal impurity, respectively.
Figure 86: X-ray powder diffraction pattern of Sr$_2$CrReO$_6$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The blue vertical marks denote the Bragg reflections.
Figure 87: X-ray powder diffraction pattern of $\text{Sr}_{2.05}\text{CrReO}_6$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The upper and lower blue vertical marks denote the Bragg reflections for $I\bar{4}/m$ symmetry and the Re metal impurity, respectively.
Figure 88: X-ray powder diffraction pattern of Sr$_{2.075}$CrReO$_6$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The upper and lower blue vertical marks denote the Bragg reflections for $I4/m$ symmetry and the Re metal impurity, respectively.
Figure 89: X-ray powder diffraction pattern of $\text{Sr}_{2.1}\text{CrReO}_6$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The upper and lower blue vertical marks denote the Bragg reflections for $I4/m$ symmetry and the $\text{Sr}_{11}\text{Re}_4\text{O}_{24}$ impurity, respectively.
Figure 90: X-ray powder diffraction pattern of Sr$_2$Cr$_{0.9}$Re$_{1.1}$O$_6$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The upper and lower blue vertical marks denote the Bragg reflections for $I4/m$ symmetry and the Re metal impurity, respectively.
Figure 91: X-ray powder diffraction pattern of $\text{Sr}_2\text{Cr}_{0.95}\text{Re}_{1.05}\text{O}_6$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The upper and lower blue vertical marks denote the Bragg reflections for $I4/m$ symmetry and the Re metal impurity, respectively.
Figure 92: X-ray powder diffraction pattern of $\text{Sr}_2\text{Cr}_{1.05}\text{Re}_{0.95}\text{O}_6$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The upper and lower blue vertical marks denote the Bragg reflections for $I4/m$ symmetry and the Re metal impurity, respectively.
Figure 93: X-ray powder diffraction pattern of Sr$_2$Cr$_{1.1}$Re$_{0.9}$O$_6$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The upper and lower blue vertical marks denote the Bragg reflections for $I4/m$ symmetry and the Re metal impurity, respectively.
**Figure 94:** X-ray powder diffraction pattern of $\text{Sr}_{1.9}\text{La}_{0.1}\text{CrReO}_6$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The upper and lower blue vertical marks denote the Bragg reflections for $I4/m$ symmetry and the Re metal impurity, respectively.
Figure 95: X-ray powder diffraction pattern of $\text{Sr}_{1.8}\text{La}_{0.2}\text{CrReO}_6$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The upper and lower blue vertical marks denote the Bragg reflections for $I4/m$ symmetry and the Re metal impurity, respectively.
Figure 96: X-ray powder diffraction pattern of $\text{Sr}_{1.9}\text{Ca}_{0.1}\text{CrReO}_6$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The blue vertical marks denote the Bragg reflections.
Figure 97: X-ray powder diffraction pattern of $\text{Sr}_{1.8}\text{Ca}_{0.2}\text{CrReO}_6$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The upper and lower blue vertical marks denote the Bragg reflections for $I4/m$ symmetry and the Re metal impurity, respectively.
Figure 98: X-ray powder diffraction pattern of SrCaCrReO$_6$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The blue vertical marks denote the Bragg reflections.
Figure 99: X-ray powder diffraction pattern of Sr$_{1.9}$K$_{0.1}$CrReO$_6$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The upper, middle, and lower blue vertical marks denote the Bragg reflections for $I4/m$ symmetry, the Re metal impurity, and the KReO$_4$ impurity, respectively.
**Figure 100:** X-ray powder diffraction pattern of $\text{Sr}_{1.8}\text{K}_{0.2}\text{CrReO}_6$ compound. The black dots, red and gray lines represent the observed, calculated and difference patterns, respectively. The upper, middle, and lower blue vertical marks denote the Bragg reflections for $I4/m$ symmetry, the Re metal impurity, and the KReO$_4$ impurity, respectively.
Figure 101: Waterfall plots of the X-ray powder diffraction patterns from Sr$_{2+x}$CrReO$_6$ (x = -0.07, 0, 0.05, 0.075, and 0.1) systems. The bottom waterfall plot has a 2θ range of 15-50 degrees with the intensity adjusted. The black circle in the bottom plot indicates the Sr$_{11}$Re$_4$O$_{24}$ impurity.
Figure 102: Waterfall plots of the X-ray powder diffraction patterns from \( \text{Sr}_2\text{Cr}_{1+y}\text{Re}_{1-y}\text{O}_6 \) \((y = -0.1, -0.05, 0, 0.05, \text{and} 0.1)\) systems. The bottom waterfall plot has a 2θ range of 15-50 degrees with the intensity adjusted. The black circles in the bottom plot indicate the Re metal impurity.
Figure 103: Waterfall plots of the X-ray powder diffraction patterns from $\text{Sr}_{2.2}A_{2}\text{CrReO}_6$ ($A = \text{K, Ca, and La}$; $z = 0, 0.1, 0.2$; $z = 1$ only for Ca) systems. The bottom waterfall plot has a 2θ range of 15-60 degrees with the intensity adjusted. The red and black circles on certain peaks in the bottom plot indicate the KReO$_4$ and Re metal impurities, respectively.
Table 23: Comparing the X-ray powder diffraction Rietveld refinements from different compositions in Sr$_{2+x}$CrReO$_6$ system. All have $I4/m$ symmetry.

<table>
<thead>
<tr>
<th>$x$</th>
<th>-0.07</th>
<th>0</th>
<th>0.05</th>
<th>0.075</th>
<th>0.10</th>
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<tbody>
<tr>
<td>$a$ (Å)</td>
<td>5.5338(1)</td>
<td>5.53205(9)</td>
<td>5.5312(1)</td>
<td>5.5310(2)</td>
<td>5.5309(2)</td>
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<tr>
<td>$c$ (Å)</td>
<td>7.8104(3)</td>
<td>7.8117(2)</td>
<td>7.8097(3)</td>
<td>7.8097(7)</td>
<td>7.8098(4)</td>
</tr>
<tr>
<td>$a_p$ (Å)</td>
<td>3.9103(2)</td>
<td>3.9099(1)</td>
<td>3.9090(2)</td>
<td>3.9090(4)</td>
<td>3.9089(2)</td>
</tr>
<tr>
<td>$\xi$ (%)</td>
<td>64.60(3)</td>
<td>72.92(1)</td>
<td>74.14(1)</td>
<td>72.30(2)</td>
<td>73.16(2)</td>
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<tr>
<td>Impurity (%)</td>
<td>Re 0.35</td>
<td>Re 0.09</td>
<td>Re 0.16</td>
<td>Re 0.49</td>
<td>Sr$<em>{11}$Re$</em>{24}$O$_{24}$ 0.70%</td>
</tr>
<tr>
<td>$R_{wp}$</td>
<td>23.842</td>
<td>19.423</td>
<td>20.182</td>
<td>23.692</td>
<td>24.680</td>
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Table 24: Comparing the X-ray powder diffraction Rietveld refinements from different compositions in Sr$_2$Cr$_{1+y}$Re$_{1-y}$O$_6$ system. All compounds have $I4/m$ symmetry.

