AN ABSTRACT OF THE DISSERTATION OF

Joshua Flynn for the degree of Doctor of Philosophy in Chemistry presented on March 7, 2017.

Title: Substitution Effects on the Structure and Electronic Behavior of Ternary Precious Metal Oxides.

Abstract approved: ____________________________________________________________

Munirpallam A. Subramanian

Due to the high cost of precursor materials, complex oxides of 4d and 5d transition metals are under-studied compared to their 3d counterparts. Recent studies have shown that oxides containing heavier transition metals can exhibit exotic electronic states due to presence of strong spin-orbit coupling. The goal of this dissertation is to investigate and to learn more about the chemical and electronic behavior of Ir and Rh. Four oxide systems were prepared and studied: \( \text{Ba}_2\text{In}_{2-x}\text{Ir}_x\text{O}_{5+\delta} \), \( \text{Ba}_{2-x}\text{La}_x\text{InIrO}_6 \), \( \text{BaLaIn}_{1-y}\text{Ca}_y\text{IrO}_6 \), and \( \text{A}_{1+x}\text{Rh}_{2-x}\text{O}_4 \) (\( \text{A}^{2+} = \text{Co, Ni, Cu} \)).

The solid solution series \( \text{Ba}_2\text{In}_{2-x}\text{Ir}_x\text{O}_{5+\delta} \) (\( x = 0\text{–}1.4, 2 \)) was synthesized and its structural, magnetic, and charge transport properties were measured. With increasing Ir content, three transitions in the room temperature structure were observed: orthorhombic to tetragonal, tetragonal to cubic, and cubic to a monoclinic distortion of a hexagonal \( \text{BaTiO}_3 \) structure. Neutron diffraction refinements showed \( \text{Ba}_2\text{In}_{1.6}\text{Ir}_{0.4}\text{O}_{5.4} \) was cubic and \( \text{Ba}_2\text{InIrO}_6 \) was monoclinic. The latter result contradicts previously published XRD refinements. Magnetization measurements show Curie-Weiss behavior for \( x = 0.2\text{–}0.6 \), which arises from near 50:50 ratio
of Ir(V) and Ir(VI). To our knowledge, this is the first time Ir(VI) has been stabilized with standard solid state methods under ambient conditions. Electrical resistivity measurements show all the compounds studied were semiconducting, and that resistivity decreases with increasing Ir content which suggests proximity to a metal-insulator transition. A sign reversal in the high-temperature Seebeck coefficient is observed indicating both electron and hole charge transport.

Two novel solid solution series, $\text{Ba}_{2-x}\text{La}_x\text{InIrO}_6$ ($x = 0–1.0$) and $\text{BaLaIn}_{1-y}\text{Ca}_y\text{IrO}_6$ ($y = 0–1.0$), were prepared and several changes in structure, magnetic moment, and charge transport were observed. The $\text{Ba}_{2-x}\text{La}_x\text{InIrO}_6$ series exhibits a transition from a 6M polytype to an orthorhombic perovskite structure with increased La content whereas the $\text{BaLaIn}_{1-y}\text{Ca}_y\text{IrO}_6$ series transitioned from a disordered orthorhombic perovskite to an ordered cubic perovskite with increased Ca content. Seebeck measurements for both systems showed that Ir(IV)-rich compounds tended to have a n-type conduction mechanism while Ir(V)-rich compounds appeared to be p-type. Both systems were found to be semiconducting and the magnitude of the resistivity is dependent on the crystal structure and Ir environment. Magnetic measurements show that the $\mu_{\text{eff}}$ values for both systems are significantly less than predicted for Ir(IV) ($1.73 \mu_B$) and greater than predicted for Ir(V) ($0 \mu_B$). These results are compared to other iridate compound families.

The spinels $A_{1+2}\text{Rh}_{2-x}\text{O}_4$ ($A^{2+} = \text{Co, Ni, Cu}$) were previously reported but information on their structures and magnetic behavior was lacking. $\text{CoRh}_2\text{O}_4$, $\text{CuRh}_2\text{O}_4$, and the novel composition $\text{Ni}_{1.25}\text{Rh}_{1.75}\text{O}_4$ were prepared using standard solid state methods and characterized using diffraction and magnetic susceptibility techniques. $\text{CoRh}_2\text{O}_4$ was found to have the cubic
spinel structure \((Fd\bar{3}m)\) whereas \(\text{CuRh}_2\text{O}_4\) and \(\text{Ni}_{1.25}\text{Rh}_{1.75}\text{O}_4\) crystallized in tetragonally distorted spinel structures \((I4_1/amd)\) due to Jahn-Teller effects. Antiferromagnetic behavior was observed in \(\chi(T)\) data for \(\text{CoRh}_2\text{O}_4\) \((T_N = 24.9(1) \text{ K}, \mu_{\text{eff}} = 4.42(1) \mu_\text{B})\) and \(\text{CuRh}_2\text{O}_4\) \((T_N = 24(1) \text{ K}, \mu_{\text{eff}} = 1.97(1) \mu_\text{B})\) and their magnetic structures while determined be an antiferromagnetic \(A\)-type and an \(ab\)-plane helical structure, respectively. An upward deviation from Curie-Weiss behavior in the \(\chi(T)\) data and a positive \(\theta\) value for \(\text{Ni}_{1.25}\text{Rh}_{1.75}\text{O}_4\) suggests the presence of competing ferromagnetic and antiferromagnetic correlations. A divergence in ZFC and FC \(\chi(T)\) data was observed for \(\text{Ni}_{1.25}\text{Rh}_{1.75}\text{O}_4\) as well as a lack of long-range ordering in low temperature neutron data both of which suggest spin-glass behavior.
Substitution Effects on the Structure and Electronic Behavior of Ternary Precious Metal Oxides

by

Joshua Flynn

A DISSERTATION

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of
Doctor of Philosophy

Presented March 7, 2017
Commencement June 2017
Doctor of Philosophy dissertation of Joshua Flynn presented on March 7, 2017

APPROVED:

____________________________________________________________
Major Professor, representing Chemistry

____________________________________________________________
Chair of the Department of Chemistry

____________________________________________________________
Dean of the Graduate School

I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

____________________________________________________________
Joshua Flynn, Author
ACKNOWLEDGEMENTS

First, I would like to thank my PhD advisor Dr. Mas Subramanian for the patience, guidance and support that he has shown me over the course of my graduate career. He has stood behind me since I joined his group and brought many development opportunities to my attention including summer workshops and presenting my work multiple prestigious solid state conferences. The knowledge and skills I learned during my time in Dr. Subramanian’s lab have helped me become a better researcher and solid state chemist and I will continue to utilize them in the future.

I am grateful to all the past and present members of Dr. Subramanian’s group I’ve had the pleasure of working with. Dr. Jun Li, Dr. Alvin Gatimu, Dr. Peng Jiang, Dr. Geneva Laurita, Dr. Whitney Schmidt, and Dr. Rosa Grajczyk, thank you for sharing your knowledge, expertise, and patience when answering my “stupid” questions. My research would have been much more difficult without your help. I would also like to thank Joseph Tang, Sarah Synnestvedt, Bella Giampaoli, Elena Medina, Maxwell Wallace for creating a fun work environment and helping me hone my understanding of chemistry through numerous research discussions.

I would also like to thank Dr. Michael Lerner, Dr. Janet Tate, Dr. Brady Gibbons, and Dr. David McIntyre for taking the time to sit on my graduate committee and for reviewing this work. Dr. Lerner, Dr. Tate, and Dr. Gibbons have also been excellent teachers and their courses gave me different perspectives on the science of solid state materials and helped me become a more rounded scientist.
My time in graduate school would have been a lot less enjoyable if not for both old friends and new ones I’ve made throughout the department and community. Thank you to Wes Surta, Joseph Tang, and Dr. Ashley Mason for reviewing and helping me improve this dissertation. Additionally, I’d like to thank Ryan McQuade, Dr. Lauren McQuade, Dr. Geneva Laurita, Michelle Jenyns, Jonathan King, Victor Mendiola, Nick Genovia, and Ryan Flynn for helping keep me grounded and sane through the rite of passage that is graduate school.

I would also like to acknowledge the collaborators I’ve had the privilege of working with: Dr. Arthur Ramirez, Dr. Jennifer Trinh, Dr. Martin Mourigal, Luwei Ge, and Dr. Joe Paddison. Your discussions have taught so much more about solid state materials than I would have discovered on my own and this dissertation would certainly be lacking without your efforts.

Last but certainly not least, I thank my parents, David and Debbie Flynn. Without your guidance and insistence that I better myself, I would not where I am today. Thank you for your unwavering support and love.
CONTRIBUTION OF AUTHORS

Chapter 2: Dr. Mas Subramanian, Dr. Jun Li, Dr. Art Sleight, Dr. Arthur Ramirez contributed in the preparation and review of the manuscript on which this chapter is primarily based; J. Flynn, J. Li, A.W. Sleight, A.P. Ramirez, M.A. Subramanian, Structure and Properties of Ir-Containing Oxides with Large Spin–Orbit Coupling: Ba$_2$In$_{2-x}$Ir$_x$O$_{5+\delta}$, Inorg. Chem. 55 (2016) 2748–2754. Dr. Jun Li also contributed to discussions of structure refinements and performed Rietveld refinements for Ba$_2$In$_{1.6}$Ir$_{0.4}$O$_{5.4}$. Dr. Ramirez also performed magnetic experiments at UC Santa Cruz using a Magnetism Property Measurement System (MPMS) and contributed to the analysis and discussion of the provided data.

Chapter 3: Dr. Mas Subramanian, Dr. Jun Li, Dr. Arthur Ramirez contributed in the preparation and review of the manuscript on which this chapter is primarily based; J. Flynn, J. Li, A.P. Ramirez, M.A. Subramanian, The effect of iridium oxidation state on the electronic properties of perovskite-type solid solutions: Ba$_2$$_{4-x}$La$_x$InIrO$_6$ and BaLaIn$_{1-x}$Ca$_x$IrO$_6$, J. Solid State Chem. 247 (2017) 53–59. Dr. Jun Li also contributed to discussions of structure refinements. Dr. Ramirez also performed magnetic experiments at UC Santa Cruz using a MPMS and contributed to the analysis and discussion of the provided data.

Chapter 4: Dr. Mas Subramanian, Dr. Arthur Ramirez, Dr. Martin Mourigal, Dr. Joseph Paddison, and Luwei Ge contributed to in the preparation of the manuscripts on which this
chapter is primarily based; L. Ge, J. Flynn, J.A.M. Paddison, M.B. Stone, S. Cadler, A.P. Ramirez, M.A. Subramanian, M. Mourigal, Spin order and dynamics in the perfect and distorted diamond-lattice Heisenberg antiferromagnets CoRh$_2$O$_4$ and CuRh$_2$O$_4$ and J. Flynn, J. Li, M.A. Subramanian, The true composition of NiRh$_2$O$_4$. Dr. Jun Li contributed to discussions of room-temperature structure refinements. Dr. Ramirez also performed magnetic experiments at UC Santa Cruz using a MPMS and contributed to the analysis and discussion of the provided data. Dr. Mourigal, Dr. Paddison, and Luwei collected and performed refinements of low-temperature neutron diffraction data and contributed to discussions of magnetic structures.

Appendix A: Dr. Ramirez and Dr. Jennifer Trinh of UC Santa Cruz collected and analyzed magnetotransport data for the BaIrO$_3$ single crystals. The data is published in Dr. Trinh’s PhD thesis, “Low temperature properties of strong spin-orbit systems”.
## TABLE OF CONTENTS

1 Introduction to Structure-Property Relationships in a Material ........................................ 1

1.1 Transition Metal Oxides ................................................................................................. 1

1.2 Preparation of Solid State Oxides ................................................................................ 2

1.2.1 Ceramic Method ....................................................................................................... 2

1.2.2 Crystal Growth via Flux Method ............................................................................. 3

1.3 Structures of Crystalline Materials ............................................................................. 4

1.3.1 Symmetry operations ............................................................................................... 4

1.3.2 Close packing of atoms and ions .......................................................................... 6

1.4 Crystal Structures in this Dissertation ....................................................................... 8

1.4.1 The Perovksite Structure ....................................................................................... 8

1.4.1.1 Non-stoichiometry in Perovskites .................................................................. 13

1.4.1.2 Hexagonal Polytypes ...................................................................................... 15

1.4.1 The Spinel Structure ............................................................................................ 17

1.5 Structural Analysis .................................................................................................... 19

1.5.1 Scattering of Light by Crystalline Materials ......................................................... 19

1.5.2 Powder Diffraction ................................................................................................... 21

1.5.2.1 X-ray Diffraction ............................................................................................. 21

1.5.2.2 Time-of-Flight Neutron Diffraction ................................................................ 23

1.5.2.3 Structure Modeling .......................................................................................... 24

1.5.3 Diffraction Instrumentation ................................................................................... 26

1.6 Magnetism ..................................................................................................................... 27
# TABLE OF CONTENTS (Continued)

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6.1 Fundamentals</td>
<td>27</td>
</tr>
<tr>
<td>1.6.2 Magnetic Ordering</td>
<td>30</td>
</tr>
<tr>
<td>1.6.3 Spin Glasses</td>
<td>33</td>
</tr>
<tr>
<td>1.6.4 Spin-Orbit Coupling</td>
<td>34</td>
</tr>
<tr>
<td>1.6.5 Magnetism Instrumentation</td>
<td>34</td>
</tr>
<tr>
<td>1.7 Electrical Properties</td>
<td>39</td>
</tr>
<tr>
<td>1.7.1 Electrical Conduction</td>
<td>39</td>
</tr>
<tr>
<td>1.7.2 Seebeck Effect</td>
<td>43</td>
</tr>
<tr>
<td>1.7.3 Electronic Transport Instrumentation</td>
<td>44</td>
</tr>
<tr>
<td>1.7.3.1 High-Temperature Measurements</td>
<td>44</td>
</tr>
<tr>
<td>1.7.3.2 Low-Temperature Measurements</td>
<td>45</td>
</tr>
<tr>
<td>1.8 References</td>
<td>47</td>
</tr>
<tr>
<td>2 Solid Solution Between Ba$_2$In$_2$O$_5$ and BaIrO$_3$</td>
<td>52</td>
</tr>
<tr>
<td>2.1 Introduction to Ba$_2$In$_2$O$_5$ and BaIrO$_3$</td>
<td>54</td>
</tr>
<tr>
<td>2.2 Investigation of Ba$_2$In$_2$Ir$_x$O$_5$+$\delta$</td>
<td>55</td>
</tr>
<tr>
<td>2.2.1 Motivation for Solid Solution</td>
<td>55</td>
</tr>
<tr>
<td>2.2.2 Structural Characterization</td>
<td>56</td>
</tr>
<tr>
<td>2.2.3 Magnetism</td>
<td>65</td>
</tr>
<tr>
<td>2.2.4 Electronic Transport Properties</td>
<td>69</td>
</tr>
<tr>
<td>2.3 Conclusions</td>
<td>70</td>
</tr>
<tr>
<td>2.4 Methods and Materials</td>
<td>71</td>
</tr>
</tbody>
</table>
TABLE OF CONTENTS (Continued)

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5 References</td>
<td>73</td>
</tr>
<tr>
<td>3 Tuning Ir Oxidation State in Ba$_2$InIrO$_6$ and BaLaInIrO$_6$ via A- and B-site Substitutions</td>
<td>77</td>
</tr>
<tr>
<td>3.1 Motivation for Solid Solutions</td>
<td>79</td>
</tr>
<tr>
<td>3.2 Substitutions and Structural Characterization</td>
<td>80</td>
</tr>
<tr>
<td>3.2.1 Ba$_{2-x}$La$_x$InIrO$_6$</td>
<td>80</td>
</tr>
<tr>
<td>3.2.2 BaLaIn$_{1-y}$Ca$_y$IrO$_6$</td>
<td>86</td>
</tr>
<tr>
<td>3.3 Electronic Properties</td>
<td>89</td>
</tr>
<tr>
<td>3.3.1 Transport Characterization</td>
<td>89</td>
</tr>
<tr>
<td>3.3.2 Magnetism</td>
<td>91</td>
</tr>
<tr>
<td>3.4 Conclusions</td>
<td>95</td>
</tr>
<tr>
<td>3.5 Materials and Methods</td>
<td>96</td>
</tr>
<tr>
<td>3.6 References</td>
<td>97</td>
</tr>
<tr>
<td>4 Structural Refinement and Magnetic Characterization of A$<em>{1+x}$Rh$</em>{2-x}$O$_4$ (A$^{2+}$ = Co, Ni, Cu) Spinels</td>
<td>103</td>
</tr>
<tr>
<td>4.1 Motivation for Study</td>
<td>105</td>
</tr>
<tr>
<td>4.2 Structural Characterization</td>
<td>106</td>
</tr>
<tr>
<td>4.3 Magnetic Characterization</td>
<td>116</td>
</tr>
<tr>
<td>4.3.1 CoRh$_2$O$_4$</td>
<td>116</td>
</tr>
<tr>
<td>4.3.2 Ni$<em>{1.25}$Rh$</em>{1.75}$O$_4$</td>
<td>119</td>
</tr>
<tr>
<td>4.3.3 CuRh$_2$O$_4$</td>
<td>123</td>
</tr>
</tbody>
</table>
### TABLE OF CONTENTS (Continued)