<table>
<thead>
<tr>
<th>$y$</th>
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<th>0.05</th>
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<td>$a$ (Å)</td>
<td>5.5365(3)</td>
<td>5.5336(2)</td>
<td>5.5304(2)</td>
<td>5.5283(2)</td>
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<td>$c$ (Å)</td>
<td>7.8213(8)</td>
<td>7.8163(5)</td>
<td>7.8082(5)</td>
<td>7.8038(6)</td>
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<tr>
<td>$a_p$ (Å)</td>
<td>3.9135(4)</td>
<td>3.9113(3)</td>
<td>3.9084(3)</td>
<td>3.9067(4)</td>
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<tr>
<td>$\xi$ (%)</td>
<td>58.36(5)</td>
<td>66.14(1)</td>
<td>75.54(1)</td>
<td>79.14(1)</td>
</tr>
<tr>
<td>Re Impurity (%)</td>
<td>0.21</td>
<td>0.62</td>
<td>0.54</td>
<td>0.72</td>
</tr>
<tr>
<td>$R_{wp}$</td>
<td>24.365</td>
<td>19.329</td>
<td>18.624</td>
<td>18.143</td>
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### Table 25

Comparing the X-ray powder diffraction Rietveld refinements from different compositions in Sr$_{2-x}$A$_x$CrReO$_6$ ($A = K$, Ca, and La) system. All compounds have $I4/m$ symmetry.

<table>
<thead>
<tr>
<th></th>
<th>Lax</th>
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<tbody>
<tr>
<td></td>
<td>0.10</td>
<td>0.20</td>
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<tr>
<td>a (Å)</td>
<td>5.5347(2)</td>
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<td>c (Å)</td>
<td>7.8134(4)</td>
<td>7.819(1)</td>
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<td>a$_p$ (Å)</td>
<td>3.9113(3)</td>
<td>3.9126(2)</td>
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<tr>
<td>$\xi$ (%)</td>
<td>65.68(2)</td>
<td>64.26(3)</td>
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<tr>
<td>Re Impurity (%)</td>
<td>0.04</td>
<td>0.14</td>
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<tr>
<td>R$_{wp}$</td>
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<tr>
<td>R$_p$</td>
<td>16.939</td>
<td>17.281</td>
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<tr>
<td></td>
<td>0.10</td>
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<td>1</td>
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<tr>
<td>a (Å)</td>
<td>5.5290(1)</td>
<td>5.5273(2)</td>
<td>5.4826(7)</td>
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<tr>
<td>c (Å)</td>
<td>7.7993(3)</td>
<td>7.7982(4)</td>
<td>7.747(2)</td>
</tr>
<tr>
<td>a$_p$ (Å)</td>
<td>3.9063(2)</td>
<td>3.9053(3)</td>
<td>3.8757(4)</td>
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<tr>
<td>$\xi$ (%)</td>
<td>80.42(5)</td>
<td>81.40(9)</td>
<td>79.92(3)</td>
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<tr>
<td>Re Impurity (%)</td>
<td>0</td>
<td>0.11</td>
<td>0</td>
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<tr>
<td>R$_{wp}$</td>
<td>24.202</td>
<td>24.549</td>
<td>24.107</td>
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<tr>
<td>R$_p$</td>
<td>17.757</td>
<td>17.892</td>
<td>17.606</td>
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<table>
<thead>
<tr>
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<th>Kx, z</th>
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<tbody>
<tr>
<td></td>
<td>0.10</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>a (Å)</td>
<td>5.5319(1)</td>
<td>5.5196(3)</td>
<td></td>
</tr>
<tr>
<td>c (Å)</td>
<td>7.8074(3)</td>
<td>7.8185(9)</td>
<td></td>
</tr>
<tr>
<td>a$_p$ (Å)</td>
<td>3.9090(2)</td>
<td>3.9050(6)</td>
<td></td>
</tr>
<tr>
<td>$\xi$ (%)</td>
<td>81.00(2)</td>
<td>64.68(4)</td>
<td></td>
</tr>
<tr>
<td>Impurities (%)</td>
<td>KReO$_4$ 0.28 %</td>
<td>KReO$_4$ 3.81 %</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Re 0.30 %</td>
<td>Re 4.31 %</td>
</tr>
<tr>
<td>R$_{wp}$</td>
<td>16.881</td>
<td>22.318</td>
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<tr>
<td>R$_p$</td>
<td>12.358</td>
<td>17.461</td>
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All compositions were either phase pure solid solutions or nearly phase pure with negligible levels of un-reacted Re metal present (< 0.75 %), except for two compounds. Sr$_{2.1}$CrReO$_6$ had ~ 0.70 % Sr$_{11}$Re$_4$O$_{24}$ impurity, and Sr$_{1.8}$K$_{0.2}$CrReO$_6$ had 3.81 % KReO$_4$ and 4.31 % Re impurities. Sr$_{1.9}$K$_{0.1}$CrReO$_6$ is considered nearly phase pure since its level of KReO$_4$ is miniscule (0.28 %). On-stoichiometric Sr$_2$CrReO$_6$ is nearly phase pure and has a $\xi$ of 72.92(1) %. The B-site occupancy is refined separately from each Wyckoff site (2a Wyckoff site is 0,0,0 and 2b Wyckoff site is $\frac{1}{2}$, $\frac{1}{2}$, 0), and the highest attainable $\xi$ is reported between the two sites. Figures 104-106 show the highest attainable B-site ordering from each Sr$_{2+x}$CrReO$_6$ (x = -0.07, 0, 0.05, 0.075, and 0.10), Sr$_2$Cr$_{1+y}$Re$_{1-y}$O$_6$ (y = -0.1, -0.05, 0, 0.05, and 0.10), and Sr$_{2-z}$A$_z$CrReO$_6$ (A = K, Ca, and La; z = 0, 0.1, 0.2; z = 1 only for Ca) system, respectively. For the Sr$_{2+x}$CrReO$_6$ (x = -0.07, 0, 0.05, 0.075, and 0.10) system, the $\xi$ hovers around an average of ~ 71 %. Unfortunately there is not a linear trend for the $\xi$ observed, which could be to the system not incorporating the Sr substitution well into the system. As the Cr-substitution increases in the Sr$_2$Cr$_{1+y}$Re$_{1-y}$O$_6$ (y = -0.1, -0.05, 0, 0.05, and 0.10) system, the $\xi$ increases as well. This is expected since the Re valency is increasing, which promotes higher ordering due to the larger differences between the Cr and Re oxidation states. For isovalent A-site substitutions, the $\xi$ increases from the Sr$_2$CrReO$_6$ composition and then hovers around 80.5 %. It is expected that the $\xi$ should stay about the same, despite the different levels of Ca$^{2+}$ substitution. As for the aliovalent substitutions, the $\xi$ shows expected trends. Since K$^{1+}$ substitution causes the Re valency to increase, this promotes higher ordering. The reason why Sr$_{1.8}$K$_{0.2}$CrReO$_6$ shows a decrease in the $\xi$ and is not reported in Figure 106 is
because the level of K\textsuperscript{1+} substitution is not incorporated well into the composition. This is obvious since the amount of impurities is much higher than the other compositions. In the case of La\textsuperscript{3+} substitution, the $\xi$ decreases because Re is being reduced. The smaller charge difference between the $B$-site cations causes the $\xi$ to decrease. The two highest $B$-site orderings were observed for Sr\textsubscript{1.9}K\textsubscript{0.1}CrReO\textsubscript{6} and Sr\textsubscript{1.8}Ca\textsubscript{0.2}CrReO\textsubscript{6}, which are 81.00(2) % and 81.40(9) %, respectively. This is not surprising for the 5% K-substitution. However, it appears that somehow the smaller $A$-site cation (Ca\textsuperscript{2+}) substitution is influencing the $B$-site ordering and is causing the $\xi$ to be on the same level as the K\textsuperscript{1+} substitution.
Figure 104: The $B$-site ordering found for the $\text{Sr}_{2+x}\text{CrReO}_6$ ($x = -0.07, 0, 0.05, 0.075,$ and 0.10) system.
Figure 105: The B-site ordering found for the Sr$_2$Cr$_{1+y}$Re$_{1-z}$O$_6$ ($y = -0.1$, -0.05, 0, 0.05, and 0.10) system.
The pseudo-cubic lattice parameters for \( \text{Sr}_{2+x}\text{CrReO}_6 (x = -0.07, 0, 0.05, 0.075, \text{and } 0.10) \), \( \text{Sr}_2\text{Cr}_{1+y}\text{Re}_{1-y}\text{O}_6 (y = -0.1, -0.05, 0, 0.05, \text{and } 0.10) \), and \( \text{Sr}_2\text{A}_z\text{CrReO}_6 (A = K, \text{Ca, and La; } z = 0, 0.1, 0.2; z = 1 \text{ only for Ca}) \) systems are shown in Figures 107-111. When the Sr and the Cr levels increase in \( \text{Sr}_{2+x}\text{CrReO}_6 (x = -0.07, 0, 0.05, 0.075, \text{and } 0.10) \) and \( \text{Sr}_2\text{Cr}_{1+y}\text{Re}_{1-y}\text{O}_6 (y = -0.1, -0.05, 0, 0.05, \text{and } 0.10) \) systems, respectively, the lattice parameters and unit cell volume decrease. From a view of steric effects, adding more large Sr cations in the \( \text{Sr}_{2+x}\text{CrReO}_6 (x = -0.07, 0, 0.05, 0.075, \text{and } 0.10) \) system should increase the unit cell volume. However, a decrease is observed, which could be
due to cation vacancies. Effective nuclear charge or steric effects from the change in valency of the Re cation is responsible for the observed decrease in unit cell volume as the Cr content increases in $\text{Sr}_2\text{Cr}_{1+y}\text{Re}_{1-y}\text{O}_6$ ($y = -0.1, -0.05, 0, 0.05, \text{and } 0.10$) system. Since Re is becoming oxidized with increased levels of Cr content, the effective ionic radii decreases. In the aliovalent substitutions where $K^{1+}$ replaces $\text{Sr}^{2+}$, the lattice parameters and unit cell volume should increase due to steric effects from the larger A-site cation substitution, but instead the lattice parameters decrease. This is a result from the Re cations becoming oxidized; thus, effective electron removal from the Re $t_{2g}$ band. Whereas, the lattice parameters and unit cell volume increase when $\text{Sr}^{2+}$ is substituted by $\text{La}^{3+}$. From steric effects, the replacement of the larger $\text{Sr}^{2+}$ cation by the smaller $\text{La}^{3+}$ cation should decrease the lattice parameters. Instead there is an increase. This is attributed to the Re cations becoming reduced and the effective electron injection into the Re $t_{2g}$ band. As $\text{Sr}^{2+}$ is isovalently substituted by $\text{Ca}^{2+}$, the lattice parameters and unit cell volume decrease as expected because $\text{Ca}^{2+}$ is the smaller cation; hence steric effects.
**Figure 107:** Pseudo-cubic lattice parameters and unit cell volume for \( \text{Sr}_{2+x}\text{CrReO}_6 \) (\( x = -0.07, 0, 0.05, 0.075, \) and 0.10) system.
Figure 108: Pseudo-cubic lattice parameters and unit cell volume for \( \text{Sr}_2\text{Cr}_{1+y}\text{Re}_{1-y}\text{O}_6 \) (\( y = -0.1, -0.05, 0, 0.05, \) and 0.10) system.
Figure 109: Pseudo-cubic lattice parameters and unit cell volume for Sr$_{2-z}$La$_z$CrReO$_6$ ($z = 0, 0.1, \text{and } 0.2$) system.
Figure 110: Pseudo-cubic lattice parameters and unit cell volume for $\text{Sr}_{2-z}\text{Ca}_z\text{CrReO}_6$ ($z = 0, 0.1, 0.2, \text{ and } 1$) system.
Figure 111: Pseudo-cubic lattice parameters and unit cell volume for Sr$_{2-z}$K$_z$CrReO$_6$ ($z = 0$ and 0.1) system.

The $A$-site occupancies were refined for each compound to observe the effects of the substitutions. Figures 112-116 show this for Sr$_{2+x}$CrReO$_6$ ($x = -0.07$, 0, 0.05, 0.075, and 0.10), Sr$_2$Cr$_{1+y}$Re$_{1-y}$O$_6$ ($y = -0.1$, -0.05, 0, 0.05, and 0.10), Sr$_{2-z}$La$_z$CrReO$_6$ ($z = 0$, 0.1, 0.2), Sr$_{2-z}$Ca$_z$CrReO$_6$ ($z = 0$, 0.1, 0.2, and 1), and Sr$_{2-z}$K$_z$CrReO$_6$ ($z = 0$, 0.1, 0.2) compounds, respectively.
Figure 112: Refined A-site occupancy for \( \text{Sr}_x\text{CrReO}_6 \) (\( x = 1.93, 2.0, 2.05, 2.075, \) and 2.10) system.
Figure 113: Refined A-site occupancy for \( \text{Sr}_2\text{Cr}_y\text{Re}_{2-y}\text{O}_6 \) \((y = 0.90, 0.95, 1.0, 1.05, \text{ and } 1.10)\) system.
Figure 114: Refined A-site occupancies for Sr$_{2-z}$La$_z$CrReO$_6$ ($z = 0$, 0.1, and 0.2) system.
Figure 115: Refined A-site occupancies for Sr$_{2-z}$Ca$_z$CrReO$_6$ ($z = 0, 0.1, 0.2, \text{ and } 1$) system.
Figure 116: Refined A-site occupancies for $\text{Sr}_{2-z}\text{K}_z\text{CrReO}_6$ ($z = 0, 0.1, \text{and} 0.2$) system.

In Figure 112, the refined Sr occupancy for the $\text{Sr}_{2+x}\text{CrReO}_6$ ($x = -0.07, 0, 0.05, 0.075, \text{and} 0.10$) system does not show a linear trend, meaning that the system is not responding well to the substitutions. It is possible that different levels of cation vacancies could be responsible for this observation. In particular, the refined Sr occupancy outlier for $\text{Sr}_{1.93}\text{CrReO}_6$ does not make logical sense, which clearly shows that Sr is not substituting well into this compound. In Figure 113, there is a general increasing trend for the Sr occupancy for $\text{Sr}_2\text{Cr}_{1+y}\text{Re}_{1-y}\text{O}_6$ ($y = -0.1, -0.05, 0, 0.05, \text{and} 0.1$) system, except for $\text{Sr}_2\text{Cr}_{1.05}\text{Re}_{0.95}\text{O}_6$. During the synthesis reaction, this compound could have produced slightly more cation vacancies, which would cause this outlier to be slightly off from the
increasing trend. The substitutions made by the La, Ca, and K cations all show linear trends in the refined Sr and A-site substitutions; see Figures 114-116. These results show that the Sr and A-site cation substitutions are incorporating well into the Sr$_{2-z}$A$_z$CrReO$_6$ ($A = K, Ca, and La; z = 0, 0.1, 0.2; z = 1$ only for Ca) systems. The occupancies from each A-site substituted system are approximately on par to the expected values.