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.4 Conclusions</td>
<td>126</td>
</tr>
<tr>
<td>4.5 Methods and Materials</td>
<td>127</td>
</tr>
<tr>
<td>4.6 References</td>
<td>129</td>
</tr>
<tr>
<td>General Conclusions and Future work</td>
<td>133</td>
</tr>
<tr>
<td>Bibliography</td>
<td>136</td>
</tr>
<tr>
<td>Appendix A: Linear Magnetoresistance in BaIrO$_3$</td>
<td>148</td>
</tr>
<tr>
<td>A.1 Introduction</td>
<td>148</td>
</tr>
<tr>
<td>A.1.1 BaIrO$_3$</td>
<td>148</td>
</tr>
<tr>
<td>A.1.2 Magnetoresistance</td>
<td>150</td>
</tr>
<tr>
<td>A.3 Characterization of BaIrO$_3$</td>
<td>151</td>
</tr>
<tr>
<td>A.3.1 Single Crystals</td>
<td>151</td>
</tr>
<tr>
<td>A.3.1 Electronic Properties</td>
<td>152</td>
</tr>
<tr>
<td>A.4 Conclusions</td>
<td>155</td>
</tr>
<tr>
<td>A.5 Materials and Methods</td>
<td>156</td>
</tr>
<tr>
<td>A.6 References</td>
<td>157</td>
</tr>
</tbody>
</table>
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>2</td>
</tr>
<tr>
<td>1.1 Simple diagram illustrating the formation of a new material (purple) at the interface of two larger particles.</td>
<td></td>
</tr>
<tr>
<td>1.2</td>
<td>5</td>
</tr>
<tr>
<td>1.2 The 14 Bravais lattices</td>
<td></td>
</tr>
<tr>
<td>1.3</td>
<td>6</td>
</tr>
<tr>
<td>1.3 Schematics illustrating AB and ABC stacking types</td>
<td></td>
</tr>
<tr>
<td>1.4</td>
<td>7</td>
</tr>
<tr>
<td>1.4 Illustration of the octahedral and tetrahedral holes between stacked layers</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>8</td>
</tr>
<tr>
<td>1.5 Crystal structures of NaCl and Na₂O illustrating octahedral (Oₖ) and tetrahedral (T₄) hole filling</td>
<td></td>
</tr>
<tr>
<td>1.6</td>
<td>9</td>
</tr>
<tr>
<td>1.6 Periodic table colored to indicate the elements that have been to crystallize in the perovskite structure (ABX₃)</td>
<td></td>
</tr>
<tr>
<td>1.7</td>
<td>10</td>
</tr>
<tr>
<td>1.7 Unit cell of the ideal perovskite structure with space group Pm̅3m</td>
<td></td>
</tr>
<tr>
<td>1.8</td>
<td>13</td>
</tr>
<tr>
<td>1.8 Projections of NaTaO₃ (a₀b·c⁺) demonstrating the different tilting patterns observed in distorted perovskites</td>
<td></td>
</tr>
<tr>
<td>1.9</td>
<td>15</td>
</tr>
<tr>
<td>1.9 Comparison of the perovskite and brownmillerite structures. The brownmillerite structure can be created by removing O ions from the perovskite in alternating layers along the [110]</td>
<td></td>
</tr>
<tr>
<td>1.10</td>
<td>16</td>
</tr>
<tr>
<td>1.10 Comparison of the perovskite polytype structures created by all ccp (3C) and all hcp (2H) stacking of AX₃ layers</td>
<td></td>
</tr>
<tr>
<td>1.11</td>
<td>17</td>
</tr>
<tr>
<td>1.11 Crystal structures of commonly observed perovskite polytypes created by varying the ratio of ccp and hcp stacking of the AX₃ layers</td>
<td></td>
</tr>
<tr>
<td>1.12</td>
<td>18</td>
</tr>
<tr>
<td>1.12 Unit cell of the cubic (Fd₃m) spinel crystal structure</td>
<td></td>
</tr>
<tr>
<td>1.13</td>
<td>18</td>
</tr>
<tr>
<td>1.13 Projections showing the diamond and pyrochlore sublattices formed respectively by the A and B sites of the spinel structure</td>
<td></td>
</tr>
<tr>
<td>1.14</td>
<td>20</td>
</tr>
<tr>
<td>1.14 Plot displaying the Z dependence of X-ray scattering factors and neutron scattering cross sections. Note the highly linear trend for X-rays compared to the much more irregular trend for the neutron cross sections</td>
<td></td>
</tr>
<tr>
<td>1.15</td>
<td>22</td>
</tr>
<tr>
<td>1.15 Schematic representation of conditions leading to Bragg diffraction</td>
<td></td>
</tr>
</tbody>
</table>
### LIST OF FIGURES (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.16 Photos of the exterior of the Rigaku Miniflex II diffractometer and sample chamber illustrating the geometry of the X-ray tube, sample, and detector</td>
<td>26</td>
</tr>
<tr>
<td>1.17 Schematic showing the electron spin ordering and temperature dependence of the magnetization for ferromagnetic behavior. The Curie temperature ($T_C$) indicates the beginning of magnetic ordering while $M_{sat}$ is the saturation magnetization</td>
<td>31</td>
</tr>
<tr>
<td>1.18 Schematic showing the electron spin ordering and temperature dependence of the magnetization for antiferromagnetic behavior. The Néel temperature ($T_N$) indicates the beginning of magnetic ordering</td>
<td>32</td>
</tr>
<tr>
<td>1.19 Commonly observed antiferromagnetic structures</td>
<td>33</td>
</tr>
<tr>
<td>1.20 Diagrams illustrating the geometric frustration of magnetic moment moments (arrows) in triangular and tetrahedral atomic arrangements</td>
<td>34</td>
</tr>
<tr>
<td>1.21 Schematic illustration of the magnetic field ($B_0$) for the angular momentum of an electron. The generation of $B_0$ can be rationalized by considering the motion of a nucleus with charge $+Ze$ around an electron with charge $-e$</td>
<td>35</td>
</tr>
<tr>
<td>1.22 Splittings of the Ir(IV) and Ir(V) $t_{2g}$ orbitals caused by SOC. Note that electron filling for Ir(V) leads to a non-magnetic state</td>
<td>36</td>
</tr>
<tr>
<td>1.23 Quantum Design PPMS with the ACMS equipment installed</td>
<td>37</td>
</tr>
<tr>
<td>1.24 Representation of the ACMS coilset and tube assemblage, expanded view with labels of the ACMS coilset detection unit, and mounted ‘as prepared’ sample. ACMS coilset illustrations taken and modified from Quantum Design application notes</td>
<td>38</td>
</tr>
<tr>
<td>1.25 Schematic demonstrating the formation of energy bands from molecular orbitals via the addition of an increasing number of atomic orbitals</td>
<td>40</td>
</tr>
<tr>
<td>1.26 Simple two-band diagrams for: (a) metal, (b) extrinsic semiconductor, and (c) insulator. The conduction and valence bands are labeled by CB and VB, respectively. The point at which the electron filling stops is denoted by the Fermi level ($E_F$) while $E_g$ is the energy gap between bands</td>
<td>41</td>
</tr>
<tr>
<td>1.27 Temperature-dependent plots of (a) $\rho(T)$ for a metal and semiconductor and (b) $\ln \rho$ vs. $T$ for a semiconductor. Note that in (b) $E_g = \text{Slope} \times 2k$</td>
<td>42</td>
</tr>
</tbody>
</table>
LIST OF FIGURES (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.28 Diagrams demonstrating the (a) Seebeck and (b) Peltier effects</td>
<td>44</td>
</tr>
<tr>
<td>1.29 ZEM-3 Thermoanalyzer and mounted sample in the thermal chamber</td>
<td>45</td>
</tr>
<tr>
<td>1.30 PPMS resistivity puck with a bar sample connected to position 1 using the four probe contact technique. Contacts are made using conductive silver paint and copper wires that are soldered to the puck</td>
<td>46</td>
</tr>
<tr>
<td>2.1 Crystal structures of (a) brownmillerite Ba₂In₂O₅, (b) 6H polytype Ba₂InIrO₆ and (c) monoclinic 9R polytype BaIrO₃ (Ba = green, In = purple, Ir = brown, O = red)</td>
<td>56</td>
</tr>
<tr>
<td>2.2 Powder X-ray diffraction patterns and lattice parameters for ( x = 0-0.5 ). The ( c ) parameter of the tetragonal phase (( x = 0.1 )) was divided by 2 to allow for direct comparison to the cubic phases</td>
<td>57</td>
</tr>
<tr>
<td>2.3 Structures of (a) tetragonal defect perovskite Ba₂In₁.9Ir₀.1O₅.₁, (b) cubic defect perovskite Ba₂In₁.₆Ir₀.₄O₅.₄ (Ba = green, In/Ir = purple, O = red)</td>
<td>58</td>
</tr>
<tr>
<td>2.4 Time-of-flight neutron diffraction pattern for Ba₂In₁.₄Ir₀.₄O₅.₄ with calculated intensities (red), difference (blue) and background (green) curves. The allowed reflections for ( \text{Pm}\bar{3}m ) are indicated by the magenta tick marks</td>
<td>59</td>
</tr>
<tr>
<td>2.5 Powder X-ray diffraction patterns for ( x = 0.6-1.4 )</td>
<td>60</td>
</tr>
<tr>
<td>2.6 Refined cell edges, ( \beta ) angles and cell volumes for ( x = 0.6-1.4 )</td>
<td>61</td>
</tr>
<tr>
<td>2.7 Time-of-flight neutron diffraction pattern of Ba₂InIrO₆ with calculated intensities (red) and difference curve (blue). Inset shows example of peak splitting not explained by hexagonal model ( (hkl: 1 - 224, 2 - 22\bar{4}, 3 - 223, 4 - 22\bar{3}) )</td>
<td>62</td>
</tr>
<tr>
<td>2.8 Comparison of time-of-flight neutron diffraction patterns for Ba₂InIrO₆: experimental (blue), calculated ( \text{Pm}\bar{3}m1 ) (black) and ( \text{C}2/\text{c} ) (red). Note that the 003 peak (~4.9 Å) in the ( \text{Pm}\bar{3}m1 ) pattern is absent in the experimental pattern while a small 020,110 peak (~5.1 Å) from ( \text{C}2/\text{c} ) is present</td>
<td>63</td>
</tr>
<tr>
<td>2.9 Projections of the reported hexagonal and this work’s monoclinic structure models illustrating the differences in the Ir/In ordering and canting of the octahedra</td>
<td>63</td>
</tr>
<tr>
<td>2.10 Comparison of bond distances within the face-sharing clusters and M-O-M’ bond angles between the face-sharing cluster and the corner sharing octahedra in Ba₂InIrO₆ from the two models (In = purple, Ir = brown, O = red)</td>
<td>64</td>
</tr>
<tr>
<td>Figure</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>2.11 Inverse magnetic susceptibility plot for Ba$<em>2$In$</em>{2-x}$Ir$<em>x$O$</em>{5+\delta}$. All data has been corrected for the contribution from the atomic cores of the constituent ions.</td>
<td>66</td>
</tr>
<tr>
<td>2.12 Curie-Weiss fits and ratios of the possible Ir oxidations states for Ba$<em>2$In$</em>{2-x}$Ir$<em>x$O$</em>{5+\delta}$ ($x = 0.2–0.6$).</td>
<td>67</td>
</tr>
<tr>
<td>2.13 Temperature-dependent, high temperature resistivity and Seebeck coefficient plots for Ba$<em>2$In$</em>{2-x}$Ir$<em>x$O$</em>{5+\delta}$. Note the sign change in the Seebeck coefficient for $x = 1.0$ and $1.2$ at ~550 K.</td>
<td>69</td>
</tr>
<tr>
<td>3.1 Powder X-ray diffraction patterns for Ba$_2$La$_x$InIrO$_6$ ($x = 0–1$).</td>
<td>81</td>
</tr>
<tr>
<td>3.2 Crystal structures of (a) monoclinic 6H polytype Ba$_2$IrO$_6$ (Ba = green, In = purple, Ir = light brown, O = red) and (b) orthorhombic perovskite BaLaIrO$_6$ (Ba/La = green, In/Ir = purple, O = red).</td>
<td>82</td>
</tr>
<tr>
<td>3.3 Lattice parameters for Ba$_2$La$_x$InIrO$_6$ ($x = 0–1$). The a and c parameters of the monoclinic phase (filled points) were divided by $\sqrt{3}$ for a more direct comparison to the orthorhombic parameters (open points).</td>
<td>82</td>
</tr>
<tr>
<td>3.4 Time-of-flight neutron diffraction pattern for BaLaIrO$_6$ with calculated intensities (red) and difference curve (blue). The magenta tick marks are the allowed reflections for Pbnm.</td>
<td>83</td>
</tr>
<tr>
<td>3.5 Comparison of experimental (black) and calculated Pbnm (red) and Imma (blue) XRD patterns for BaLaIrO$_6$. Note that the (111) peak (~24°) is the present in both the experimental and Pbnm patterns but is absent in the Imma pattern.</td>
<td>85</td>
</tr>
<tr>
<td>3.6 Projections of BaLaIrO$_6$ ($a’a’c’$) showing the anti-phase tilting (8.15(1)°) respect to the cubic axis and in-phase tilting (5.21(1)°) along the c axis.</td>
<td>85</td>
</tr>
<tr>
<td>3.7 Powder X-ray diffraction patterns and lattice parameters for BaLaIn$_{1-y}$Ca$_y$IrO$_6$ ($y = 0–1.0$). Successful substitution of In for Ca is indicated by the increase in the lattice parameters with increasing $y$. The orthorhombic $b$ and $c$ parameters were multiplied by $\sqrt{2}$ for a more direct comparison to the cubic phase.</td>
<td>87</td>
</tr>
<tr>
<td>3.8 Crystal structure for ordered cubic perovskite BaLaCaIrO$_6$. (Ba/La = green, Ca = blue, Ir = light brown, O = red).</td>
<td>88</td>
</tr>
<tr>
<td>3.9 High temperature resistivity ($\rho$) and Seebeck coefficient plots for (a,b) Ba$_2$La$_x$InIrO$<em>6$ ($x = 0–1.0$) and (c,d) BaLaIn$</em>{1-y}$Ca$_y$IrO$_6$ ($y = 0–0.75$).</td>
<td>90</td>
</tr>
</tbody>
</table>
### LIST OF FIGURES (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.10</td>
<td>$\mu(T)_{\text{eff}}$ plots for (a) Ba$_2$La$<em>3$InIrO$<em>6$ and (b) BaLaIn$</em>{1.5}$Ca$</em>{0.5}$IrO$_6$. The temperature independence of the data above 100 K suggests Curie-Weiss behavior</td>
</tr>
<tr>
<td>3.11</td>
<td>A plot of $\mu_{\text{eff}}$ as a function of Ir valence for Ba$_2$La$<em>3$InIrO$<em>6$ (triangles) and BaLaIn$</em>{1.5}$Ca$</em>{0.5}$IrO$<em>6$ (squares). The dashed line is the trend the expected $\mu</em>{\text{eff}}$ values should follow when considering spin-orbit coupling effects</td>
</tr>
<tr>
<td>4.1</td>
<td>Time-of-flight neutron diffraction pattern for Co(Rh$<em>{1.90(1)}$Co$</em>{0.10(1)}$)O$_4$ with calculated intensities (red) and difference (blue) and background (green) curves. The magenta tick marks indicate the allowed reflections for $Fd\bar{3}m$ and the teal tick marks indicate the “strain phase” used to model the asymmetric broadening</td>
</tr>
<tr>
<td>4.2</td>
<td>Time-of-flight neutron diffraction pattern for NiRh$<em>{1.86(1)}$Ni$</em>{0.14(1)}$O$_4$ with calculated intensities (red) and difference (blue) and background (green) curves. The magenta tick marks indicate the allowed reflections for $I\bar{4}1/amd$ and the teal tick marks indicate the “strain phase” used to model the asymmetric broadening</td>
</tr>
<tr>
<td>4.3</td>
<td>Temperature dependent plots of (top) the lattice parameters $a$ and $c$ and (bottom) the $c/\sqrt{a_{\text{cub}}}$ ratio and volume for Ni$<em>{1.25}$Rh$</em>{1.75}$O$_4$</td>
</tr>
<tr>
<td>4.4</td>
<td>Time-of-flight neutron diffraction pattern for CuRh$_2$O$_4$ with calculated intensities (red) and difference (blue) and background (green) curves. The magenta tick marks indicate the allowed reflections for $I\bar{4}1/amd$ and the teal tick marks indicate the “strain phase” used to model the asymmetric broadening</td>
</tr>
<tr>
<td>4.5</td>
<td>Orbital diagrams illustrating the splitting of the $t_2$ and $e$ orbitals caused by Jahn-Teller elongation and compression</td>
</tr>
<tr>
<td>4.6</td>
<td>Schematic showing the different stabilization energies (SE) for Ni$^{2+}$ and Cu$^{2+}$ produced by Jahn-Teller compression and elongation. The values $m$ and $n$ are the number of electrons in the lower and upper orbitals, respectively. The grey dotted line represents the relative position of the unsplit $t_2$ orbitals</td>
</tr>
<tr>
<td>4.7</td>
<td>$1/\chi(T)$ plot for CoRh$_2$O$_4$ shows antiferromagnetic (AFM) behavior ($T_N = 25$ K) with the red line showing the fit to the Curie-Weiss Law. Inset shows close-up view of the AFM transition</td>
</tr>
<tr>
<td>Figure</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>4.8</td>
<td>117</td>
</tr>
<tr>
<td>4.9</td>
<td>118</td>
</tr>
<tr>
<td>4.10</td>
<td>119</td>
</tr>
<tr>
<td>4.11</td>
<td>120</td>
</tr>
<tr>
<td>4.12</td>
<td>121</td>
</tr>
<tr>
<td>4.13</td>
<td>122</td>
</tr>
<tr>
<td>4.14</td>
<td>123</td>
</tr>
<tr>
<td>4.15</td>
<td>124</td>
</tr>
<tr>
<td>4.16</td>
<td>125</td>
</tr>
</tbody>
</table>

4.8 Rietveld refinement on CoRh$_2$O$_4$ powder neutron diffraction data collected at $T = 4$ K. Contribution from nuclear peaks (blue ticks), magnetic peaks (red ticks) and Al can (gray ticks) are considered. The inset shows the temperature dependence of the second magnetic peak intensity (highlighted with asterisk).