5.5.2 Electrical properties

To study the effects of how the electrical properties change with each substitution, the resistivity for Sr$_{2+x}$CrReO$_6$ ($x = -0.07$ and $0.075$), Sr$_2$Cr$_{1+y}$Re$_{1-y}$O$_6$ ($y = -0.1, -0.05, 0, 0.05, and 0.10$), and Sr$_{2-z}$A$_z$CrReO$_6$ ($A = K$ when $z = 0.1; A = La$ when $z = 0.2; A = Ca$ when $z = 1$) samples was measured. These representative compounds were chosen from each system to understand how the substitutions change the electrical transport. The low temperature (5 K) and room temperature resistivities are recorded in Table 26. Figure 117 shows the log scale of the conductivity, and Figures 118-120 show the log scale of the resistivity ratio ($\rho_T / \rho_{400K}$) for Sr$_{2+x}$CrReO$_6$ ($x = -0.07$, $0$, and $0.075$), Sr$_2$Cr$_{1+y}$Re$_{1-y}$O$_6$ ($y = -0.1, -0.05, 0, 0.05,$ and $0.10$), and Sr$_{2-z}$A$_z$CrReO$_6$ ($A = K$ when $z = 0.1; A = La$ when $z = 0.2; A = Ca$ when $z = 1$) system, respectively. $\rho_T$ represents the resistivity collected as the temperature varies. The resistivity from each system was normalized because of a temperature dependence observed from the samples, particularly in the higher temperature regime. This correlates to the effects of the grain boundaries due to the fair amount of the porosity from the polycrystalline samples.
Figure 117: Log of the conductivity as a function of temperature for Sr$_{2+x}$CrReO$_6$ ($x = -0.07$ and 0.075), Sr$_2$Cr$_{1+y}$Re$_{1-y}$O$_6$ ($y = -0.1$, -0.05, 0, 0.05, and 0.1), and Sr$_{2-z}$A$_z$CrReO$_6$ ($A = K$ when $z = 0.1$; $A = La$ when $z = 0.2$; $A = Ca$ when $z = 1$) systems.
**Figure 118:** Log scale plot of the normalized resistivity ($\rho_T / \rho_{400K}$) for the $\text{Sr}_{2+x}\text{CrReO}_6$ ($x = -0.07, 0, \text{ and } 0.075$) system as a function of temperature.
Figure 119: Log scale plot of the normalized resistivity ($\rho_T / \rho_{400K}$) for the $\text{Sr}_2\text{Cr}_{1+y}\text{Re}_{1-y}\text{O}_6$ ($y = -0.1, -0.05, 0, 0.05,$ and $0.10$) system as a function of temperature.
Figure 120: Log scale plot of the normalized resistivity \( \rho_T / \rho_{400K} \) for the Sr\(_{2-z}\)A\(_z\)CrReO\(_6\) (\( A = K \) when \( z = 0.1 \); \( A = La \) when \( z = 0.2 \); \( A = Ca \) when \( z = 1 \)) system as a function of temperature.
Table 26: Comparing the low temperature and room temperature resistivities for each compound.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\rho(\Omega\cdot\text{cm})$ at 5 K</th>
<th>$\rho(\Omega\cdot\text{cm})$ at 300 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Sr}_{1.92}\text{CrReO}_6$</td>
<td>$1.14 \times 10^1$</td>
<td>3.15</td>
</tr>
<tr>
<td>$\text{Sr}_2\text{CrReO}_6$</td>
<td>1.28</td>
<td>0.40</td>
</tr>
<tr>
<td>$\text{Sr}_{2.075}\text{CrReO}_6$</td>
<td>1.43</td>
<td>0.197</td>
</tr>
<tr>
<td>$\text{Sr}<em>2\text{Cr}</em>{0.3}\text{Re}_{1.1}\text{O}_6$</td>
<td>$1.30 \times 10^4$</td>
<td>514.26</td>
</tr>
<tr>
<td>$\text{Sr}<em>2\text{Cr}</em>{0.95}\text{Re}_{1.05}\text{O}_6$</td>
<td>$5.86 \times 10^3$</td>
<td>216.78</td>
</tr>
<tr>
<td>$\text{Sr}<em>2\text{Cr}</em>{1.05}\text{Re}_{0.95}\text{O}_6$</td>
<td>$1.47 \times 10^1$</td>
<td>1.60</td>
</tr>
<tr>
<td>$\text{Sr}<em>2\text{Cr}</em>{1.1}\text{Re}_{0.5}\text{O}_6$</td>
<td>2.80</td>
<td>0.132</td>
</tr>
<tr>
<td>$\text{Sr}<em>{1.9}\text{K}</em>{0.1}\text{CrReO}_6$</td>
<td>$6.57 \times 10^4$</td>
<td>157.96</td>
</tr>
<tr>
<td>$\text{Sr}\text{CaCrReO}_6$</td>
<td>$6.99 \times 10^4$</td>
<td>0.308</td>
</tr>
<tr>
<td>$\text{Sr}<em>{1.8}\text{La}</em>{0.2}\text{CrReO}_6$</td>
<td>$2.02 \times 10^6$ (at 42 K)</td>
<td>$1.17 \times 10^4$</td>
</tr>
</tbody>
</table>

The $\text{Sr}_{2+x}\text{CrReO}_6$ ($x = -0.07$ and 0.075) and $\text{Sr}_2\text{Cr}_{1+y}\text{Re}_{1-y}\text{O}_6$ ($y = -0.1$, -0.05, 0, 0.05, and 0.1) compounds are more metallic by nature than the $\text{Sr}_{2-z}\text{A}_z\text{CrReO}_6$ ($A = \text{K}$ when $z = 0.1$; $A = \text{La}$ when $z = 0.2$; $A = \text{Ca}$ when $z = 1$) compounds. The Sr-rich compound is the most metallic of all the studied compounds with little temperature dependence. It is possible that the grain boundaries could be interfering and masking the conductive nature of this sample. The Sr-deficient compound shows Mott insulating behavior. As the Cr-content increases, the resistivity decreases. There is a clear shift from the Cr-deficient ($y = -0.1$ and -0.05) compounds showing Mott insulating behavior to the Cr-rich ($y = 0.05$ and 0.1) compounds showing metallic conductivity in the low temperature regime. Had the resistivity been collected for temperatures above 400 K, we would see a clear insulator to metal transition for $\text{Sr}_2\text{Cr}_{0.9}\text{Re}_{1.1}\text{O}_6$ since the resistivity jumps by an order of magnitude...
in the temperature regime of 300-400 K in Figure 119. This validates Mott insulating behavior.

The $\text{Sr}_{1.8}\text{La}_{0.2}\text{CrReO}_6$ shows Mott insulating behavior and is the most highly resistive compound compared to the others. La-substitution is expected to increase conductivity since Re is being reduced. However, this is not observed. In the case of $\text{Sr}_{2-x}\text{La}_x\text{FeReO}_6$, the resistivity increased with increased substitutions of La.\textsuperscript{9} Reasons for this increase in resistivity is attributed to successful electron injection into the metal d-bands.\textsuperscript{9} By introducing charge carriers to the system, the electrons are effectively transferred to the Re $t_{2g}$ down spin band. This explanation is supported by the increase in lattice parameters and thus the unit cell volume for $\text{Sr}_{2-x}\text{La}_x\text{CrReO}_6$ ($z = 0$, 0.1, and 0.2) system. If this was not the case, the La-substitution should decrease the lattice parameters since La$^{3+}$ is smaller in ionic radii than Sr$^{2+}$. The $\text{Sr}_{1.9}\text{K}_{0.1}\text{CrReO}_6$ compound is the second highly resistive sample followed by the $\text{SrCaCrReO}_6$ compound. Electron hole substitution is expected to increase the resistivity since Re is being oxidized. K-substitution or electron-hole substitution has never been explored in $\text{Sr}_2\text{CrReO}_6$. As for $\text{SrCaCrReO}_6$, this compound exhibits Mott insulating behavior. This is expected since the Ca$^2$CrReO$_6$ analog is an insulator.\textsuperscript{12} Our measured resistivity for $\text{SrCaCrReO}_6$ matches well with the literature for Ca$^2$CrReO$_6$,\textsuperscript{12} in that the resistivity increases by more than 4 orders of magnitude.