4.9 Unit cells displaying (a) the nearest neighbor interactions ($J$) and (b) the A-type antiferromagnetic magnetic structure (red and yellow arrows) of CoRh$_2$O$_4$.

4.10 Schematics showing the relative position of one Co-O-Rh-O-Co superexchange pathways (green lines) within CoRh$_2$O$_4$ and illustrating how the superexchange results in AFM ordering.

4.11 $1/(\chi(T) - \chi_0)$ plot for Ni$_{1.25}$Rh$_{1.75}$O$_4$ with the fit to Curie-Weiss behavior (red line) above 90 K. Upward deviation from CW below suggests AFM correlations. Inset shows close-up view reveals of large divergence between field-cooled (FC) and zero field-cooled (ZFC) data typical of spin-glass behavior. $T_g$ is the spin-glass transition temperature.

4.12 Superexchange mechanisms in Ni$_{1.25}$Rh$_{1.75}$O$_4$. Rh on the $B$-site allows for an antiferromagnetic $A$-$A$ interaction between the. Substituting Ni for Rh interrupts the exchange and results in ferromagnetic $A$-$A$ and antiferromagnetic $A$-$B$ interactions.

4.13 Variable temperature neutron diffraction data (4–200 K) for Ni$_{1.25}$Rh$_{1.75}$O$_4$. The lack of new peaks or intensity changes indicates there is no long-range magnetic ordering.

4.14 $1/(\chi(T) - \chi_0)$ plot for CuRh$_2$O$_4$ shows AFM behavior ($T_N = 24.5$ K) with the red line showing the fit to the Curie-Weiss Law. Inset shows close-up view of the AFM transition with an upward trend beginning at ~11 K.

4.15 Rietveld refinement on CuRh$_2$O$_4$ powder neutron diffraction data at $T = 4$ K. Contribution from nuclear peaks (blue ticks) and magnetic peaks (red ticks) are considered. The inset shows the temperature dependence of the second magnetic peak intensity (highlighted with asterisk).

4.16 Unit cells displaying (a) the nearest neighbor interactions ($J_n$) with different colors to distinguish the different orders of neighbors and (b) the incommensurate helical magnetic structure (red arrows) of CuRh$_2$O$_4$. The gray rings serve as a guide to the eye for the propagation and orientation of the magnetic moments.
LIST OF FIGURES (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.1</td>
<td>Crystal structures of the (a) 9M, (b) 5M, and (c) 6M polymorphs of BaIrO$_3$ (Ba = green, Ir = brown, O = red)</td>
</tr>
<tr>
<td>A.2</td>
<td>Photos of example BaIrO$_3$ single crystals showing (a) relative size and (b) close-up view of crystal shapes</td>
</tr>
<tr>
<td>A.3</td>
<td>$\rho(T)$ plot for BaIrO$_3$ exhibiting an anomaly at $T_C \approx 160$ K. Inset is an overlay plot of $-d \log \rho / d(T^{-1})$ and $\Delta \rho / \rho_0(T)$</td>
</tr>
<tr>
<td>A.4</td>
<td>Plots of $\Delta \rho / \rho_0(H)$ for BaIrO$_3$ (a) near $T_C \approx 160$ K and (b) well below $T_C$</td>
</tr>
<tr>
<td>A.5</td>
<td>$\rho_{xy}(T)$ plot for BaIrO$_3$ for $T = 40$–$160$ K. The black arrow is a guide for the trend for decreasing $T$. The inset is a plot of $R_H(T)$ exhibiting a positive-negative-positive sign change near $T_C$</td>
</tr>
</tbody>
</table>
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 Perovskite Tilt Systems and Their Assigned Space Groups</td>
<td>12</td>
</tr>
<tr>
<td>2.1 Refined atomic parameters for Ba$<em>2$In$</em>{1.62(1)}$Ir$<em>{0.38(1)}$O$</em>{5.49(1)}$</td>
<td>59</td>
</tr>
<tr>
<td>2.2 Lattice parameter comparison of structure models for Ba$_2$InIrO$_6$</td>
<td>65</td>
</tr>
<tr>
<td>2.3 Refined atomic coordinates and occupancies for Ba$_2$IrO$_6$</td>
<td>65</td>
</tr>
<tr>
<td>2.4 Estimated band gaps for Ba$<em>2$In$</em>{2-x}$Ir$<em>x$O$</em>{5+\delta}$</td>
<td>70</td>
</tr>
<tr>
<td>3.1 Refined unit-cell, coordinate and displacement parameters for BaLaInIrO$_6$ (Pbnm)</td>
<td>84</td>
</tr>
<tr>
<td>3.2 Estimated band gaps for Ba$_2-x$La$_x$InIrO$<em>6$ and BaLaIn$</em>{1-x}$Ca$_x$IrO$_6$</td>
<td>90</td>
</tr>
<tr>
<td>4.1 Summarized crystallographic information for CoRh$<em>{1.90(1)}$Co$</em>{0.10(1)}$O$_4$</td>
<td>107</td>
</tr>
<tr>
<td>4.2 Summarized crystallographic information for NiRh$<em>{1.86(1)}$Ni$</em>{0.14(1)}$O$_4$</td>
<td>109</td>
</tr>
<tr>
<td>4.3 Summarized crystallographic information for CuRh$_2$O$_4$</td>
<td>113</td>
</tr>
</tbody>
</table>
Chapter 1: Introduction to Transition Metal Oxides and Physical Properties

1.1 Transition Metal Oxides

Transition metal oxides (TMOs) have long been of interest for applications in consumer electronic devices. Their popularity is due to both their high degree of stability as well as being able to host a wide variety of magnetic and electrical properties. Due to the close relationship between a TMO’s properties and crystal structure, the magnetic or electrical behavior can be enhanced or changed completely by manipulating metal oxidation states, distorting the crystal structure, or causing a transition to a new structure simply via elemental substitution. This is especially true of the perovskite and spinel structures.

The 4d and 5d transition metals, especially precious metals such as Ir, Rh, Pd, and Pt, have been less studied in oxides than their 3d counterparts largely due to the high cost of precursor materials. Since the orbital interactions and spin-orbit coupling of heavier transition metals have comparable energy scales, they have been of recent interest, as many have been shown to exhibit exotic states such as spin-orbit Mott insulators [1,2], quantum spin liquids [3], Weyl semimetals [4,5] and, potentially, topological insulators [6,7]. The goal of research activities discussed in this dissertation is to fill in knowledge gaps in the chemical and electronic behavior of Ir and Rh by preparing and characterizing the perovskite and spinel oxide systems: \( \text{Ba}_2\text{In}_{2-x}\text{Ir}_x\text{O}_{5+\delta}, \text{Ba}_2\text{La}_x\text{InIrO}_6, \text{BaLaIn}_{1-x}\text{Ca}_x\text{IrO}_6, \) and \( \text{A}_x\text{Rh}_{2-x}\text{O}_4 (A^{2+} = \text{Co, Ni, Cu}) \). The next sections will cover fundamentals of the characterization methods and properties that will be discussed later.
1.2 Preparation of Solid State Oxides

1.2.1 Ceramic Method

There are several approaches a solid state chemist can take when preparing complex oxides. The most common methodology is the “ceramic method” which relies on the use of thermal energy to facilitate the diffusion of atoms or ions across the interface of particles in a mixture of two or more materials (Figure 1.1). Most of the compounds characterized in this dissertation were prepared using this method.

To begin, stoichiometric amounts of metal precursors are mechanically ground and mixed together using a mortar and pestle or a ball mill. Metal oxides or carbonates are typically used as precursors though occasionally halide or elemental forms are employed. Once the precursors are mixed, the mixture is pressed into a pellet to reduce the distance between particles and make diffusion easier. The pellet is then heat treated, or “fired”, for several hours at temperatures typically ranging from 400 °C to 1700 °C. The optimal temperature to prepare
a compound can vary depending on the precursors or target structure involved and can be
determined by searching literature for similar procedures or by trial and error. The longer the
sample is held at the firing temperature, the lower the diffusion rate of the ions becomes due to
the growth of the new phase along the particle interfaces. To combat this, the heat treatment is
stopped and the sample is re-ground to both break up the old interfaces and create fresh ones.
From here mixture is again pressed into a pellet and the heat treatment is resumed. This process
of grinding, pelletizing, and heating is continued until a pure phase is obtained or the reaction
ceases to progress.

The ceramic method is preferably performed under ambient pressure and atmosphere
for reasons of simplicity though occasionally, it is desirable to stabilize crystal structures or
unusual metal oxidation states that are difficult or impossible to form under ambient conditions.
These compounds can often be realized by applying pressure or by changing the heating
environment via the flow of an oxidative or reductive gas over the sample or heating the sample
in an vacuum evacuated tube.

1.2.2 Crystal Growth via Flux Method

Compounds prepared using ceramic methods are polycrystalline meaning they are made
up of multiple randomly oriented crystallites joined by grain boundaries. A single crystal, on
the other hand, is a material where the crystal lattice of the entire sample is continuous and
unbroken to the edges of the sample. The electronic properties and behavior of single crystals
are often different from their polycrystalline analogs and can even be anisotropic. Additionally,
the absence of grain boundaries in single crystals makes them desirable for applications such as lasers, microprocessors, and gemstones.

There are several techniques that can be used to grow single crystals such as hydrothermal synthesis, sublimation, or the use of a molten flux. All single crystal samples discussed in this dissertation were grown using the flux method which involves dissolving metal precursors in a low-melting point solid solvent, typically an alkali or alkali earth metal halide or hydroxide [9]. A prototypical flux preparation begins by mixing the precursors together with the flux solvent and heating the mixture to just beyond the melting point of the solvent. After being held at this temperature for several hours, the solution is then typically cooled very slowly to give the crystals time to nucleate and grow. Once the flux has cooled, the single crystals can be extracted from the flux matrix and characterized.

1.3 Structures of Crystalline Materials

1.3.1 Symmetry operations

Crystalline solids can be thought of as atoms periodically arranged in a 3D lattice. The structure of these materials is often represented by a unit cell which is defined as the smallest unit that retains the symmetry of the structure as a whole. The crystal structure can then be “created” by translating the unit cell across three-dimensional space. The symmetry of a crystal structure can be described by one of 230 space groups that are subdivided into seven crystal systems: cubic, hexagonal, rhombohedral/trigonal, tetragonal, orthorhombic, monoclinic, and triclinic [10]. Using Hermann-Mauguin notation, space groups are expressed by combining an
uppercase letter that represents the Bravais lattice with additional symbols for representing symmetry elements. The 14 Bravais lattice symbols are $P$ for primitive, $I$ for body-centered, $F$ for face-centered, $A$, $B$ or $C$ for base-centered, and $R$ for rhombohedral (Figure 1.2). The remaining symbols specify the highest symmetry elements with respect to the crystallographic axes $a$, $b$, $c$. For example, the space group $Fd\bar{3}m$ represents a cubic crystal structure with a face-centered unit cell ($F$) that contains a diamond glide plane ($d$) along the $a$, $b$, $c$ axes, a three-fold rotation axis with a center of inversion ($\bar{3}$) along each of the body diagonals, and mirror planes ($m$) that are perpendicular to the face diagonals.

Figure 1.2. The 14 Bravais lattices (from [11]).
1.3.2 Close packing of atoms and ions

Another common way to describe crystal structures is through close packing of spheres. Close packing is the concept that spheres will tend to pack in a way that minimizes the void space between them. In 2D, this is accomplished by packing in a hexagonal manner as illustrated by the green spheres in Figure 1.3. In 3D, there are two positions for a 2nd layer to stack on to the first: a “B” position, indicated by the blue dots, and a “C” position, indicated orange dots. If the 2nd layer stacks on the B sites, a 3rd layer can stack over either the original “A” layer or the “C” positions. The former is AB stacking and the latter is ABC stacking, illustrated in Figure 1.3; repeating these stacking motifs leads to hexagonal close packing (hcp) and cubic close packing (ccp), respectively.

![2D Close Packed Array](image)

**Figure 1.3.** Schematics illustrating AB and ABC stacking types.
When considering ionic solids, the close packing is usually completed by anions rather than cations (due to their larger relative size), which then fill the interlayer voids. It should be noted that this is not always the case, as there are a few examples of “anti” structures in which the cations form the layers and the anions fill the voids. However, for simplicity, this discussion will not refer to these cases. There are two potential sites for the cations to occupy, a tetrahedral ($T_d$) site and an octahedral ($O_h$) site, as illustrated in Figure 1.4.

![Figure 1.4. Illustration of the octahedral and tetrahedral holes between stacked layers.](image)

For both hexagonal- and cubic-close packing patterns, there are two $T_d$ sites for each $O_h$ site and structures can often be described by the stacking and degree of occupation in the sites. For example, both the NaCl rocksalt structure and the anti-fluorite Na$_2$O structure (Figure 1.5)
are cubic-close packed, but NaCl has 100% of the octahedral sites filled while 100% of the tetrahedral sites are filled in Na$_2$O.

![NaCl ctp, 100% O$_h$ filled](image1.png) ![Na$_2$O ctp, 100% T$_d$ filled](image2.png)

**Figure 1.5.** Crystal structures of NaCl and Na$_2$O illustrating octahedral (O$_h$) and tetrahedral (T$_d$) hole filling.

### 1.4 Crystal Structures in this Dissertation

#### 1.4.1 Perovskite Structure

The mineral perovskite was first discovered by the mineralogist Gustav Rose in 1839 who named it after fellow mineralogist Lev Perovski [12]. The perovskite structure has a general formula of $ABX_3$ and is one of, if not the, most commonly adopted crystal structures for solid state ceramic materials. It can accommodate almost any element on the periodic table (Figure 1.6) largely due to the structure’s ability to distort and accept vacancies. This flexibility has led to perovskites and their derivative structures hosting a number of properties, such as superconductivity, ferromagnetism, and high $\kappa$ dielectric constants [13].
The perovskite structure can be described as cubic close packed anion layers with one quarter of the anions replaced with an A cation forming layers of AX3. The B cation then fills one quarter of the octahedral holes. This results in a pseudo-FCC unit cell in which the A cations reside on the corners and X anions on the faces, forming octahedral coordination around the B cation in the center (Figure 1.7). This is considered the ideal perovskite structure and has $Pm\bar{3}m$ symmetry with Wyckoff positions of 1a (0,0,0), 1b (1/2,1/2,1/2), and 3c [(0,1/2,1/2), (1/2,0,1/2), (1/2,1/2,0)] for the A, B, and X ions, respectively.

Victor Moritz Goldschmidt [14] observed that for an ideal perovskite, the A cation is similar in size to the X anion, and as such, the X-A-X distance would be $\sqrt{2}$ times greater than the X-B-X distance. The ratio of these two distances is called the tolerance factor ($t$):
where $R$ is the radii for each of the ions. For ideal perovskites, $t$ would be equal 1 and any deviation will tend to cause the structure to distort or even crystallize in a non-perovskite structure. A $t$ value of < 1 indicates that the $A$ cation is too small and as a result, the octahedra will tilt to compensate (i.e. GdFeO$_3$, $t = 0.904$). When the $A$ cation is too large ($t > 1$), the ions will displace to compensate (i.e. BaTiO$_3$, $t = 1.063$).

\[
t = \frac{(R_X + R_A)}{\sqrt{2(R_X + R_B)}}
\]  
(E1.1)

**Figure 1.7.** Unit cell of the ideal perovskite structure with space group $Pm\bar{3}m$.

If the deviation from 1 is large enough, the compound can crystallize in a completely different structure. For example, MgTiO$_3$ ($t = 0.747$) and RbNiF$_3$ ($t = 1.066$), crystallize in the ilmenite and 6H hexagonal polytype structures, respectively. It must be noted, however, that the tolerance factor is not an infallible predictor of structure type. There are many factors that influence the crystal structure other than ion size, including: degree of covalency, metal-metal...
interactions, Jahn-Teller effects, and lone pair effects. Cubic perovskites tend to form when $t$ falls within a range of 0.9–1.05. Examination of literature, however, shows that this range can be expanded to 0.81–1.11, which extends well into regions where one would expect non-cubic symmetry and/or non-perovskite structure types. The reverse is true as well. For example, PbTiO$_3$ has a $t$ value of 0.999, suggesting it would crystallize with $Pm\bar{3}m$ symmetry; however, it is actually tetragonally distorted ($P4mm$) due to large ion displacement (facilitated by the presence of a lone pair on Pb$^{2+}$).