It is expected that the aliovalent and isovalent A-site substitutions should follow the trend of La$^{3+} > \text{Ca}^{2+} > \text{K}^{1+}$ in conductivity. However, this trend is not observed in Figure 120. The grain boundaries are suspected in playing a significant role in affecting
the conductivities of these samples, particularly in the higher temperature regime, because of a temperature dependence observed across the substitutions. This is attributed to how well the sintering is affected by the density of these polycrystalline pellets considering these samples have a significant amount of porosity.

5.6 Magnetic properties

The magnetization was collected for $\text{Sr}_{2+x}\text{CrReO}_6$ ($x = -0.07$, 0, and 0.075), $\text{Sr}_2\text{Cr}_{1+y}\text{Re}_{1-y}\text{O}_6$ ($y = -0.1$, -0.05, 0, 0.05, and 0.10), and $\text{Sr}_{2-z}\text{A}_z\text{CrReO}_6$ ($A = \text{K}$ when $z = 0.1$; $A = \text{La}$ when $z = 0.2$; $A = \text{Ca}$ when $z = 1$) samples to gauge the trend from the substitutions in the magnetic properties. All hysteresis loops showed FM/FiM-like behavior (see Figures 121-124). Because $\text{Sr}_2\text{CrReO}_6$ does not saturate at 5 K using ±5 T fields (see Figure 121), the hysteresis loops for all the substitutions were taken at 300 K and swept with ±5 T fields. As shown in Figures 122-124, none of the room temperature hysteresis loops are truly saturated. Ideally a high field pulsed magnetometer, which can go as high as 100 T fields, would be needed to fully saturate these samples at room and low temperatures.
Figure 121: Measure of the magnetization as a function of field for Sr$_2$CrReO$_6$ taken at 5 K and 300 K.
Figure 122: Room temperature hysteresis for Sr$_{2+x}$CrReO$_6$ (x = -0.07, 0, and 0.075) system.
Figure 123: Room temperature hysteresis for $\text{Sr}_2\text{Cr}_{1+y}\text{Re}_{1.3}\text{O}_6$ ($y = -0.1, -0.05, 0, 0.05,$ and 0.10) system.
Figure 124: Room temperature hysteresis for Sr$_{1.9}$K$_{0.1}$CrReO$_6$, SrCaCrReO$_6$, Sr$_{1.8}$La$_{0.2}$CrReO$_6$, and Sr$_2$CrReO$_6$ samples.

The slight indent in the hysteresis curves for Sr$_{2.075}$CrReO$_6$ and SrCaCrReO$_6$ (see Figure 122 and Figure 124, respectively) is an artifact from movement of the polycrystalline powder while measuring the magnetic moment.

The magnetization from Figure 122 for Sr$_{2+x}$CrReO$_6$ ($x = -0.07, 0$, and 0.075) system changes very little but does show a slight increase in the magnetization as the Sr substitution increases. This is not expected since the Re is becoming reduced with increased levels of Sr substitution. Possible explanations for this trend could relate to cation vacancies or a small percentage of Ruddlesden-Popper phase could be present that
could not be detected from XRD. As for the Sr$_2$Cr$_{1+y}$Re$_{1-y}$O$_6$ ($y = -0.1$, -0.05, 0, 0.05, and 0.10) system, the magnetization shows an increase as the Cr-substitution increases, except for Sr$_2$Cr$_{1.1}$Re$_{0.9}$O$_6$ (see Figure 123). This trend is expected since the Re is becoming oxidized. For stability purposes, the chromium cation should maintain an oxidation state of Cr$^{3+}$ ($d^3$). Considering this and that Cr$^{3+}$ and Re$^{5+/6+}$ are antiferromagnetically coupled, the magnetization should increase with increased levels of Cr-substitution because Re is oxidized. Explanations for why the magnetization dips back down for Sr$_2$Cr$_{1.1}$Re$_{0.9}$O$_6$ is because of increased amounts of Cr substitution. Because these samples are not a 100% ordered, anti-sites where a Cr is sitting next to another Cr would cause the magnetization to decrease. Super-exchange interactions between Cr$^{3+}$ ($d^3$) and Cr$^{3+}$ ($d^3$) results in a net zero moment; thereby, localized pockets of anti-sites from Cr causes the magnetization to decrease.

As for Figure 124 that displays the room temperature hysteresis loops for Sr$_{1.9}$K$_{0.1}$CrReO$_6$, SrCaCrReO$_6$, Sr$_{1.8}$La$_{0.2}$CrReO$_6$, and Sr$_2$CrReO$_6$ samples, the magnetization shows an expected linear trend across the aliovalent substitutions compared to Sr$_2$CrReO$_6$ but not for the isovalent substitution. The magnetization for SrCaCrReO$_6$ is higher than Sr$_2$CrReO$_6$. Somehow the relative nature of calcium causing the surrounding octahedra to tilt is influencing a high magnetization for SrCaCrReO$_6$. Pertaining to the pseudo-box shaped hysteresis curve for SrCaCrReO$_6$ in Figure 124, this indicates the hardness of the magnet. As for aliovalent substitutions with La$^{3+}$, the magnetization decreases because Re is reduced. From super-exchange interactions, the antiferromagnetically coupled spins between Cr$^{3+}$ ($d^3$) and Re$^{4+/5+}$ ($d^3$ / $d^2$) causes the
ferrimagnetic moment to decrease. Likewise for $K^{1+}$-substitution, the magnetization increases since Re is oxidized. For similar arguments, the antiferromagnetically coupled spins between $Cr^{3+}$ ($d^3$) and $Re^{5+/6+}$ ($d^2/d^1$) causes the ferrimagnetic moment to increase.

The ZFC and FC susceptibilities curves support FM/FiM-like behavior (see Figures 125-127). The Curie temperatures from the FC curves are reported in Table 27. The overlay of the ZFC and FC curves from each sample clearly shows robust FM/FiM behavior. Figure 125 shows that as the Sr substitution increases, the $T_C$ is approximately the same. Significant changes in the $T_C$ are not expected. The $T_C$ is expected to slightly decrease for $Sr_{1.93}CrReO_6$ compared to $Sr_2CrReO_6$ because the Re valency increases; thereby less delocalized electrons are present. As for the slight decrease in $T_C$ for $Sr_{2.075}CrReO_6$, this could be due to an undetectable amount of the Ruddlesden-Popper phase. Segueing to the $Sr_2Cr_{1+y}Re_{1-y}O_6$ ($y = -0.1, 0$, and $0.1$) system, Figure 126 shows that the $T_C$ decreases as the Cr-substitution increases. This is attributed to the Re valency increasing; thereby causing less delocalized electrons to be present. The aliovalent and isoential $A$-site substitutions also show expected trends in the $T_C$ (see Figure 127). The $La^{3+}$ substitution is expected to increase the $T_C$ because of increased carriers and double exchange from more delocalized electrons. Other compounds explored with $La^{3+}$ substitution, such as $Sr_{2-x}La_xFeReO_6$ ($x \leq 0.5$) and $Sr_{2-x}La_xFeMoO_6$ ($1 \geq x \geq 0$), have also found an increase in $T_C$ as the La content increased. However, these studies also showed that as a consequence of La substitution, the $M_{sat}$ decreases, which is on par with what we observe. The $T_C$ decreases with $K^{1+}$-substitution since less delocalized electrons are present from Re becoming oxidized. As for isovalent substitution, the $T_C$ decreases as
well but for entirely different reasons. When the smaller cation Ca\textsuperscript{2+} replaces the larger cation Sr\textsuperscript{2+}, octahedral tilting occurs for energetic reasons and causes the bond angles to become more bent. Therefore the pathway of the super-exchange magnetic interactions is hindered in that the bond angles are not linear, which results in a decrease in the T\textsubscript{C}. SrCaCrReO\textsubscript{6} compound has the lowest T\textsubscript{C} of all the studied compounds.