The most commonly observed distortion in perovskites is tilting of the $BX_6$ octahedra and occurs in order to achieve a lower energy mode when the A cation is too small (i.e. $t < 1$). This distortion also necessitates a lowering of symmetry from the ideal $Pm\bar{3}m$ symmetry. The tilting mechanisms have been heavily studied and classified by Glazer, Woodward and others [15–17]. Woodward and Glazer are credited for linking the possible tilting schemes to their respective space groups (Table 1.1). Glazer notation is used to classify the $BX_6$ tilting with respect to the Cartesian axes of the ideal cubic unit cell. Each unique tilting angle along the $x$, $y$, $z$ axes is represented by the letters $a$, $b$, $c$. For example, an $aab$ scheme indicates that the tilt angles along $x$ and $y$ are the same while the $z$ angle is different. Superscripts are used to give an indication of the how the octahedra tilt with respect to their neighbors. Positive superscripts indicate an in-phase rotation of octahedra in successive layers in the same direction while an anti-phase tilt is represented by a negative superscript. If no rotation is present, a zero subscript is used.
Table 1.1. Perovskite Tilt Systems and Their Assigned Space Groups [15]

<table>
<thead>
<tr>
<th>Number</th>
<th>Symbol</th>
<th>Space Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-Tilt System</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>$a^+b^+c^+$</td>
<td>Immm (#71)</td>
</tr>
<tr>
<td>2</td>
<td>$a^+b^+b^+$</td>
<td>Immm (#71)</td>
</tr>
<tr>
<td>3</td>
<td>$a^+a^+a^+$</td>
<td>Im3 (#204)</td>
</tr>
<tr>
<td>4</td>
<td>$a^+b^+c^-$</td>
<td>Pmmn (#59)</td>
</tr>
<tr>
<td>5</td>
<td>$a^+a^+c^-$</td>
<td>$P4_2/nmc$ (#137)</td>
</tr>
<tr>
<td>6</td>
<td>$a^+b^+b^-$</td>
<td>Pmmn (#59)</td>
</tr>
<tr>
<td>7</td>
<td>$a^+a^+a^-$</td>
<td>$P4_2/nmc$ (#137)</td>
</tr>
<tr>
<td>8</td>
<td>$a^+b^+c^-$</td>
<td>$P2_1/m$ (#11)</td>
</tr>
<tr>
<td>9</td>
<td>$a^+a^+c^-$</td>
<td>$P2_1/m$ (#11)</td>
</tr>
<tr>
<td>10</td>
<td>$a^+b^+b^-$</td>
<td>Pnma (#62)</td>
</tr>
<tr>
<td>11</td>
<td>$a^+a^+a^-$</td>
<td>Pnma (#62)</td>
</tr>
<tr>
<td>12</td>
<td>$a^+b^+c^-$</td>
<td>F-1 (#2)</td>
</tr>
<tr>
<td>13</td>
<td>$a^+a^+a^-$</td>
<td>I2/a (#15)</td>
</tr>
<tr>
<td>14</td>
<td>$a^+b^+b^-$</td>
<td>R-3c (#167)</td>
</tr>
<tr>
<td>2-Tilt System</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>$a^0b^+c^+$</td>
<td>Immm (#71)</td>
</tr>
<tr>
<td>16</td>
<td>$a^0b^+b^+$</td>
<td>I4/mmm (#139)</td>
</tr>
<tr>
<td>17</td>
<td>$a^0b^+c^-$</td>
<td>Cmcm (#63)</td>
</tr>
<tr>
<td>18</td>
<td>$a^0b^+b^-$</td>
<td>Cmcm (#63)</td>
</tr>
<tr>
<td>19</td>
<td>$a^+b^+c^-$</td>
<td>I2/m (#12)</td>
</tr>
<tr>
<td>20</td>
<td>$a^+b^+b^-$</td>
<td>Imma (#74)</td>
</tr>
<tr>
<td>1-Tilt System</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>$a^0a^0c^+$</td>
<td>$P4/mbm$ (#127)</td>
</tr>
<tr>
<td>22</td>
<td>$a^0a^0c^-$</td>
<td>$I4/mcm$ (#140)</td>
</tr>
<tr>
<td>0-Tilt System</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>$a^0a^0a^0$</td>
<td>$Pm\bar{3}m$ (#221)</td>
</tr>
</tbody>
</table>

To illustrate, NaTaO$_3$ crystallizes as an orthorhombic perovskite ($Cmcm$) at high temperature and has a Glazer tilting scheme of $a^0b^+c^+$. The different tilting patterns can be
easily observed upon the examination of projections of NaTaO$_3$ along the [100], [010], and [001] directions (Figure 1.8). Tilting of octahedra can have a drastic effect on the properties of a material. For example, Subramanian et al. showed that substitution of Te for Se in ferromagnetic SeCuO$_3$ can induce a transition to an antiferromagnetic state by tuning the tilting angle of the CuO$_6$ octahedra [18].

![Image of NaTaO$_3$ projections](image)

**Figure 1.8.** Projections of NaTaO$_3$ ($a^0b^0c^0$) demonstrating the different tilting patterns observed in distorted perovskites.

1.4.1.1 Non-stoichiometry in Perovskites

The two major ways non-stoichiometry is achieved in perovskites are either A-site or anion vacancies. B-site vacancies can occur in thin films [19] but have never been reported in bulk. A-site vacancies have a general formula of $A_{1-x}BX_3$ where $0 < x < 1$. Although there is no strict rule, compounds with $x < 0.75$ are generally classified as “bronzes” and those where $x > 0.75$ are simply called A-site deficient perovskites [20].
Anion-deficient or defect perovskites can be generalized with the formula $ABX_{3-\delta}$ where $0 \leq \delta \leq 0.5$. These vacancies typically occur in order to compensate for a charge imbalance when a cation in the structure is substituted for another of lower charge. This can be demonstrated by considering a solid solution between $\text{LaFeO}_3$ and $\text{La}_2\text{Ni}_2\text{O}_5$. When the $\text{Fe}^{3+}$ is substituted for $\text{Ni}^{2+}$ the positive charge on the B-site is lowered meaning the negative charge produced by the full oxygen content is too high and must be reduced by the production of a vacancy ($\Box$):

$$\text{Fe}^{3+} + 6\text{O}^{2-} \leftrightarrow \text{Ni}^{2+} + 5\text{O}^{2-} + \Box$$

Anion vacancies can be ordered or randomly oriented depending on the quantity and, in some cases, temperature. Generally, vacancy ordering occurs when one sixth of the anion positions are vacant giving a general formula of $A_2B_2\text{O}_5$ ($\delta = 0.5$). There are a few ways these compounds can order, but one of the most common orderings is along the [011], which forms the orthorhombic brownmillerite structure (Figure 1.9) named for Dr. Lorrin Thomas Brownmiller. This structure typically forms when $A$ = late alkali earth and $B^{3+} =$ Al, Sc, Fe, In, Cr, Ga. Examples of reported brownmillerites include $\text{Ca}_2\text{FeAlO}_5$, $\text{Ba}_2\text{In}_2\text{O}_5$, $\text{Ca}_2\text{FeCoO}_5$, and $\text{Sr}_2\text{MnGaO}_5$; they have been investigated for their magnetic and electronic transport behaviors, as well as their potential as pigments, oxide ion conductors, catalysts and thermoelectric materials [21–28].
The brownmillerite structure can be created by removing O ions from the perovskite in alternating layers along the [110].

1.4.1.2 Hexagonal Polytypes

The ideal cubic perovskite can also be described in terms of a hexagonal unit cell where \( a_{\text{hex}} = a_{\text{cub}} \sqrt{2} \) and \( c_{\text{hex}} = a_{\text{cub}} \sqrt{3} \). Using this cell, the \( AX_3 \) layers stack perpendicular to [001] in a cubic-close packed manner. Because of this a cubic perovskite is often called a “3C” polytype due a \( ccc \) repeat sequence where \( c \) denotes corner sharing octahedra (Figure 1.10). There is also an ideal hexagonal perovskite structure where the \( AX_3 \) layers follow a hexagonal-close packing scheme. In this structure, the \( O_h \) sites are oriented to where they share faces. The ideal hexagonal perovskite is also called the 2H polytype as the repeat sequence is \( hh \) where \( h \) denotes face-sharing octahedra (Figure 1.10). 2H polytypes typically form when the \( A \) cation is too large (i.e. \( t > 1 \)); therefore, a majority of 2H compounds are composed of an alkali or alkali earth \( A \) cation and a transition metal \( B \) cation (e.g. \( \text{BaNiO}_3 \)).
Between the two ideal structures exists the possibility to create new structures by mixing cubic and hexagonal stacking motifs. In theory, there is a near-infinite number of possible structures. In practice, however, this number is limited to relatively few stacking sequences. Some of the more commonly occurring examples include the 6H, 4H, and 9R polytypes (Figure 1.11). The 6H and 4H polytypes both have hexagonal symmetry (hence the H) with the space group $P6_3/mmc$. The ratio of hexagonal to cubic stacking is 1:2 for 6H and 1:1 for 4H and therefore they have stacking sequences of $hcchcc$ and, $hcch$ respectively. The 9R polytype, on the other hand, has rhombohedral symmetry with the $R3m$ space group. It has hexagonal-cubic ratio of 2:1 with the stacking sequence $hhchhhch$ or $(hch)_3$. While the 4H, 6H, and 9R polytypes are most common, more complex polytypes have been reported. Examples include: 8H, 10H, 14H, 12R, 15R, and 27R which have stacking sequences of $(cchc)_2$, $(cchcc)_3$, $(cchcchc)_2$, $(cchh)_3$, $(cchch)_3$, and $(cchchchch)_3$, respectively. Examples of these structures include $\text{Ba}_4\text{Ru}_3\text{NaO}_{12}$, $\text{Ba}_6\text{Nd}_2\text{Ti}_4\text{O}_{17}$, and $\text{SrMn}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ [29–31].
Figure 1.11. Crystal structures of commonly observed perovskite polytypes created by varying the ratio of ccp and hcp stacking of the AX₃ layers.

1.4.2 The Spinel Structure

Spinels have the general formula AB₂X₄ where A and B are metal cations and X is an anion, usually oxygen. Their well-studied structure (shown in Figure 1.12), from a close packing point-of-view, can be described as a cubic-close packed X anion lattice with 1/8 of the tetrahedral sites filled by the A cations and 1/2 of the octahedral sites filled by the B cations. The robust and rigid nature of the spinel structure leads most examples to crystallize with cubic symmetry and a space group of $Fd\bar{3}m$ with Wyckoff positions of 8a (1/8,1/8,1/8), 16d (1/2,1/2,1/2) and 32e (x,x,x) for the A, B, and X ions, respectively. The most common distortion in cubic is displacement of the X ion from its ideal position ($x = 1/4$) toward or away from the B-site. This results in distortion of octahedral bonds angles away from 90°. The tetrahedral sites typically remain rigid with ideal 109.4° bond angles and the cubic symmetry always remains intact. There are, however, a few reported examples of spinels, such as CuCr₂O₄ and NiCr₂O₄, that are tetragonally distorted due to Jahn-Teller effects at the A-site [32–34].
The spinel structure can be broken down into diamond and pyrochlore sublattices (Figure 1.13) created by the $A$ and $B$ sites, respectively. The atomic arrangement in these sublattices makes them useful systems for inducing and studying geometric frustration [35].

Figure 1.12. Unit cell of the cubic ($Fd\bar{3}m$) spinel crystal structure.

Figure 1.13. Schematics showing the (left) diamond and (right) pyrochlore sublattices formed respectively by the $A$ and $B$ sites of the spinel structure.
1.5 Structural Analysis

1.5.1 Scattering of Light by Crystalline Materials

When a material is irradiated with a beam of particles or light of an appropriate wavelength, the beam will be scattered. Depending on the type of beam, scattering, and interactions between the beam and the material, a variety of information about the material can be extracted. There are two main types of scattering: elastic and inelastic. In elastic scattering, there is a complete transfer of energy and momentum from the incident beam to the scattered beam. In inelastic scattering, the transfer is incomplete and some of the energy and momentum is transferred to the material.

For experiments on the atomic scale, the wavelength of the beam must be on the order of 0.01–100 Å, in which the best choices for crystal structure or chemical composition determination are electrons, neutrons and X-rays. While all three beams can yield crystallographic information, each type of beam has advantages or disadvantages depending on how it interacts with atoms. Electrons are scattered by repulsive forces from the electron cloud of the atom and due to the short wavelength (typically ~ 0.02 Å), the strong atomic scattering, and the ability to examine tiny sample sizes (~10 nm³), electron scattering is sensitive to small structural deviations caused by structural distortions, ordering, short-range ordering, or defects [36]. The biggest drawback of electron scattering is that the penetration depth of electrons in solid materials is relatively shallow. This means experiments must be performed using transmission electron microscopy (TEM), an expensive and time-consuming process. Scattering experiments using TEM also requires that samples be thin enough to allow for electron transmission (< 100 nm) which can be difficult to achieve for some samples.
X-rays also interact with the atomic electron cloud but have a deeper penetration depth than electrons because they lack charge. This allows for extraction of more detailed structural information such as lattice parameters and atomic positions to be obtained. One of the drawbacks for X-rays, however, is that their atomic scattering factors scale linearly (Figure 1.14) with atomic number, $Z$. Atomic scattering factors also vary as a function of $(\sin \theta)/\lambda$ meaning scattering gets weaker as the angle of the incident beam, $\theta$, or the radiation wavelength, $\lambda$, increases.

![Figure 1.14](image.png)

**Figure 1.14.** Plot illustrating the $Z$ dependence of X-ray scattering factors and neutron scattering cross sections. Note the highly linear trend for X-rays compared to the much more irregular trend for the neutron cross sections.

A consequence of the linear relationship of scattering factors and $Z$ is that X-rays are sufficient for determining position and occupancy of heavier elements, such as Pb or Ir, but poor for lighter elements, such as H or O; this can be problematic when dealing with oxides.
This also implies that elements that are close on the periodic table will have similar scattering factors and therefore be indistinguishable when they share a crystallographic site. Neutrons, on the other hand, interact directly with the atomic nucleus, and the atomic scattering cross sections are independent of Z. This effectively removes the limitations for lighter elements and those in close with similar values of Z. Neutrons, while lacking charge, have inherent spin, and are therefore subject to electron spin interactions throughout the crystal structure; this characteristic allows for refinement of the magnetic structure of a magnetically ordered material. Using neutrons, however, does introduce other challenges. Although they are more sensitive to certain elements, others, e.g. Cd and Gd, are very good neutron absorbers, and therefore any sample containing these would be very difficult to analyze. Additionally, the neutron sources used for structural analysis are expensive and large which limits viability of neutron diffraction experiments to national laboratories. X-rays, on the other hand, can be generated with small X-ray tubes which can be fitted in benchtop instruments making them more accessible to academic labs. Both X-rays and neutrons were employed in this dissertation and will be the focus of additional discussion.

1.5.2 Powder Diffraction

1.5.2.1 X-ray Diffraction

The most common method used for crystal structure elucidation is powder X-ray diffraction (PXRD). Diffraction is a special case of scattering in which, under the right conditions, scattered rays mutually reinforce each other resulting in a diffracted ray of greater intensity. The conditions for diffraction to occur can be illustrated using a simple diagram of a
crystal lattice with spacing \( d \) such as in Figure 1.15. The incident (1, 2) and diffracted (1’, 2’) beams will have the same wavelength, \( \lambda \), and angle, \( \theta \), relative to the plane of atoms. Due to the interplanar spacing, beam 2 must travel further to reach atom C than beam 1 must to reach atom A. This can be stated for the diffracted beams as well. Geometrically, the total additional distance traveled by 2 and 2’, shown in red, can be written in terms of \( d \) and \( \theta \):

\[
BC + CD = d \sin \theta + d \sin \theta
\]

(E1.2)

When this sum is some integer multiple of \( \lambda \), the diffracted beams will completely in phase and constructive interference occurs, or

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

(E1.3)

This relationship was first developed by father and son William Henry Bragg and William Lawrence Bragg in 1913 [37] and is appropriately called Bragg’s Law.

Figure 1.15. Schematic representation of conditions leading to Bragg diffraction.
According to Bragg’s law, different \( d \) spacings will yield constructive interference at different angles. Therefore, by irradiating a material with a constant wavelength of X-rays from various angles and detecting the intensity of the diffracted beams, a PXRD pattern can be generated showing a series of peaks, typically as a function of scattering angle, \( 2\theta \). Based on the relative intensities and positions of these peaks, a large amount of information about the materials crystal structure can be extracted including atomic positions and thermal vibrations, site occupancies, and overall unit cell dimensions. Each peak is related to one or more crystallographic planes, labelled by Miller indices \((hkl)\), formed by the atoms. The spacing of these planes is directly related to the dimensions of the unit cell based on the its symmetry [11]. For example, for an orthorhombic unit cell:

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

(E1.4)

where \( a, b \) and \( c \) are the unit cell dimensions. For additional crystallographic information, modeling the entire pattern is required and will be discussed in §1.4.2.3.