![Graph](image_url)

**Figure 125:** Zero-field cooled and field-cooled susceptibility plot for Sr\textsubscript{2+x}CrReO\textsubscript{6} (x = -0.07, 0, and 0.075) system. The field was set to 8 kG.
Figure 126: Zero-field cooled and field-cooled susceptibility plot for $\text{Sr}_2\text{Cr}_{1+y}\text{Re}_{1-y}\text{O}_6$ ($y = -0.10, 0, \text{and} 0.10$) system. The field was set to 8 kG.
Figure 127: Zero-field cooled and field-cooled susceptibility plot for Sr$_{2-x}$A$_x$CrReO$_6$ ($A = K$ when $z = 0.1$; $A = La$ when $z = 0.2$; $A = Ca$ when $z = 1$; $z = 0$) system. The field was set to 8 kG.
Table 27: Comparing the room temperature magnetizations, Curie temperatures, and coercivities for each sample collected from the superconducting quantum interference device.

The room temperature magnetizations and coercivities for these samples are reported in Table 27. The hardest magnet observed is SrCaCrReO$_6$. Figures 128-132 recap the magnetizations and $T_C$ for each system. The highest magnetization of all the studied compounds is the 5% K-substituted compound with 0.756 $\mu_B$/f.u. (see Figure 128). The magnetizations for SrCaCrReO$_6$ and Sr$_{1.8}$La$_{0.2}$CrReO$_6$ compounds are 0.745 $\mu_B$/f.u. and 0.482 $\mu_B$/f.u., respectively (see Figures 129-130). With electron-hole substitution, the moment increases, but as charge carriers are introduced into the Sr$_2$CrReO$_6$ compound, the moment decreases. Both trends are expected due to the change in valency of the Re cation. The K$^{1+}$-substitution causes Re to be oxidized; thereby resulting in an increase in magnetization. Likewise, the La$^{3+}$-substitution causes Re to be reduced, which results in a decrease in magnetization. The magnetizations for Sr$_2$CrReO$_6$ and SrCaCrReO$_6$ are 0.651 $\mu_B$/f.u. and 0.745 $\mu_B$/f.u., respectively. Somehow the relative

<table>
<thead>
<tr>
<th>Compound</th>
<th>$M$ ($\mu_B$/f.u.) at 300 K</th>
<th>$T_C$ (K)</th>
<th>$H_C$ (kG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr$_{1.22}$CrReO$_6$</td>
<td>0.590</td>
<td>643</td>
<td>11.1</td>
</tr>
<tr>
<td>Sr$_2$CrReO$_6$</td>
<td>0.651</td>
<td>645</td>
<td>12.5</td>
</tr>
<tr>
<td>Sr$_{2.072}$CrReO$_6$</td>
<td>0.658</td>
<td>640</td>
<td>10.3</td>
</tr>
<tr>
<td>Sr$<em>2$Cr$</em>{0.5}$Re$_{1.5}$O$_6$</td>
<td>0.441</td>
<td>655</td>
<td>9.37</td>
</tr>
<tr>
<td>Sr$<em>{2.102}$Cr$</em>{0.6}$Re$_{0.95}$O$_6$</td>
<td>0.576</td>
<td>647</td>
<td>13.1</td>
</tr>
<tr>
<td>Sr$<em>2$Cr$</em>{1.1}$Re$_{0.5}$O$_6$</td>
<td>0.911</td>
<td>640</td>
<td>12.2</td>
</tr>
<tr>
<td>Sr$<em>{1.5}$K$</em>{0.2}$CrReO$_6$</td>
<td>0.564</td>
<td>630</td>
<td>14.3</td>
</tr>
<tr>
<td>SrCaCrReO$_6$</td>
<td>0.756</td>
<td>621</td>
<td>13.0</td>
</tr>
<tr>
<td>Sr$<em>{1.8}$La$</em>{0.2}$CrReO$_6$</td>
<td>0.745</td>
<td>570</td>
<td>26.2</td>
</tr>
<tr>
<td>Sr$<em>{1.8}$La$</em>{0.2}$CrReO$_6$</td>
<td>0.482</td>
<td>650</td>
<td>8.42</td>
</tr>
</tbody>
</table>
nature of the calcium cation causing the surrounding octahedra to tilt could be influencing the magnetization. As the Sr level increases in $\text{Sr}_{2+x}\text{CrReO}_6$, the magnetization increases (see Figure 131). With increased Cr substitutions in $\text{Sr}_2\text{Cr}_{1+y}\text{Re}_{1-y}\text{O}_6$ system, there is a rise and fall in the magnetizations (see Figure 132).

Figure 128: Magnetization and Curie temperature for $\text{Sr}_{1.9}\text{K}_{0.1}\text{CrReO}_6$ and $\text{Sr}_2\text{CrReO}_6$ compounds.
Figure 129: Magnetization and Curie temperature for SrCaCrReO$_6$ and Sr$_2$CrReO$_6$ compounds.
Figure 130: Magnetization and Curie temperature for Sr$_{1.8}$La$_{0.2}$CrReO$_6$ and Sr$_2$CrReO$_6$ compounds.
Figure 131: Magnetization and Curie temperature for Sr$_{2+x}$CrReO$_6$ (x = -0.07, 0, and 0.075) system.
Figure 132: Magnetization and Curie temperature for Sr$_2$Cr$_{1+y}$Re$_{1-y}$O$_6$ ($y = -0.1, -0.05, 0, 0.05, \text{ and } 0.1$) system.

5.7 Discussion

We have successfully synthesized and characterized Sr$_{2+x}$CrReO$_6$ ($x = -0.07, 0, 0.05, \text{ and } 0.075, \text{ and } 0.1$), Sr$_2$Cr$_{1+y}$Re$_{1-y}$O$_6$ ($y = -0.1, -0.05, 0.05, \text{ and } 0.1$), and Sr$_{2-z}$A$_z$CrReO$_6$ ($A = \text{K, Ca, and La; } z = 0, 0.1, 0.2; z = 1 \text{ only for Ca}$) systems. All compounds adopt $I4/m$ symmetry. We show that with significant amounts of substitutions the compositions are either phase pure solid solutions or nearly phase pure for all but two compounds.

We observe that the Sr$_{2+x}$CrReO$_6$ ($x = -0.07$ and $0.075$) and Sr$_2$Cr$_{1+y}$Re$_{1-y}$O$_6$ ($y = -0.1, -0.05, 0, 0.05, \text{ and } 0.1$) compounds are more metallic than the Sr$_{2-z}$A$_z$CrReO$_6$ ($A = \text{K when } z = 0.1; A = \text{La when } z = 0.2; A = \text{Ca when } z = 1$) compounds. Grain boundaries are
suspected in interfering with the conductivities of the more metallic compounds. We note that the $\text{Sr}_2\text{Cr}_{0.9}\text{Re}_{1.1}\text{O}_6$ compound shows an insulator to metal transition in the temperature regime of 300-400 K, which marks Mott insulating behavior. The aliovalent and isovalent $A$-site substituted compounds all show Mott insulating behavior and are the more resistive samples by several orders of magnitude. Considering that these are polycrystalline samples, there is a significant amount of porosity caused by how well the pellets were sintered. As a result, there is temperature dependence in the higher temperature regime, which is attributed to the effects of grain boundaries. It is also certainly plausible that other phases may be present but are not detectable by XRD that could be responsible for preventing electrical conductivity.