1.5.2.2 Time-of-Flight Neutron Diffraction

Neutron powder diffraction (NPD), often done in conjunction with PXRD, is typically performed using one of two methods; this can be done using a beam of neutrons of a constant wavelength, similar to PXRD, or by using a pulsed beam containing a wide band of neutron wavelengths and therefore velocities. The latter of these is called time-of-flight (TOF) diffraction. In TOF diffraction, the neutron beam is directed down a long path, \( L \), to the sample.
and the time, $t$, it takes the neutrons to go from source to sample to detector, or time-of-flight, is recorded in addition to the scattering angle $2\theta$. Since the beam contains neutrons of different wavelengths and therefore different velocities, whether or not a neutron will be diffracted depends on the relationship between the neutron’s wavelength, and therefore its time-of-flight, and the $d$ spacing in the sample. This relationship can be obtained by combining the de Broglie equation with Bragg’s law:

$$\lambda = \frac{ht}{m_nL} = 2d \sin \theta$$  \hspace{1cm} (E1.5)

where $h$ is Planck’s constant and $m_n$ is the neutron mass. Patterns generated by NPD, generally expressed as a function of $t$, contain the same structural information as their PXRD counterparts.

1.5.2.3 Structure Modeling

The method most often used to obtain crystallographic information from a diffraction pattern is Rietveld method [38]. The basis of this method relies on accounting for fitting the peak shapes and intensities. The peak intensity, $I$, for a particular $hkl$ value can be defined as:

$$I_{hkl} = F_{hkl}^2 \times M_{hkl} \times D$$  \hspace{1cm} (E1.6)

where $F_{hkl}$ is the structure factor, $M_{hkl}$ is the multiplicity of the $hkl$ family and $D$ is the displacement factor. For X-rays, the structure factor accounts for the contributions of the scattering factor, $f$, and location of atom $j$:

$$F_{hkl} = \sum_j f_j \exp(-2\pi i(hx_j + ky_j + lz_j))$$  \hspace{1cm} (E1.7)
where \( x_j, y_j \) and \( z_j \) are the positional coordinates of \( j \) \cite{11}. The displacement factor accounts for, as the name implies, any average displacement of the atom caused by structural distortion or thermal vibration. It is related to \( \lambda \) and \( \theta \) through

\[
D = \exp \left( \frac{U \sin \theta}{8\pi^2 \lambda} \right) \tag{E1.8}
\]

The value \( U \) is the atomic displacement parameter and is usually reported in scientific reports involving crystal structure refinements.

The Rietveld method involves using the above relationships to calculate intensities and fits them against the observed experimental data using least-squares analysis. The structure model and calculated intensities are tuned by methodically refining instrumental background, unit cell parameters, peak shape and broadening parameters, atomic positions, site occupancies, and atomic displacement parameters. Due to the sheer number of variables, however, it can be difficult to make progress if little is known about the structure. To facilitate this, refinements are usually begun with the LeBail method \cite{39} which uses the same Rietveld algorithm but sets all \( F_{hkl} \) values to 1 thereby removing the dependency on the atomic identities and positions. This allows for space group determination, if needed, through peak indexing as well as refinement of the unit cell parameters and peak shapes. Once this information is extracted, it can be used directly to start a Rietveld refinement; the intensity determining parameters can then be refined, and the overall structure model can subsequently be fine-tuned and finalized.
1.5.3 Diffraction instrumentation

All XRD measurements discussed in this dissertation were performed using a Rigaku Miniflex II bench top diffractometer (Figure 1.16) over a range of 10–80° 2θ using Cu Kα radiation (λ = 1.54 Å). The X-rays are generated by accelerating a beam of electrons from a heated tungsten filament toward an anode with a Cu metal target by applying a large voltage (> 10 kV). The striking incident electrons ionize some of the Cu 1s electrons. Characteristic X-ray radiation is then given off when electrons from the outer orbitals relax to occupy the 1s vacancy [40]. These X-rays are directed out a Be window toward the sample to be measured. A graphite monochromator is often employed to absorb Cu Kβ radiation which is undesirable. The Miniflex II operates at fixed tube voltage of 30 kV and a fixed tube output current of 15 mA [41].

Figure 1.16. Photos of (left) the exterior of the Rigaku Miniflex II diffractometer and (right) sample chamber illustrating the geometry of the X-ray tube, sample, and detector.

The Miniflex II utilizes either a 6-sample changer which rotates the sample during the measurement, or a single sample holder without rotation. Generally, the 6-sample changer is used for most fast scan measurements (scans where the 2θ variation is > 2°/min) when phase
identification is the only objective. For analysis of unit cell parameters and structural refinements, high peak resolution and intensities are required which can be obtained by using a slower scan. This is done by decreasing the $2\theta$ step increment and increasing the scan time at each step, allowing the intensity to reach its maximum.

Neutron diffraction data for the samples in this dissertation were collected at the Spallation Neutron Source (SNS) at Oak Ridge National Lab in Oak Ridge, Tennessee using the BL–11A (POWGEN) neutron powder diffractometer [42]. Sample masses were 1–2 g and samples were loaded into 6 mm vanadium sample cans and data was collected over approximately 2–4 h.

1.6 Magnetism

“Few subjects in science are more difficult to understand than magnetism.”

– Encyclopedia Britannica, 1989

1.6.1 Fundamentals

Everything, whether it be an oxide, polymer, wood, living, or dead, exhibits a response to a magnetic field. All substances are diamagnetic to an extent, meaning all electrons are paired and any external magnetic field would disturb the energy state. Consequently, a diamagnetic material repels an external magnetic field by generating its own field in the opposite direction resulting in a small negative magnetic moment that is temperature independent and on the order of $10^{-6}$ emu/mol. A paramagnetic material, on the other hand, has unpaired electrons whose spins are oriented randomly in the absence of a magnetic field. When a paramagnetic material is exposed to an external field, it responds by aligning some of its unpaired electron spins in the
same direction as the external field. This generates a positive magnetic moment that usually has a magnitude around $10^1$ emu/mol. Thermal agitation (i.e. temperature) works against this alignment, with only a small portion of the unpaired spins aligning with the external field. This portion can, however, be increased by lowering the temperature of the material. Paramagnetic materials also have a diamagnetic electron core but since the diamagnetic moment is several orders of magnitude lower, it is often overshadowed and ignored.

When a material is put under the influence of a magnetic field, $B$, the response can be quantified by the magnetization, $M$. These two quantities are proportionally related by

$$ M = \mu_0 \chi B $$

(E1.6)

where $\mu_0$ is the permeability of free space and $\chi$ is the magnetic susceptibility of the material. The intensity of $B$, labeled as $H$, can be calculated via:

$$ H = \mu_0 B $$

(E1.7)

Solving E1.6 for $\chi$ and substituting for $\mu_0 B$ yields a definition of magnetic susceptibility in terms of magnetization and external field strength:

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

(E1.8)

The observed magnetic susceptibility ($\chi_{\text{obs}}$) of a material can be considered as the sum of several magnetic susceptibilities:

$$ \chi_{\text{obs}} = \chi_{\text{para}} + \chi_{\text{dia}} + \chi_{\text{VV}} + \chi_{\text{Pauli}} $$

(E1.9)

where $\chi_{\text{para}}$ and $\chi_{\text{dia}}$ are the paramagnetic and diamagnetic susceptibilities. The Van Vleck term ($\chi_{\text{VV}}$) is a type of temperature independent paramagnetism that occurs when the electron
configuration of an atom or ion results in a state in which the total orbital momentum is equal to zero. $\chi_{\text{Pauli}}$ is the term for Pauli paramagnetism, which is a phenomenon only seen in materials that conduct electrons metallically; as none of the compounds described in this dissertation are metallic, it will not be discussed further. Most often with transition metal oxides, the most interesting term out of these four is $\chi_{\text{para}}$, as a great deal of information can be extracted from it. $\chi_{\text{para}}$ can be isolated from $\chi_{\text{obs}}$ by subtracting out the other $\chi$ terms (or ignoring them if they are negligible) and it is defined by the Curie Law to be inversely proportional with temperature:

$$\chi_{\text{para}} = \frac{C}{T} \quad (\text{E1.10})$$

The Curie constant, $C$, is defined as

$$C = \frac{\mu_0 N_A}{3k_B} \mu_{\text{eff}}^2 \mu_B^2 \quad (\text{E1.11})$$

where $N_A$ is Avogadro’s number, $k_B$ is Boltzmann’s constant, $\mu_B$ is the Bohr magneton, and $\mu_{\text{eff}}$ is the effective magnetic moment of the material. Often the orbital contribution is small enough to be ignored, especially in 3$d$ TMs, and the moment is considered “spin-only”. The spin-only moment, $\mu_S$, can be estimated by:

$$\mu_S^2 = g_S^2 S(S + 1) \quad (\text{E1.12})$$

where $g_S$ is the electronic spin $g$-factor (usually estimated as 2) and $S$ is the spin quantum number for the magnetic ion in the material.

Although there are some examples (e.g. Gd$_2$O$_3$, gaseous O$_2$), very few materials are “pure” paramagnets due to electron-electron interactions. Consequently, a “corrected” variation
of E1.10, called the Curie-Weiss Law, is more often used when characterizing magnetic materials:

\[ \chi_{\text{para}} = \frac{c}{T-\theta} \]  

(E1.13)

where \( \theta \) is the Weiss constant which can give an indication of any magnetic ordering that may be present. When analyzing \( \chi \) data, the Curie-Weiss law is often used in its linear form:

\[ \frac{1}{\chi} = \frac{1}{c} (T) + \frac{\theta}{c} \]  

(E1.14)

Using this form, the values for \( c \) and \( \theta \) can be extracted by fitting the linear paramagnetic region in a plot of \( \chi^{-1} \) vs. \( T \). This process is commonly done to infer or confirm oxidation states by comparing the \( \mu_{\text{eff}} \) and \( \mu_S \) values calculated using E1.12 and E1.13.

1.6.2 Magnetic Ordering

Some materials, while paramagnetic at high temperatures, are known to undergo spontaneous long-range ordering of their electron spins at sufficiently low temperatures. The two simplest types of magnetic ordering are ferromagnetism and antiferromagnetism. In ferromagnetism, the electron spins spontaneously coalign resulting in a large, sudden increase in the magnetization (Figure 1.17).
Figure 1.1. Schematic showing the (left) electron spin ordering and (right) temperature dependence of the magnetization for ferromagnetic behavior. The Curie temperature ($T_C$) indicates the beginning of magnetic ordering while $M_{\text{sat}}$ is the saturation magnetization.

Similar to paramagnetism, the alignment is resisted by thermal agitation but as $T \to 0$, the magnetization approaches a saturation magnetization, $M_{\text{sat}}$. The temperature below which the ordering occurs is called the Curie temperature, $T_C$. Above this temperature, paramagnetic behavior is observed according to the Curie-Weiss law (E1.10) and for ferromagnetic materials, $\theta > 0$. Ferromagnetic materials tend to be metallic conductors, examples of which include metallic iron, Fe$_2$O$_3$, and CrO$_2$.

Antiferromagnetism is much more commonly observed in oxides than ferromagnetism and in contrast, results from spontaneous anti-alignment of electron spins (Figure 1.18). This causes, as one might suspect, a sudden decrease in the magnetization. This alignment and corresponding decrease in magnetization increases as $T \to 0$ due to the effects of thermal agitation.
Figure 1.18. Schematic showing the (left) electron spin ordering and (right) temperature dependence of the magnetization for antiferromagnetic behavior. The Néel temperature ($T_N$) indicates the beginning of magnetic ordering.

This also means that, like its counterpart, antiferromagnetism only occurs below a certain threshold temperature called the Néel temperature, $T_N$, above which the material is paramagnetic and $\theta < 0$. For antiferromagnetic materials, there are several different ways the spins can order while still achieving long range antiferromagnetic order. Interestingly, many of these orderings are observed in the La$_{1-x}$Ca$_x$MnO$_3$ solid solution and were first labeled A through G by Wollan and Koehler [43]. A-, C- and G-types are illustrated in Figure 1.19 and the magnetic structures can be described in terms of the spin interactions within and between layers along the $z$ axis. The G-type structure is the most commonly ordering seen outside La$_{1-x}$Ca$_x$MnO$_3$ and has antiferromagnetic ordering within the horizontal layers as well as between them. A- and C-type structures are a bit more complex. The A-type magnetic structure has intralayer ferromagnetic ordering while the interlayer interactions are antiferromagnetic. C-type
is the reverse with the intralayer ordering is antiferromagnetic with ferromagnetic interlayer ordering.

![Diagram of magnetic structures](image)

**Figure 1.19.** Commonly observed antiferromagnetic structures.

The remaining magnetic structure types labeled by Wollan and Koehler are more complex with the exception of $B$-type, which is actually the ferromagnetic structure. It should be noted that more exotic and complex antiferromagnetic structures exist that are not covered by these labels, such as those seen in $\text{La}_2\text{CuO}_4$ and $\text{La}_2\text{NiO}_4$ [44].

1.6.3 **Spin Glasses**

It is often observed that not all materials fit neatly into the types of magnetic behavior described above and many oxides exhibit unusual or exotic magnetic states. One of these states is called a spin glass. If the magnetic atoms in a material are arranged in a certain way, it’s possible to create a situation where electron spins that want to order antiferromagnetically are not able to do so due to competing interactions. This is called geometrically frustrated magnetism [45] and, as illustrated in Figure 1.20, often occurs in triangular or tetrahedral arrangements of magnetic atoms or ions. These frustrated motifs occur in several lattices. Some
common ones include the FCC lattice, the Kagome lattice seen in layered honeycomb and magnetoplumbite structures [46,47], and the pyrochlore lattice seen in pyrochlores as well as spinels [48–50].

Magnetic frustration can cause a variety of unique and interesting magnetic states, many of which result in the absence of any long-range ordering. One of these states is called a spin glass. In this state, the electron spins are essentially frozen in a random pattern below a glass temperature, \( T_G \). Spin glasses manifest themselves experimentally through many characteristics. The common ones include [45]: divergence between the field-cooled and zero field-cooled DC magnetic susceptibilities below \( T_G \), a strong frequency dependence in the AC susceptibility, and the absence of long-range order in low temperature neutron diffraction data.

![Diagrams illustrating the geometric frustration of magnetic moment moments (arrows) in triangular and tetrahedral atomic arrangements.](image)

**Figure 1.20.** Diagrams illustrating the geometric frustration of magnetic moment moments (arrows) in triangular and tetrahedral atomic arrangements.

### 1.6.4 Spin-Orbit Coupling

Spin-orbit coupling (SOC) occurs when the spin of an electron magnetically interacts with its own orbital angular momentum. From the point of view of an observer at the electron,
the nucleus will appear to orbit the electron (Figure 1.21). This creates a magnetic field \( \mathbf{B}_o \) that interacts with the magnetic moment of the electron.

**Figure 1.21.** Schematic showing the magnetic field \( \mathbf{B}_o \) for the angular momentum of an electron. The generation of \( \mathbf{B}_o \) can be rationalized by considering the motion of a nucleus with charge \( +Ze \) around an electron with charge \( -e \).

For a many-electron state, the energy of the spin-orbit interaction \( E_{so} \) scales with nuclear charge \( Z \) and be defined in terms of the spin and orbital angular momentum quantum numbers \( S \) and \( L \):

\[
E_{so} = \frac{\mu_0 e^2 g_s}{8\pi m_e^2 r^3} S \cdot L
\]  

(E1.15)

where \( e \) is the charge of an electron, \( m_e \) is the electron mass, and \( r \) is the average radius of the electron cloud [51]. All elements have SOC to a degree but it much more prominent in heavier elements, such as the 5d TMs. E1.14 can be simplified to:

\[
E_{so} = \lambda_{so} \frac{S \cdot L}{\hbar^2}
\]  

(E1.16)
where $\lambda_{so}$ is the SOC constant. It is useful at this point to define a total angular momentum quantum number $J = S + L$. The allowed values for $J$ are $L + S, L + S - 1, \ldots, |L - S|$ and each $J$ state has a degeneracy of $2J + 1$. For example, an $^3F$ state would be allowed $J = 4, 3, \text{and } 2$. Thus, SOC manifests itself by splitting the energy states which can have a direct effect on the electronic properties of a material. For instance, when SOC is applied to Ir(V) ($d^5$) and Ir(IV) ($d^5$) configurations in a strong octahedral field, the $t_{2g}$ orbitals are split into new $J$ states of $J = 2, 1, 0 \text{ and } J = 3/2, 1/2$, respectively [52] (Figure 1.22).

![Figure 1.22. Splittings of the Ir(IV) and Ir(V) $t_{2g}$ orbitals caused by SOC. Note that electron filling for Ir(V) leads to a non-magnetic state.](image)

The $J$ states can be thought of as “shells” and if a shell is partially filled, the state is magnetic. If the shells are filled, the state is non-magnetic. Thus, whether or not SOC is applied for Ir(IV), the result is effectively equivalent to $S = 1/2$ or one unpaired electron. For Ir(V), however, accounting for SOC is important. Without SOC, Ir(V) should have a magnetic ground state with two unpaired electrons while applying SOC results in the four $d$ electrons completely filling the $J = 1$ and 0 states leading to a non-magnetic state. The role SOC plays in the electronic behavior of Ir oxides has been of much recent debate and discussion [53–56].
### 1.6.5 Magnetic Instrumentation

All of the magnetic susceptibility measurements discussed in this dissertation were done using either a Quantum Design Physical Property Measurement System (PPMS) at Oregon State University (Figure 1.23) or a Quantum Design Magnetic Property Measurement System (MPMS) at University of California Santa Cruz.

![Quantum Design PPMS with the ACMS equipment installed.](image)

**Figure 1.23.** Quantum Design PPMS with the ACMS equipment installed.

The AC/DC Magnetometry System (ACMS) is an attachment of the PPMS which allows for AC susceptibility and DC magnetization. Most of the magnetic measurements performed in this dissertation utilize a technique for DC measurements known as extraction magnetometry. The ACMS coil set, Figure 1.24, is inserted into the main dewar chamber,
connected to the instrument via a 12-pin connector at the base of the sample chamber. The sample, loaded in a polycarbonate straw is vibrated vertically through the coil set by the DC servo motor. Sample preparation is an important aspect of the measurement process as the sample should not be allowed to move freely in the straw as it can affect the sample centering if the sample does not move according to the DC servo motor. Thus, the sample can be measured as a sintered mass or as a tightly packed powder.

An applied field induces a magnetization in the sample that is detected by the ACMS coil set as an induced voltage. The amplitude of the voltage signal is thus related to the magnetic moment and the speed of vertical movement for a given extraction. Although automated, an important aspect of the measurement is the speed in which an extraction is made. A faster speed for an extraction generally results in enhanced signal strength and thus directly relates to the

**Figure 1.24.** Representation of the ACMS coilset and tube assemblage (left), expanded view with labels of the ACMS coilset detection unit (center), and mounted “as prepared” sample (right). ACMS coil set illustrations taken and modified from Quantum Design application notes [57].
measurement accuracy. Equally important then is the samples location with respect to the
detection coils. Thus, it is necessary to locate the sample using a single point DC extraction.
This allows the instrument to correct for the sample displacement when the DC servo motor is
engaged. If the sample has not been centered, the operator runs the risk of inaccurate
magnetization measurements. Generally, locating with an AC excitation is more accurate as
there is better resolution, but it is recommended to locate the sample using the method employed
for actual measurements [57].

For DC magnetization measurements, an applied field is necessary. The PPMS at
Oregon State University utilizes a superconducting magnet capable of magnetic fields as high
as 7 T, however an applied field of 0.1–1 T is generally sufficient for temperature dependent
measurements. It should be noted that if attempting to determine the effective moment, Curie
constant and transition temperatures through the Curie-Weiss relationship, a sufficient
temperature range above any transition temperature is required. This temperature range would
be well into the paramagnetic region. Thus, it is necessary to have some insight into the potential
magnetic interactions present for a sample, and may require several measurements to resolve
temperature discrepancies.

1.7 Electronic Transport Properties

1.7.1 Electrical Conduction

A material’s crystal structure, and therefore the arrangement of atoms, has a direct
impact on the band structure of the material. In Molecular Orbital theory, molecular orbitals are
created from linear combinations of atomic orbitals. As more and more atomic orbitals are introduced, the molecular orbitals begin to cluster in high and low energy bands. When this concept is applied to an infinitely repeating lattice, the spacing between orbitals decreases to the point that they begin to mix and the bands become continuous (Figure 1.25). The relative position of these bands and the number of available electrons in a given material determines the nature of its electrical conductivity. This can be illustrated using a simple two-band diagram with a valence band and a conduction band [58].

![Diagram showing the creation of energy bands from molecular orbitals.]  

**Figure 1.25.** Schematic demonstrating the creation of energy bands from molecular orbitals via the addition of an increasing number of atomic orbitals.

The energy to which the available electrons fill is called the Fermi level \( (E_F) \). If the electrons partially fill one of the bands (i.e. \( E_F \) falls within a band) as in Figure 1.26a, they can freely flow to available energy levels and the material is said to be a metallic conductor. On the other hand, when \( E_F \) falls in a gap between bands (Figures 1.26b and c), the electrons must
jump from the valence band and across the band gap \( (E_g) \) to the conduction band in order for electronic conduction to occur.

**Figure 1.26.** Simple two-band diagrams for: (a) metal, (b) extrinsic semiconductor, and (c) insulator. The conduction and valence bands are labeled by CB and VB, respectively. The point at which the electron filling stops is denoted by the Fermi level \( (E_F) \) while \( E_g \) is the energy gap between bands.

When \( E_g \) is large, the electrons need a sizable amount of energy to jump the gap, which leads to a low conduction band population and poor conduction, or insulator, behavior. Conversely, if \( E_g \) is small enough, the thermal energy of electrons is sufficient which allows more of them to populate the conduction band. The result is a material called a semiconductor that has decent conductivity. An insulator can be made more conductive though processes called n-type or p-type doping. This is accomplished by replacing, or “doping”, a small amount of the atoms for ones with more (n-type) or less (p-type) electrons which adds donor or acceptor levels to the band structure. These levels allow electrons to populate conduction bands more easily, thereby increasing conductivity. Doped conductors are labeled extrinsic semiconductors where as non-doped ones are intrinsic semiconductors.
The temperature dependence of conductivity ($\sigma$) and its reciprocal, resistivity ($\rho$), for each type of conductor is well known. For metals, resistivity is directly proportional with temperature (Figure 1.27a). In metals, the flow of electrons is interrupted only by scattering caused by collisions with atoms in the lattice. As temperature increases, thermal vibrations are intensified, causing more scattering events to occur, inhibiting conduction. In semiconductors, the proportionality of resistivity and temperature is an inverse trend. As temperature is increased, more electrons are able to jump across $E_g$ into the conduction band, and resistivity decreases.

![Temperature-dependent plots of (a) $\rho(T)$ for a metal and semiconductor and (b) $\ln \rho$ vs. $1/T$ for a semiconductor. Note that in (b) $E_g = \text{Slope} \times 2k$.](image)

The temperature dependence of semiconductor resistivity can be expressed mathematically as an Arrhenius relationship:

$$\rho = \rho_0 \exp \left( \frac{E_g}{2kT} \right)$$  \hspace{1cm} (E1.17)
where $\rho_0$ is a preexponential constant and $k$ is the Boltzmann constant. By taking the natural log of both sides, a linear relationship (Figure 1.27b) between $\ln \rho$ and $T^{-1}$ can be established:

$$
\ln \rho = \left( \frac{E_g}{2k} \right) \frac{1}{T} + \ln \rho_0
$$

(E1.18)

$E_g$ can then be estimated by multiplying the slope of the line by $2k$.

1.7.2 Seebeck Effect

Thermoelectric materials have the ability to produce electricity from thermal energy and vice versa. They can be utilized in devices for energy production and refrigeration, which rely on one of two thermoelectric effects: the Peltier effect or the Seebeck effect. Both effects involve the concept of heat conduction by the dominant charge carriers [59]. The first of these effects to be discovered was the Seebeck effect, in which a current is produced when a temperature gradient is applied to a material (Figure 1.28a). This effect is generally observed by measuring the voltage ($\Delta V$) generated by the gradient ($\Delta T = T_H - T_C$), related through a proportionality constant, $S$, called the Seebeck coefficient:

$$
\Delta V = S\Delta T
$$

(E1.19)

The magnitude and sign of $S$ can give an impression of how well a material produces current under a thermal gradient and the type of dominant charge carrier.
If $S$ is negative, it indicates the charge carriers are electrons while a positive value suggests hole carriers. Semiconductors tend to have higher $S$ values than metals (e.g. 200 vs. 10 $\mu$V·K$^{-1}$). While this phenomenon seems counterintuitive (since metals are better electrical conductors relative to semiconductors), metallic materials tend to be very good thermal conductors, which increases the difficulty in establishing a large temperature gradient. The complement to the Seebeck effect is the Peltier effect, which describes the production of a temperature gradient by applying current through a material (Figure 1.28b).

**Figure 1.28.** Diagrams demonstrating the (a) Seebeck and (b) Peltier effects.

1.7.3 Electronic Transport Instrumentation

1.7.3.1 High-Temperature Measurements

High-temperature (300–800 K) resistivity and Seebeck coefficients were measured using ULVAC-RIKO ZEM-3 Thermoanalyzer, Figure 1.29. The main components of the ZEM-3 consist of a heater and water cooling unit that encloses the sample chamber and probe contacts.
The sample is placed on the spring-loaded electrode blocks (Ni contacts) which are then tightened against the sample. The Pt probes are then brought into contact with sample from the side. Once the sample is held firmly in place and electrical contact is confirmed, the chamber is sealed, evacuated, and filled with a low pressure static helium atmosphere. The voltage across the sample ($\Delta V$) is measured using the Pt probes which are connected to a digital multi-meter. The current is flowed through the Ni side electrodes which are also used to generate and measure the thermal gradient ($\Delta T$) across the sample. The sign of the Seebeck coefficient is determined by the charge flow for the thermal gradient. The cold end is then positive for holes and negative for electrons. An external thermocouple is used to measure the set furnace temperature of the thermal chamber [60].

1.7.3.2 Low-Temperature Measurements

In addition to magnetic susceptibility, the PPMS can be easily set up to perform low-temperature (5–300 K) DC resistivity measurements. The resistivity puck shown in Figure 1.30 uses the same 12-pin connector at the base of the sample chamber as that used for a connection.
to the ACMS coil set mentioned previously. The PPMS resistivity puck is designed to measure four probe resistivity on 3 samples independently. Four probe resistivity is one of two general techniques used for measuring resistivity based on the resistivity of the sample. Normally the four-probe technique is employed when the sample resistivity is $\rho < 10 \, \Omega\text{-cm}$. This is necessary as the voltage leads and current leads are separated thus removing the contribution of the lead wire and contact resistance.

**Figure 1.30.** PPMS resistivity puck with a bar sample connected to position 1 using the four-probe contact technique. Contacts are made using conductive silver paint and copper wires that are soldered to the puck.

Samples with resistivities above $\rho = 10 \, \Omega\text{-cm}$ can be measured by the two-probe technique where the contact and lead wire resistance will not have much effect on the total resistivity. For samples measured in the PPMS, the four-probe technique is the only option. As shown in Figure 1.30, four contact wires are attached to the sample bar of known dimension by
means of silver paste or silver epoxy. Once the sample and contacts are in place, the puck is connected to the bottom of the PPMS sample chamber and the measurement can be started.

1.8 References


Chapter 2: Structural, Magnetic and Transport Characterization of the Solid Solution Between Ba$_2$In$_2$O$_5$ and BaIrO$_3$: Ba$_2$In$_{2-x}$Ir$_x$O$_{5+\delta}$

Abstract

The solid solution series Ba$_2$In$_{2-x}$Ir$_x$O$_{5+\delta}$ ($x = 0–1.4, 2$) was prepared and its structural, magnetic, and charge transport properties were measured. With increasing Ir content, three transitions in the room temperature structure were observed: orthorhombic to tetragonal, tetragonal to cubic, and cubic to a monoclinic distortion of a hexagonal BaTiO$_3$ structure. Neutron diffraction refinements showed Ba$_2$In$_{1.6}$Ir$_{0.4}$O$_{5.4}$ was cubic and Ba$_2$InIrO$_6$ was monoclinic. The latter result contradicts previously published XRD refinements. Magnetization measurements show Curie-Weiss behavior for $x = 0.2–0.6$, which arises from near 50:50 ratio of Ir(V) and Ir(VI). To our knowledge, this is the first time Ir(VI) has been stabilized with standard solid state methods under ambient conditions. Electrical resistivity measurements show all the compounds studied were semiconducting, and that resistivity decreases with increasing Ir content which suggests proximity to a metal-insulator transition. A sign reversal in the high-temperature Seebeck coefficient is observed indicating both electron and hole charge transport.
Publications based on this chapter:

2.1 Introduction to $\text{Ba}_2\text{In}_2\text{O}_5$ and $\text{BaIrO}_3$

The compounds $\text{Ba}_2\text{In}_2\text{O}_5$ and $\text{BaIrO}_3$ both crystallize in perovskite-related structures. $\text{Ba}_2\text{In}_2\text{O}_5$ is known to adopt the brownmillerite structure (Figure 2.1a) at room temperature. There has been some debate as to whether the correct space group is $Ibm2$ or $Icmm$ [1–5] which differ primarily in the periodicity of the orientation of tetrahedra. $\text{Ba}_2\text{In}_2\text{O}_5$ is often indexed as $Ibm2$ but more recent spectroscopic and computational studies have suggested that the short-range structure contains $Icmm$ symmetry [6]. The oxygen vacancies in $\text{Ba}_2\text{In}_2\text{O}_5$ at room temperature are ordered along the [001], but at higher temperatures, the oxygen vacancies begin to disorder. It transitions from the orthorhombic brownmillerite to a tetragonal perovskite phase at 925 °C and then to a cubic defect perovskite at 1116 °C [1]. The cubic phase has been found to have a relatively high oxide ion conductivity [7] and some substitutions for In have been reported in an effort to stabilize the cubic phase at room temperature [7–11]. Additionally, the solid solution $\text{Ba}_2\text{In}_{2-x}\text{Mn}_x\text{O}_{5+x}$ yielded green and turquoise colors the cause of which was determined to be $d$-$d$ transitions in tetrahedrally coordinated $\text{Mn}^{5+}$ ions [12].

The crystal structure for $\text{BaIrO}_3$ at ambient pressure and temperature is a monoclinic distortion of the 9R $\text{BaRuO}_3$ structure with space group $C2/m$. The structure (Figure 2.1b) can be described as corner-sharing clusters made up of face-sharing $\text{IrO}_6$ octahedra. It displays unusual ferromagnetic charge ordering behavior [13–15].
2.2 Investigation of \( \text{Ba}_2\text{In}_{2-x}\text{Ir}_x\text{O}_{5+\delta} \)

2.2.1 Motivation for Study

Interest in topological insulators has sparked the search for materials with large spin orbit coupling, among which are oxides containing \(5d\) transition metals, and iridium in particular [16–18]. The most common oxidation state of iridium in oxides is \(\text{Ir(IV)}\) although \(\text{Ir(V)}\) [19–23] and \(\text{Ir(VI)}\) [24–27] have been stabilized as well. These higher oxidation states have been observed in oxides of the types \(\text{Ba}_2\text{MIrO}_6\) and \(\text{Ba}_3\text{MIr}_2\text{O}_9\), both of which crystallize in perovskite-related structures [28,29]. Limited work has been done on solid solutions of these families and the brownmillerite structure.

Two members of the related compound series \(\text{Ba}_2\text{In}_{2-x}\text{Ir}_x\text{O}_{5+\delta}\) have been previously reported in the literature, \(\text{Ba}_2\text{InIrO}_6\) (\(x = 1, \delta = 1\)) and \(\text{Ba}_2\text{In}_{0.67}\text{Ir}_{1.33}\text{O}_6\) (\(x = 1.33, \delta = 1\)), with average Ir oxidation states of 5+ and 4.5+, respectively [28,30,31]. While the physical properties for \(\text{Ba}_2\text{InIrO}_6\) have previously not been reported, \(\text{Ba}_2\text{In}_{0.67}\text{Ir}_{1.33}\text{O}_6\) is known to be paramagnetic with short-range magnetic order which is supported by the susceptibility and specific heat data [28]. Both \(\text{Ba}_2\text{InIrO}_6\) and \(\text{Ba}_2\text{In}_{0.67}\text{Ir}_{1.33}\text{O}_6\) are reported to crystallize in the 6H hexagonal \(\text{BaTiO}_3\) structure (Figure 2.1c) adopting different space groups of \(P\overline{3}m1\) and \(P6_3/mmc\), respectively. The differences in symmetry is presumably due to steric constraints on spatial ordering of In and Ir ions.

The difference in structure between known members of the \(\text{Ba}_2\text{In}_{2-x}\text{Ir}_x\text{O}_{5+\delta}\) system motivates the present study to explore possible related physical states. In this work, we present the partial solid solution between \(\text{Ba}_2\text{In}_2\text{O}_5\) and \(\text{BaIrO}_3\) with a focus on the evolution of structural and physical behavior.
2.2.2 Structural Characterization

For Ba$_2$In$_2$Ir$_x$O$_{5+\delta}$, single phase samples were prepared for $x = 0–1.4$. For $x = 1.5–1.9$, mixed phase samples were formed containing various barium indium oxides and barium iridium oxides. The XRD diffraction data shown in Figure 2.2 illustrates two structural transitions as Ir content is increased from $x = 0$ to 0.6.

When $x$ is increased to 0.1, the structure transforms from the orthorhombic brownmillerite structure with space group Icmmm to a tetragonal defect perovskite structure with space group $P4/mmm$ (Figure 2.3a). In this structure, the oxygen vacancies become disordered within the $ab$ plane but are confined to alternating layers along the $c$ axis. Upon increasing $x$ to 0.2, a cubic defect perovskite phase (Figure 2.3b) with space group $Pm\overline{3}m$ forms where the oxygen vacancies are now completely disordered throughout the entire lattice. This structure persists until $x$ is increased beyond 0.5.
Figure 2.2. (Top) Powder X-ray diffraction patterns and (Bottom) lattice parameters for \( x = 0 - 0.5 \). The \( c \) parameter of the tetragonal phase \( (x = 0.1) \) was divided by 2 to allow for direct comparison to the cubic phases.
Figure 2.3. Structures of (a) tetragonal defect perovskite $\text{Ba}_2\text{In}_{1.9}\text{Ir}_{0.1}\text{O}_{5.1}$, (b) cubic defect perovskite $\text{Ba}_2\text{In}_{1.6}\text{Ir}_{0.4}\text{O}_{5.4}$ (Ba = green, In/Ir = purple, O = red).