While the magnetization does not change significantly for the $\text{Sr}_{2+x}\text{CrReO}_6$ ($x = -0.07, 0, 0.05, \text{ and } 0.10$) system, the magnetizations and Curie temperatures change in expected trends for $\text{Sr}_2\text{Cr}_{1+y}\text{Re}_{1-y}\text{O}_6$ ($y = -0.10, -0.05, 0, \text{ and } 0.05$) and $\text{Sr}_{2-z}A_z\text{CrReO}_6$ ($A = \text{K when } z = 0.1; A = \text{La when } z = 0.2$) compounds. As the Cr substitutions increase, the magnetization increases, except for $\text{Sr}_2\text{Cr}_{1.1}\text{Re}_{0.9}\text{O}_6$, and the Curie temperatures steadily decrease across the substitutions. This is attributed to Re being oxidized. For the same reason, the magnetization increases and the Curie temperatures decrease for electron-hole substitutions. For charge carrier substitutions, the opposite occurs in that the magnetization decreases and the Curie temperatures increase. This is because Re is reduced. As for isovalent substitutions, the role of the smaller cation Ca$^{2+}$ substitutions is responsible for why we observe a decrease in the Curie temperature and is suspected in
influencing the magnetization. From steric effects, the smaller cation causes the surrounding octahedra to tilt.

Considering these findings, it is interesting how we can manipulate the magnetic and electrical properties when deviating away from on-stoichiometry and with aliovalent and isovalent substitutions. These types of substitutions have not been explored in $\text{Sr}_2\text{CrReO}_6$; thus this project sheds new light. Furthermore this work may help gain understandings of the electrical and magnetic properties observed in thin films of $\text{Sr}_2\text{CrReO}_6$ and may lay the ground work for future directions in growing thin films of this material.

5.8 Acknowledgement

Financial support from the NSF through a Materials World Network grant (MWN-0603128) is gratefully acknowledged.
5.9 References

CHAPTER 6: SYNTHESIS AND CHARACTERIZATION OF POLYCRYSTALLINE Sr₂CrOsO₆

6.1 Contribution

The focus of this project is to better understand the magnetic and electrical properties of phase pure Sr₂CrOsO₆ double perovskites. This chapter will be published, and the following are the authors in order: Jennifer R. Soliz, Adam J. Hauser, Michael A. Susner, Michael D. Sumption, Fengyuan Yang, and Patrick M. Woodward. Jennifer R. Soliz has synthesized, collected and analyzed the structural properties from X-ray diffraction, and measured the electrical transport using the physical property measurement system. Adam J. Hauser and Fengyuan Yang have measured the susceptibility as a function of temperature using the vibrating sample magnetometer in Fengyuan Yang’s lab and measured the low and high temperature saturated magnetization using the vibrating sample magnetometer at the National High Magnetic Field Laboratory. Michael A. Susner measured the low and high temperature saturated magnetization using the physical property measurement system in Michael D. Sumption’s lab. Patrick M. Woodward is Jennifer’s adviser and has been informed about the details of this work. Future studies will be neutron powder diffraction results that will be collected by Ryan Morrow. This work will be added to the manuscript for publishing,
which will take place after the completion of this dissertation, and Ryan will be added as a contributing author.

6.2 Abstract

We investigate the structural, magnetic, and electrical properties of phase pure polycrystalline Sr$_2$CrOsO$_6$. From X-ray powder diffraction, Sr$_2$CrOsO$_6$ adopts the $R3$ symmetry and is 73.6(3) % ordered. Our magnetic results show Sr$_2$CrOsO$_6$ to be a ferrimagnet with a small net moment of 0.224 μ$_B$/f.u. at 4.5 K in a field strength of 35 T, and the Curie temperature is 660 K. Sr$_2$CrOsO$_6$ is strongly insulating with resistivity of 8.61x10$^2$ Ω·cm at 300K and shows a linear function for the variable range hopping model.

6.3 Introduction

Perovskites have been broadcasted to display an expansive array of properties.\textsuperscript{1} With further complexity, double perovskites combine a first row transition metal and a second or third row transition metal on the $B/B'$ sites, which allows the presence of localized and itinerant electrons, respectively. This is key for potentially enabling highly spin polarized magnetism which can be used in magnetoresistive (MR) applications.\textsuperscript{2,3} Since the discovery over a decade ago of large MR at room temperature in the ferrimagnetic half-metallic Sr$_2$FeMoO$_6$ ($T_C = 420$ K),\textsuperscript{4,5} the quest to find other high $T_C$ half-metallic materials with such properties has been a strong motive, in particular for spintronic applications.
Of the theoretically studied Cr-based $A_2CrB'O_6$ double perovskites ($A =$ Sr and Ca; $B' =$ W, Mo, Re, and Os), calculations have predicted $Sr_2CrOsO_6$ to be a Mott insulating ferrimagnet with a high $T_C$ of 725 K. In fact because $Sr_2CrOsO_6$ has the highest $T_C$ amongst all simple and double perovskites and is found to be an insulator makes this compound highly intriguing. While some high $T_C$ FiM double perovskites have been extensively studied such as $Sr_2FeMoO_6$ and $Sr_2FeReO_6$ ($T_C = 400$ K), $Sr_2CrOsO_6$ has not been well explored experimentally. Krockenberger et al. combines band structure calculations and an experimental study of the structural and magnetic properties, where $Sr_2CrOsO_6$ is reported as a high $T_C$ (725 K) FiM insulator. This study also reports the room temperature resistivity (10 Ω·cm) without showing how the temperature dependence of experimental resistivity. This leaves some ambiguity in how the resistivity changes in the low temperature regime? Is it truly an insulator or due to some extrinsic effect such as sample imperfections? To date, no other experimental work has been done to reveal further electrical characteristics of $Sr_2CrOsO_6$. In this study, we characterized the structural, magnetic, and electrical properties for polycrystalline $Sr_2CrOsO_6$.

6.4 Experimental Section

Polycrystalline powder of $Sr_2CrOsO_6$ was prepared using stoichiometric amounts of SrO (Sigma Aldrich, 99.9 % purity), CrO$_3$ (Sigma Aldrich, 99.99 %), Cr$_2$O$_3$ (Fisher Scientific, 99 %), and Os (Fisher Scientific, 99.9 %). The mixture was weighed using an analytical balance with an accuracy of 0.1 mg and ground using an agate mortar and pestle inside a glove box with O$_2$ and H$_2$O at part-per-million levels. The mixture was
loaded into high density (99.8 % dense) alumina tubes in order to maintain purity and then sealed in an evacuated quartz tube. The sample was heated to 1000 °C for 44 h. The obtained sample was reground and heated further to 400 °C under flowing O₂ gas for 13.5 h to remove excess osmium metal. The finished product appears as a black powder.

A Bruker D8 Advance diffractometer with Cu Kα₁ radiation (λ = 1.54059 Å) at a power of 40 kV, 50 mA and a Ge 111 incident beam monochromator was used to collect the X-ray powder diffraction scans to verify phase purity. The scans were taken in the 2θ range of 10-90°. The step size was 0.014286° (2θ) and the count time was 2.0 s/step. The pattern was refined by the Rietveld method using Topas academic software.¹⁰

Sr₂CrOsO₆ was sintered as a 55% dense rectangular pellet with 1x0.5x0.25 cm dimensions. Silver paint was applied to attach copper leads to the pellet. We measured the dc resistivity over a temperature range of 140 K to 350 K using four-point probe method in a Quantum Design model 6000 physical property measurement system (PPMS). The magnetic field was zero during the measurements. No corrections were made for porosity.