A similar series of transitions is seen in pure $\text{Ba}_2\text{In}_2\text{O}_5$ at high temperatures [1]. A decrease in the unit cell parameters with increasing Ir content was observed as shown in Figure 2.2b. This trend is expected due to the large difference between the ionic radii of $\text{Ir}^{5+}$ and $\text{In}^{3+}$ (0.57 and 0.80 Å, respectively [32]). Refinement of neutron diffraction data for a sample with the nominal composition of $\text{Ba}_2\text{In}_{1.6}\text{Ir}_{0.4}\text{O}_{5.4}$ is depicted in Figure 2.4 and there is no evidence for ordering of the In and Ir ions; the refined formula was determined to be $\text{Ba}_2\text{In}_{1.62(2)}\text{Ir}_{0.38(2)}\text{O}_{5.49(6)}$. Table 2.1 contains a summary of the crystallographic data for $\text{Ba}_2\text{In}_{1.62(2)}\text{Ir}_{0.38(2)}\text{O}_{5.49(6)}$. The refined and nominal compositions correlate well and the additional oxygen content, represented by $\delta = 0.49(1)$, is slightly larger than the Ir content of $x = 0.38(2)$. This gives an average Ir oxidation state of 5.57(2) which indicates that a majority (~57%) of the Ir is in the 6+ state. This result is unexpected since stabilizing Ir(VI) typically requires the use of high oxygen pressures during heating [24,25,33,34] or the use of flux methods to grow single crystals [26,27,35].
$\chi^2 = 2.23, R_{wp} = 3.97\%$

**Figure 2.4.** Time-of-flight neutron diffraction pattern for Ba$_{2}$In$_{1.6}$Ir$_{0.4}$O$_{5.4}$ with calculated intensities (red), difference (blue) and background (green) curves. The allowed reflections for $Pm\bar{3}m$ are indicated by the magenta tick marks.

**Table 2.1.** Refined atomic parameters for Ba$_{2}$In$_{1.62(2)}$Ir$_{0.38(2)}$O$_{5.49(6)}$.

<table>
<thead>
<tr>
<th></th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>Occupancy</th>
<th>$U_{iso}$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>1/2</td>
<td>1/2</td>
<td>1/2</td>
<td>1.0</td>
<td>0.0317(5)</td>
</tr>
<tr>
<td>In</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.84(1)</td>
<td>0.0151(4)</td>
</tr>
<tr>
<td>Ir</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.16(1)</td>
<td>0.0151(4)</td>
</tr>
<tr>
<td>O</td>
<td>1/2</td>
<td>0</td>
<td>0</td>
<td>0.89(1)</td>
<td>0.0313</td>
</tr>
</tbody>
</table>

Anisotropic atomic displacement parameters (Å$^2$)

<table>
<thead>
<tr>
<th></th>
<th>$U_{11}$</th>
<th>$U_{22}$</th>
<th>$U_{33}$</th>
<th>$U_{12}$</th>
<th>$U_{13}$</th>
<th>$U_{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>0.0223(6)</td>
<td>0.0374(4)</td>
<td>0.0374(4)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Iodometric titrations performed on the same sample used for neutron diffraction gave an average Ir oxidation state of 5.68(6) which compares well with the value obtained the
refinements and supports the presence of Ir(VI) in the samples with low Ir content. To our knowledge, this is the first time Ir(VI) has been stabilized using standard solid state methods with ambient pressure and atmosphere.

On increasing $x$ beyond 0.6, a third structural transition is indicated by the emergence of several new diffraction peaks in the XRD data (Figure 2.5). These peaks increase further in intensity as Ir content approaches $x = 1.0$. Initial XRD refinements indexed the new peaks to a hexagonal 6H BaTiO$_3$-type phase which persists on increasing $x$ to 1.4. Thus, in the region spanning $x = 1$, our XRD measurements are in agreement with the previously reported 6H polytype structure of Ba$_2$InIrO$_6$ [31].

*Figure 2.5.* Powder X-ray diffraction patterns for $x = 0.6$–1.4.
**Figure 2.6.** Refined (Left) cell edges and (Right) β angles and cell volumes for $x = 0.6–1.4$.

Examination of the changes in the lattice parameters with increasing Ir content reveals a couple trends (Figure 2.6). The unit cell edges $a$ and $b$ decrease linearly whereas there are two linear trends in $c$, $\beta$, and $V$ on either side of $x = 0.9$. This change in slope suggests that the cubic to hexagonal transition is completed after once the Ir content is increased beyond 0.8. Neutron diffraction refinements (Figure 2.7) for Ba$_2$InIrO$_6$ show a splitting in several of the peaks, in disagreement with the reported model (Figure 2.7 inset). These splittings, which were not observed in XRD data, can be indexed to a monoclinic distortion of 6H BaTiO$_3$ structure with a $C2/c$ space group. The absence of these splittings in the XRD patterns is likely due to lower resolution which causes the splittings to appear simply as peak broadening. Additionally, examination of the pattern at higher $d$-spacing reveals the presence of a peak at about 5.1 Å that indexes to reflections for 020 and 110. This peak is absent in a calculated pattern of the structure proposed by Thumm, *et. al.* (Figure 2.8). After the monoclinic model was determined, all XRD
refinements for $0.6 \leq x \leq 1.4$ were revised using this model. As with the lower Ir content samples discussed previously, a decrease in all lattice parameters was observed with increasing Ir content due to the difference in ionic radii.

The monoclinic model has important implications for the structure. First, in this model, the In and Ir are not ordered in alternating layers along the $c$ axis. Instead, the corner-sharing sites are 100% In and the face-sharing site In:Ir ratio is 0.27:0.73. This gives a refined formula of $\text{Ba}_2\text{In}_{1.03(2)}\text{Ir}_{0.97(2)}\text{O}_6$ which correlates well to the nominal composition. In the previously published hexagonal model [31], all octahedra are oriented parallel to the $c$ axis. The monoclinic model yields a slight canting with respect to the $a$ axis in the corner-sharing octahedra and the
face-sharing clusters of 7.3° and -3.3°, respectively (Figure 2.9). Similar canting is seen in Ir-octahedra in Ba$_3$BiIr$_2$O$_9$ and Ba$_3$NdIr$_2$O$_9$ [36,37].

![Image](image_url)

**Figure 2.8.** Comparison of time-of-flight neutron diffraction patterns for Ba$_2$InIrO$_6$: experimental (blue), calculated $P\bar{3}m1$ (black) and $C2/c$ (red). Note that the 003 peak (~4.9 Å) in the $P\bar{3}m1$ pattern is absent in the experimental pattern where as a small 020,110 peak (~5.1 Å) from $C2/c$ is present.

![Image](image_url)

**Figure 2.9.** Projections of the hexagonal structure reported by Thumm et al. and this work’s monoclinic structure models comparing the Ir/In ordering and the canting of the octahedra.
Figure 2.10 shows a comparison of bond angles and distances for the Thumm model and those from this work. When the Ir-O and In-O bond distances from the two models are compared with calculated lengths based on Shannon radii [32] (1.97 and 2.14 Å respectively), the bond lengths from our refinements are closer to theoretical values and thus more reasonable than those from the previously reported model. A comparison of the lattice parameters between this work’s structure model for Ba$_2$InIrO$_6$ and that proposed by Thumm, et al. (Table 2.2) shows little difference in the size of the unit cell. Table 2.3 summarizes additional atomic parameters from our neutron refinements for Ba$_2$InIrO$_6$.

**Figure 2.10.** Comparison of bond distances within the face-sharing clusters (top) and M-O-M’ bond angles between the face-sharing cluster and the corner sharing octahedra in Ba$_2$InIrO$_6$ (bottom) from the two models (In = purple, Ir = brown, O = red).
Table 2.2. Lattice parameter comparison of structure models for Ba$_2$InIrO$_6$.

<table>
<thead>
<tr>
<th></th>
<th>SG</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$\beta$ (°)</th>
<th>$V$ (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>$C2/c$</td>
<td>5.885(1)</td>
<td>10.19(1)</td>
<td>14.65(1)</td>
<td>90.48(1)°</td>
<td>878.4(1)</td>
</tr>
<tr>
<td>Thumm et al.</td>
<td>$P\overline{3}m1$</td>
<td>5.873</td>
<td>10.17</td>
<td>14.63</td>
<td>90°</td>
<td>873.8</td>
</tr>
</tbody>
</table>

*a Lattice parameters transformed from reported hexagonal values [31] for comparison

Table 2.3. Refined atomic coordinates and occupancies for Ba$_2$InIrO$_6$.

<table>
<thead>
<tr>
<th></th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>Occupancy</th>
<th>$U_{iso}$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba1</td>
<td>0</td>
<td>0.0012(1)</td>
<td>1/4</td>
<td>1.0</td>
<td>0.0061(7)</td>
</tr>
<tr>
<td>Ba2</td>
<td>0.5030(6)</td>
<td>0.8322(9)</td>
<td>0.0918(2)</td>
<td>1.0</td>
<td>0.0084(6)</td>
</tr>
<tr>
<td>In1</td>
<td>0.4945(3)</td>
<td>0.8330(4)</td>
<td>0.8453(1)</td>
<td>0.27(1)</td>
<td>0.0012(3)</td>
</tr>
<tr>
<td>Ir1</td>
<td>0.4945(3)</td>
<td>0.8330(4)</td>
<td>0.8453(1)</td>
<td>0.73(1)</td>
<td>0.0012(3)</td>
</tr>
<tr>
<td>In2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.0</td>
<td>0.0027(8)</td>
</tr>
<tr>
<td>O1</td>
<td>0.7725(10)</td>
<td>0.7411(6)</td>
<td>0.2473(3)</td>
<td>1.0</td>
<td>0.0116(9)</td>
</tr>
<tr>
<td>O2</td>
<td>0.5</td>
<td>0.0158(9)</td>
<td>0.25</td>
<td>1.0</td>
<td>0.0188(21)</td>
</tr>
<tr>
<td>O3</td>
<td>0.2602(10)</td>
<td>0.5858(6)</td>
<td>0.0924(3)</td>
<td>1.0</td>
<td>0.0157(11)</td>
</tr>
<tr>
<td>O4</td>
<td>0.0108(14)</td>
<td>0.8287(7)</td>
<td>0.0840(4)</td>
<td>1.0</td>
<td>0.0194(13)</td>
</tr>
<tr>
<td>O5</td>
<td>0.7657(12)</td>
<td>0.5863(8)</td>
<td>0.0761(4)</td>
<td>1.0</td>
<td>0.0226(12)</td>
</tr>
</tbody>
</table>

2.2.3 Magnetism

The magnetization, $M$, was measured for $x = 0.2$–1.33 in a magnetic field, $H$, of 0.5 T, and converted to susceptibility ($\chi$) via $\chi = M / H$. The susceptibility has been corrected for the contribution from the atomic cores of the constituent ions [38]. Field scans, $M(H)$, exhibit linear behavior over the range 0–4 T and $\chi(T)$ data had no anomalies from 2–300 K, consistent with
paramagnetism over the entire measurement range. When viewed as $1/\chi(T)$ (Figure 2.11), three distinct regimes of Ir concentration emerge. For low Ir content, $0.2 < x < 0.6$, $1/\chi(T)$ displays Curie-Weiss behavior. Fitting $1/\chi(T)$ between 200 and 300 K for these compounds yields $\mu_{\text{eff}}$ values in the range of 3.2–2.9 $\mu_B$ per Ir ion. Since the average Ir oxidation state is greater than 5.5, we expect to have a mixture of different oxidation states among the ions. It is also expected that Ir(V) has a free spin of zero and thus does not contribute to the susceptibility, apart from a Van Vleck temperature independent moment [39]. Thus, since the expected spin-only $\mu_{\text{eff}}$ value for Ir(IV) in octahedral coordination is 1.73 $\mu_B$, corresponding to $s = 1/2$, the measured moment must possess a contribution from Ir(VI), which has $s = 3/2$ by Hund’s rule and no Van Vleck term.

Figure 2.11. Inverse magnetic susceptibility plot for Ba$_2$In$_{2-x}$Ir$_x$O$_{5+\delta}$. All data has been corrected for the contribution from the atomic cores of the constituent ions.
Based on these concepts, we used the following procedure to fit the $\chi(T)$ data, letting the relative contributions of Ir(IV), Ir(V), and Ir(VI) be variable. The first step is to determine the fraction of Ir(V) by demanding that the resulting $\chi(T)$ be Curie-Weiss like (i.e. forms a straight line) in the temperature range 100-300 K after subtracting the Ir(V) Van Vleck contribution, $\chi_{VV}$ [39]. For $x = 0.2$ and 0.4, the resulting Ir(V) content was very close to 50% of the total Ir population, and the Weiss constant was extracted from the resulting ($\chi(T) - \chi_{VV}$). We found that, by assigning the remainder of the Ir ions to be Ir(VI), we obtained good fits to a Curie-Weiss form using the extracted Weiss constant.

![Curie-Weiss fits and ratios of the possible Ir oxidations states for Ba$_2$In$_{2-x}$Ir$_x$O$_{5+\delta}$ ($x = 0.2$–$0.6$).](image)

**Figure 2.12.** Curie-Weiss fits and ratios of the possible Ir oxidations states for Ba$_2$In$_{2-x}$Ir$_x$O$_{5+\delta}$ ($x = 0.2$–$0.6$).
The data, plotted as $\chi(T)$ multiplied by temperature (Figure 2.12), show a deviation from the Curie-Weiss fit at temperatures below 50 K, where super-paramagnetic effects due to spin clusters play a role. For $x = 0.6$, it was not possible to model the data with only Ir(V) and Ir(VI). Instead, we allowed the ratio of Ir(IV) to Ir(VI) to vary after determining the Ir(V) in the same manner as above until a reasonable fit was achieved. This ratio was found to be approximately 1:1 among the ~60% of non Ir(V) ions. Thus the $\chi(T)$ data suggest average Ir oxidation states of 5.5, 5.5, and 5.0 for $x = 0.2$, 0.4, and 0.6 respectively, consistent with the titration and neutron refinement values found for $x = 0.4$.

A second regime of magnetic behavior is seen for $x = 0.6–1.2$ as cubic perovskite structure transitions to the 6H structure. In this $x$ range, $\chi(T)$ decreases significantly, possibly indicating the compensation of moments through local spin cluster singlet formation. Given the large $\theta$ values observed for smaller $x$, long range order might be expected, but the two-dimensionality of the Ir site arrangement and quenched atomic disorder would suppress both its formation and detection via $\chi(T)$, similar to the behavior seen in Ba$_2$IrO$_4$ [40]. If an ordered moment exists in $x = 0.6–1.2$, it might be detectable using $\mu$SR techniques as in the Ba$_2$IrO$_4$ study.

Finally, $1/\chi(T)$ for the $x = 1.33$ compound has a significantly larger slope than $x = 1.0$ and 1.2, which might reflect the development of magnetization in a state that has already developed long-range antiferromagnetic order. In this structure, the double-layer block has 100% Ir occupancy and the intermediate layers contain only In. Since the average oxidation state of Ir is 4.5+ for this compound, the double-layer most likely possesses a random 1:1 mixture of Ir(IV) and Ir(V). The average $\chi_{VV}$ for octahedral Ir(IV) and Ir(V) is $8 \times 10^{-4}$.
emu/mole [39]. This value is larger than the room temperature $\chi(T)$ which is $7 \times 10^{-4}$ emu/mole suggesting the Ir environment for $x = 1.33$ is distorted from that described by Hayashi, *et al.* [39].

### 2.2.4 Electronic Transport Properties

High-temperature Seebeck and resistivity data for $x = 0.8–1.4$, 2 are displayed in Figure 2.13. Semiconductor behavior was observed for all samples and resistivity decreased with increasing Ir content. The band gaps ($E_g$) for each sample were extracted using $\sigma = \sigma_0 \exp(E_g/k_BT)$ and are listed in Table 2.4. The band gaps tend to decrease with increasing Ir content and decreasing Ir oxidation state.

![Figure 2.13](image.png)

**Figure 2.13.** Temperature-dependent, high temperature resistivity (left) and Seebeck (right) coefficient plots for Ba$_2$In$_{2-x}$Ir$_x$O$_{5+y}$. Note the sign change in the Seebeck coefficient for $x = 1.0$ and 1.2 at ~550 K.

Below 600 K, the system changes from p-type to n-type as denoted by the sign change in the Seebeck coefficient when the Ir content is increased from $x = 0.8$ to $x = 1.0$ and then
changes back to p-type at $x = 1.33$. A transition from n-type to p-type is observed in Seebeck coefficient for $x = 1.0, 1.2$ which suggests the presence of carriers of both signs, but with different temperature dependencies.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>0.713(13)</td>
</tr>
<tr>
<td>1.0</td>
<td>0.450(11)</td>
</tr>
<tr>
<td>1.2</td>
<td>0.406(8)</td>
</tr>
<tr>
<td>1.33</td>
<td>0.254(1)</td>
</tr>
<tr>
<td>1.4</td>
<td>0.174(1)</td>
</tr>
<tr>
<td>2.0</td>
<td>0.0907(19)</td>
</tr>
</tbody>
</table>

2.3 Conclusions

The solid solution $\text{Ba}_2\text{In}_{2-x}\text{Ir}_x\text{O}_{5+\delta}$ yielded three structural transitions with variation of the Ir content. A complete solid solution was not possible as samples for $x = 1.5–1.9$ resulted in a mixture of several phases. Neutron diffraction refinements showed that where $x \leq 1$, the increase in oxygen content is the greater than the Ir content which indicates that the Ir oxidation state is a mixture of Ir(IV), Ir(V), and Ir(VI) in these samples. While Ir(VI) has been previously reported in oxides, it was stabilized for the first time without the use of high oxygen pressures or molten flux techniques. The oxygen content in the Ir-poor phases is likely lower at our preparation temperature of 1200 °C than what we observe at room temperature. Thus, the Ir(VI) that we find in these samples may be due to the oxidation of Ir that occurred upon cooling our samples in air aided by the high electropositivity of Ba and the filling of oxygen vacancies. The monoclinic structure model for $\text{Ba}_2\text{InIrO}_6$ obtained from our neutron diffraction refinements
appears to be a better fit than the hexagonal model originally reported by Thumm, et al. This monoclinic structure is present through $x = 1.4$.