Magnetic hysteresis loops of the Sr₂CrOsO₆ pellet were measured using the Vibrating Sample Magnetometer (VSM) option of the PPMS with the maximum field of 14 T at 5 K, 300 K, and 400 K. Higher magnetic fields (± 35 T) were used to measure the hysteresis loops at 4.5 K and 295 K using the VSM from the National High Magnetic Field Laboratory (NHMFL). Magnetic susceptibility of the field cooled (FC) sample was obtained using a LakeShore VSM. The sample was heated to 800 K and then cooled in a
1.5 T field to field cooling the sample. The field cooled susceptibility curve was then measured in a field strength of 1 kG in the temperature range from 300 K to 800 K.

### 6.5 Results and Discussion

#### 6.5.1 X-ray powder diffraction

Using Rietveld refinements on the polycrystalline Sr$_2$CrOsO$_6$ samples, we found that the compound was nearly phase pure with a small amount of osmium metal (0.65%). Sr$_2$CrOsO$_6$ adopts the $R3$ space group symmetry and is found to be 73.6(3)% ordered. **Figure 133** shows the X-ray powder diffraction pattern. **Table 28** reports the refinement values and the structural parameters.
Figure 133: X-ray powder diffraction scan of \( \text{Sr}_2\text{CrOsO}_6 \). The dark grey dots, light grey and black lines represent the observed, calculated and difference patterns, respectively. The blue vertical marks denote the Bragg reflections.
Table 28: Rietveld refinement values and structural parameters for Sr$_2$CrOsO$_6$ from X-ray powder diffraction.

### 6.5.2 Electrical properties

The resistivity data collected over a temperature range of 140-350 K shows that Sr$_2$CrOsO$_6$ is indeed an insulator with activated electron transport. This matches well with theoretical band structure calculations.\textsuperscript{6, 7, 9} Resistivity below 140 K is not available due to the large resistance of Sr$_2$CrOsO$_6$ beyond the instrument limitation of our PPMS. The resistivity values are $2.52 \times 10^6 \ \Omega \cdot \text{cm}$ and $8.61 \times 10^2 \ \Omega \cdot \text{cm}$ at 140 K and 300 K, respectively. From 140 K to room temperatures, the resistivity changes by more than 3
orders of magnitude; thus indicating that Sr$_2$CrOsO$_6$ is an insulator. It is expected that the resistivity difference between 10 K and 300 K would be several orders of magnitude. In comparison to Krockenberger et al.,$^9$ our resistivity is 2 orders of magnitude higher at room temperature, which can be attributed to the difference in synthesis procedures. An acceptable fit of the resistivity data to the variable-range hopping model in the temperature range of 141-256 K is shown in Figure 134. The inset plot in Figure 134 is the resistivity as a function of $T$. Sr$_2$CrOsO$_6$ shows a linear function for the variable-range hopping model, which supports localized electrons that can hop from one localized atom site to another.
Figure 134: Log plot of the resistivity versus temperature -$1/4$ for Sr$_2$CrOsO$_6$. The excellent linear behavior indicates variable-range hopping. The inset figure plots the resistivity as a function of temperature.

6.5.3 Magnetic properties

The susceptibility was measured using the VSM, and the hysteresis loops were measured using the PPMS and VSM from the NHMFL. The FC susceptibility curve was measured in the temperature range from 300 K to 800 K with a field strength of 1 kG (see Figure 135). The $T_C$ is found to be 660 K, which is lower than the reported $T_C$ of 725 K. As shown in Figure 135, the magnetization curve increases in the 300 K to 500 K range.
temperature regime. This can be attributed to Sr$_2$CrOsO$_6$ undergoing non-monotonicity in the net magnetization and that the spins from the Os sub-lattice are frustrated.\textsuperscript{7} According to Meetei et al.\textsuperscript{7} when the temperature is above 150 K, the canted Os spins are less rigid than the canted Cr spins; thereby causing the magnetization to increase. Near the $T_C$, the magnetization plunges due to that the Cr and Os moments decrease and the materials enters paramagnetic region above $T_C$.

![Field cooled susceptibility plot as a function of temperature. The pressed pellet was cooled in a field strength of 1.5 T from 800 K and then the susceptibility was measured using a 1 kG field.](image)

**Figure 135:** Field cooled susceptibility plot as a function of temperature. The pressed pellet was cooled in a field strength of 1.5 T from 800 K and then the susceptibility was measured using a 1 kG field.
The hysteresis loops from **Figure 136** and **Figure 137** show ferro-/ferrimagnetic behavior and large coercivities. At a magnetic field of 14 T, the magnetizations ($M$) are 0.133 $\mu_B$/f.u., 0.144 $\mu_B$/f.u., and 0.171 $\mu_B$/f.u. at 5 K, 300 K, and 400 K, respectively (shown in **Figure 136**). Our raw moment values (moments in emu are not shown) at 5 K and 300 K are at least an order of magnitude greater than Krockenberger *et al.* However, none of these loops are fully saturated; thus a higher magnetic field from NHMFL was used to saturate the moment. The $M$ is 0.224 $\mu_B$/f.u. and 0.220 $\mu_B$/f.u. for 4.5 K and 295 K, respectively, at a magnetic field strength of 35 T (shown in **Figure 137**). To the best of our knowledge, these experimental moments are the highest reported. Possible reasons for why the moment does not completely saturate are due to canting and spin frustration between the Os moments.
Figure 136: Three hysteresis loops are shown from different temperatures. The magnetization is 0.133 μB/f.u., 0.144 μB/f.u., and 0.171 μB/f.u. at 5 K, 300 K, and 400 K, respectively.
Figure 137: Hysteresis loops gathered from two different temperatures. The magnetization is 0.224 μB/f.u. and 0.220 μB/f.u. for 4.5 K and 295 K, respectively.

Considering that the t$_{2g}$ orbitals for both Cr$^{3+}$ and Os$^{5+}$ are half-filled and are aligned antiferromagnetically to each other from super-exchange interactions, this should yield a zero net moment based on simple arguments. However, this is clearly not the case based on our experimental results. Some theoretical explanations for not observing a zero net moment have been attributed to either spin-orbit coupling (SOC) or canting and spin frustration.\textsuperscript{6, 7, 11} Lee and Pickett\textsuperscript{6} predicted a net total moment of 0.54 μB/f.u. mainly due to the large SOC from Os. Another study by Meetei \textit{et al.}\textsuperscript{7} has shown that the spins are canted, which is the main contribution to why there is a net magnetic moment than from
the arguments of SOC. This report also finds that SOC contradicts their results because the Os moment originates from just the spin ($S = 3/2$) and not the orbital angular momentum. Since Os$^{5+}$ has half-filled $t_{2g}$ orbitals, the orbital angular momentum is quenched.\textsuperscript{7} SOC cannot be a contributing factor to the net moment but rather the spin origin. Therefore, the presence of canting and spin contribution from Os explains why the net magnetic moment is greater than zero.

6.6 Discussion

In this study, we have synthesized nearly phase pure Sr$_2$CrOsO$_6$ with a Cr/Os ordering of 73.6(3) %. Our results verify that this material is an insulating ferrimagnet with a high $T_C$ of 660 K. Our magnetization values are the highest reported for this material and confirm that strongly canted spins must be playing a factor. If a 100% ordering had been achieved and a higher field strength has been used to saturate the moment, the magnetization would increase even further. From resistivity measurements, Sr$_2$CrOsO$_6$ supports the variable-range hopping model. Since the charge is localized and the $T_C$ is high, Sr$_2$CrOsO$_6$ shows support for Mott insulating behavior.

6.7 Acknowledgement

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6.8 **References**

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