Our magnetic measurements suggest that the lower Ir content embers ($x = 0.2–0.6$) display Curie-Weiss behavior due to the presence of Ir(VI). For $0.8 \leq x \leq 1.2$, the susceptibility rapidly decreases with the Ir concentration. The $x = 1.33$ exhibited no signs of magnetic ordering and its paramagnetic behavior did not obey the Curie-Weiss law. A modified Curie-Weiss fit yielded $\mu_{\text{eff}}$ values that were much lower than hypothetical spin-only values likely due to high degrees of spin-orbit coupling in the Ir. Electrical measurements showed semiconductor behavior for $x = 0.8–1.4$, and increasing Ir content resulted in a decrease in resistivity. The resistivities for member with $x < 0.8$ were found to be above the upper limit for the instrument and were not measured. The Seebeck measurements revealed increased Ir content caused a p-to n-type transition. A very gradual n- to p-type transition was also observed in the $x = 1.0$ and 1.2 samples with increasing temperature.

2.4 Methods and Materials

Black, single-phase polycrystalline samples were prepared by intimately mixing and grinding stoichiometric amounts of BaCO$_3$ (Cerac, 99.9%), IrO$_2$, and In$_2$O$_3$ (Stanford Materials, 99.99%) using an agate mortar and pestle. The BaCO$_3$ was dried at 120 °C overnight, and the IrO$_2$ was obtained by decomposing IrCl$_3$ (Alfa Aesar, 99.9%) at 750 °C for 10 h under air flow. The samples were then pelletized and sintered at 1200 °C for 36 h with intermittent grinding.
Iodometric titrations were performed on $x = 0.2–0.6$ to confirm the Ir oxidation state by first dissolving ~25 mg of each sample in 5 mL of a 10% HCl solution then adding excess KI. The $I^-$ in an acidic environment reduces the Ir ions from their original oxidation state to Ir$^{3+}$ and produces $I_3^-$:

$$2\text{Ir}^{x+} + (3x - 9)\text{I}^- \rightarrow 2\text{Ir}^{3+} + (x - 3)\text{I}_3^-$$

The resulting solutions were then titrated with Na$_2$S$_2$O$_3$ solution of a known concentration. The reaction of S$_2$O$_3^{2-}$ with the generated I$_3^-$ can be monitored by using a starch solution as an end-point indicator. The Ir oxidation state can then be calculated from the volume of Na$_2$S$_2$O$_3$.

Initial X-ray diffraction (XRD) characterization of the samples was done on a Rigaku Miniflex II diffractometer using Cu Kα radiation and a graphite monochromator. Single-crystal Si sample holders were used to maximize peak intensity and aid detection of minor impurities. A fixed-time scan was used with collection parameters of a 2θ range of 10-70° with a step size of 0.02° and a dwell time of 2.0 s. Lattice parameters for all samples were extracted using the Le Bail method [41] on the GSAS software with EXPGUI user interface [42,43]. Room-temperature (298 K) time-of-flight neutron diffraction data for $x = 0.4$ and 1.0 were collected at Oak Ridge National Laboratory on the POWGEN (BL-11A) beam line using center wavelengths of 1.33 and 2.66 Å. Approximately 2 g of each sample was loaded into 6 mm vanadium sample cans and data was collected over about 4 h. Structure refinement was performed using the Rietveld method [44] on the GSAS software with EXPGUI user interface [42,43]. Crystal structures were generated using the VESTA software [45]. Seebeck and resistivity measurements were performed at high temperatures (300–800 K) on an ULVAC-
RIKO ZEM 3 under a static helium atmosphere. Low-temperature (5–300 K) magnetization measurements were obtained using a Quantum Design MPMS.

2.5 References


[7] J.B. Goodenough, Oxide-ion conduction in Ba₂In₂O₅ and Ba₂In₂MO₈ (M = Ce, Hf, or Zr), Solid State Ionics. 44 (1990) 21–31.


P. Jiang, J. Li, A. Ozarowski, A.W. Sleight, M.A. Subramanian, Intense Turquoise and Green Colors in Brownmillerite-Type Oxides Based on Mn$^{5+}$ in Ba$_2$In$_{2-x}$Mn$_x$O$_{5+x}$, Inorg. Chem. 52 (2013) 1349–57. doi:10.1021/ic3020332.


Chapter 3: Tuning the Ir Oxidation State in Ba$_2$InIrO$_6$ and BaLaInIrO$_6$ via A- and B-site Substitutions

Abstract

Two novel solid solution series, Ba$_{2-x}$La$_x$InIrO$_6$ ($x = 0–1.0$) and BaLaIn$_{1-y}$Ca$_y$IrO$_6$ ($y = 0–1.0$), were prepared and several changes in structure, magnetic moment, and charge transport were observed. The Ba$_{2-x}$La$_x$InIrO$_6$ series exhibits a transition from a 6M polytype to an orthorhombic perovskite structure with increased La content whereas the BaLaIn$_{1-y}$Ca$_y$IrO$_6$ series transitioned from a disordered orthorhombic perovskite to an ordered cubic perovskite with increased Ca content. Seebeck measurements for both systems showed that Ir(IV)-rich compounds tended to have a n-type conduction mechanism while Ir(V)-rich compounds appeared to be p-type. Both systems were found to be semiconducting and the magnitude of the resistivity is dependent on the crystal structure and Ir environment. Magnetic measurements show that the $\mu_{\text{eff}}$ values for both systems are significantly less than predicted for Ir(IV) (1.73 $\mu_B$) and greater than predicted for Ir(V) (0 $\mu_B$). These results are compared to other iridate compound families.
Publications based on this chapter:

3.1 Motivation for Study

Iridium oxides are of interest due to their novel magnetic properties [1–3] and potential as topological insulators [4–6]. A large amount of work has been done on iridate families with specific perovskite stoichiometries, such as $A_2B\text{IrO}_6$ [7–11] and $A_3B\text{Ir}_2\text{O}_9$ [12–14]), and numerous $A_2\text{Ir}_2\text{O}_7$ pyrochlores [15–18]. Fewer studies have focused on diluting the Ir content or tuning the Ir oxidation state. Since tuning the oxidation state and content of transition metals has long been known to bring about exotic and unexpected properties in oxides, such studies are important for determining the structure-property relationships of iridate systems.

The magnetism of iridates especially those containing Ir(IV) or Ir(V) has been the subject of recent debate and interest. One of the most informative physical properties is the value of the effective moment ($\mu_{\text{eff}}$). Iridate compounds exhibit large variability in the reported moments. When including the splitting of the $t_{2g}$ orbitals due to spin-orbit coupling (SOC), Ir(IV) should have an $\mu_{\text{eff}}$ value close to $1.73 \mu_B$ in an octahedral environment while Ir(V) should have no moment, but should instead exhibit Van Vleck temperature-independent paramagnetism [19]. However, this is not always the case. For example, compounds containing Ir(IV) as the only magnetic ion have reported $\mu_{\text{eff}}$ values ranging from close to the spin-only value for a low spin $d^5$ metal ($1.73 \mu_B$) [7,20–22] to much lower values ($0.1–0.5 \mu_B$) [13,23–27]. While SOC is an important factor to consider when defining magnetism in iridates, the on-site Coulombic interaction, $U$ (not to be confused with $U_{\text{iso}}$), as well as the bandwidth, $W$, also play a role. The latter of these will affect the degree of localization for a particular system [28]. In particular, we note that when $W$, $U$, and SOC conspire to yield delocalized charges, the value of $\mu_{\text{eff}}$ will be less than the local moment value of $1.73 \mu_B$. Since $W$ and $U$ can depend on the
difference in orbital overlap (which is controlled by the spatial configuration of Ir ions in the lattice), one cannot assume that the local moment in one crystal structure can be compared with that in another. Therefore, the origin for variation of moment, and hence the degree of electron localization, needs to be examined for each structure type.

Iridium in oxides is somewhat flexible with respect to the oxidation state. The most common state is Ir(IV) though it is not difficult to stabilize Ir(V) and even Ir(VI) under the right conditions [29–33]. Ir(III) is most common in transition metal complexes but a few occurrences in extended oxide structures have been reported, including BaIrO$_{3.6}$, K$_{1.3}$Ir$_4$O$_8$ and Sr$_{2.3}$La$_4$IrO$_4$ [34–36]. To explore the influence of structure and Ir oxidation state on the magnetic and electrical properties, the other cations in the structure must have a closed shell configuration. In this work, the Ir oxidation state is systemically tuned between 4+ and 5+ in perovskite-related structures via A-site and B-site substitutions while monitoring the variation of structure, magnetic moment, and charge transport.

### 3.2 Substitutions and Structural Characterization

#### 3.2.1 Ba$_{2-x}$La$_x$InIrO$_6$

Ba$_2$InIrO$_6$ crystallizes in a monoclincally distorted 6H polytype structure [29] similar to Ba$_3$BiIr$_2$O$_9$ and Ba$_3$NdIr$_2$O$_9$ [37,38] and was determined to be an ideal candidate for A-site substitution due to inflexibility of the Ba and In oxidation states. Despite its significantly smaller ionic radius, La(III) has been reported to substitute well for Ba(II) in a handful of BaLa$M$IrO$_6$ ($M =$ Fe(III), Co(II), Mg(II), Ni(II)) perovskites [7]. Thus, for the potential series
$\text{Ba}_{2-x}\text{La}_x\text{InIrO}_6$, substituting La for Ba in the $A$-site will force Ir to reduce from 5+ to 4+ to compensate for the charge difference. As demonstrated below, this substitution was successful and single phase samples were prepared for $x = 0–1$.

Powder XRD diffraction data (Figure 3.1) reveal a structural transition from the monoclinic $\text{Ba}_2\text{InIrO}_6$ $C2/c$ structure (Figure 3.2a) to a disordered orthorhombic $Pbnm$ perovskite structure (Figure 3.2b) with increasing La content. The transition starts gradually with the characteristic peaks of the 6H polytype slowly decreasing in intensity while a small peak corresponding to the 110 and 002 reflections of orthorhombic perovskite begins to appear at $\sim 21.5^\circ$.

![Figure 3.1. Powder X-ray diffraction patterns for $\text{Ba}_{2-x}\text{La}_x\text{InIrO}_6 (x = 0–1)$.](image-url)
Figure 3.2. Crystal structures of (a) monoclinic 6H polytype Ba$_2$InIrO$_6$ (Ba = green, In = purple, Ir = light brown, O = red) and (b) orthorhombic perovskite BaLaInIrO$_6$ (Ba/La = green, In/Ir = purple, O = red).

Figure 3.3. Lattice parameters for Ba$_{2-x}$La$_x$InIrO$_6$ ($x = 0$–1). The $a$ and $c$ parameters of the monoclinic phase (filled points) were divided by $\sqrt{3}$ for a more direct comparison to the orthorhombic parameters (open points).
Increasing $x$ beyond 0.5 causes the monoclinic phase to disappear very quickly until only the orthorhombic perovskite phase is present at $x = 1$. Successful substitution of the La(III) for the Ba(II) is supported by the change in the lattice parameters (Figure 3.3) which show an overall decrease in the unit cell volume in both crystal structures despite the increase in the $a$ parameter of the monoclinic phase.

Refinements of the TOF neutron diffraction data for BaLaInIrO$_6$ were performed for both $P2_1/n$ and $Pbnm$ to model order and disorder, respectively, on the $B$-site. The $P2_1/n$ model refined to show very little $B$-site ordering (< 5%) and yielded a goodness-of-fit similar to that of the $Pbnm$ model so the latter was chosen due to its higher symmetry. Neither model showed ordering of the $A$-site.

**Figure 3.4.** TOF diffraction pattern for BaLaInIrO$_6$ with calculated intensities (red) and difference curve (blue). The magenta tick marks are the allowed reflections for $Pbnm$. 
Table 3.1. Refined unit-cell, coordinate and displacement parameters for BaLaInIrO$_6$ (Pbnm)$^a$

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
<th>$U_{\text{iso}}$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba/La</td>
<td>-0.0155(17)</td>
<td>0.5187(11)</td>
<td>0.25</td>
<td>0.5/0.5</td>
<td>0.0026(6)</td>
</tr>
<tr>
<td>In/Ir</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.5/0.5</td>
<td>0.0010(4)</td>
</tr>
<tr>
<td>O1</td>
<td>-0.0505(17)</td>
<td>-0.003(21)</td>
<td>0.25</td>
<td>1.0</td>
<td>0.0112(12)</td>
</tr>
<tr>
<td>O2</td>
<td>0.2321(17)</td>
<td>0.2768(14)</td>
<td>0.0358(8)</td>
<td>1.0</td>
<td>0.0210(11)</td>
</tr>
</tbody>
</table>

$^a$The unit-cell parameters are $a = 5.789(1)$ Å, $b = 5.796(1)$ Å, $c = 8.174(1)$ Å, and $V = 274.28(2)$ Å$^3$; the reliability parameters are $\chi^2 = 1.68$, $R_{wp} = 3.88\%$.

The Rietveld refinement for Pbnm is shown in Figure 3.4 and the extracted crystallographic data is summarized in Table 3.1. Imma was also considered as a possible space group and fit the neutron data as well as Pbnm; however, it was ruled out due to the presence of a peak in the XRD pattern at ~24° which indexes to the 111 reflection under Pbnm but is not allowed under Imma (Figure 3.5). The orthorhombic distortion from the ideal perovskite is two-fold: a slight displacement of the Ba/La site along the [110] direction as well as tilting of the octahedral sites. The Pbnm space group has a $a^+a^+c^+$ Glazer tilt scheme [39] (Figure 3.6). The tilting angles $\theta$ and $\phi$ were calculated using anion coordinates [40] and found to be 8.158° and 5.208°, respectively. These tilt angles are somewhat lower than expected when compared to values observed for other orthorhombic perovskites [41,42].
Figure 3.5. Comparison of experimental (black) and calculated $Pbnm$ (red) and $Imma$ (blue) XRD patterns for $\text{BaLaInIrO}_6$. Note that the 111 peak (~$24^\circ$) is present in both the experimental and $Pbnm$ patterns but is absent in the $Imma$ pattern.

Figure 3.6. Projections of $\text{BaLaInIrO}_6$ showing the anti-phase tilting respect to the $a_{\text{cubic}}$ axis and in-phase tilting along the $c$ axis.
3.2.2 \textit{BaLaIn}_{1-y}Ca_{y}IrO_{6}

Although BaLaInIrO$_6$ had not been previously reported in the literature, the double perovskite Ba$_2$CaIrO$_6$ had [31], suggesting BaLaCaIrO$_6$ would a viable target in a BaLaIn$_{1-y}Ca_{y}IrO_{6}$ series allowing for tuning of the Ir oxidation state from 4+ to 5+. Single phase samples were successfully prepared for $y = 0–1$. XRD diffraction data (Figure 3.7) shows that as Ca content is increased, the structure transitions from the disordered orthorhombic perovskite ($y = 0–0.75$) to an ordered cubic perovskite ($y = 1.0$) with the space group $Fm\bar{3}m$ (Figure 3.8). The orthorhombic lattice parameters (Figure 3.7) gradually come together with increasing Ca content. There is also an overall increase in the size of the unit cell, which is expected due to the larger ionic radius of Ca compared to In. The transition is gradual and although the intermediate members can be indexed to the $Pbnm$ space group, the degree of $B$-site ordering likely increases with Ca content suggesting these members would have a partially ordered, yet distorted, structure with a likely space group of $P2_1/n$. The ordering in BaLaCaIrO$_6$ is due to the large size and charge separation between Ca(II) and Ir(V). It is unexpected to see the transition to higher symmetry (orthorhombic to cubic) given that the tolerance factor decreases from 0.966 for BaLaInIrO$_6$ to 0.934 for BaLaCaIrO$_6$ though there is literature on cubic rhenium-based double perovskites with tolerance factors [43] similar to the value observed for BaLaCaIrO$_6$. 
Figure 3.7. (Top) Powder X-ray diffraction patterns and (bottom) lattice parameters for BaLaIn$_{1.3}$Ca$_{y}$IrO$_6$ ($y = 0–1$). Successful substitution of In for Ca is indicated by the increase in the lattice parameters with increasing $y$. The orthorhombic $b$ and $c$ parameters were multiplied by $\sqrt{2}$ for a more direct comparison to the cubic phase.
The presence of In(III) in the B-site seems to induce disorder, which is unexpected considering the size difference between Ir(IV) and In(III). One might suggest that the charge separation is too small; however, no ordering is observed in the \( \text{Ba}_2\text{In}_{2-x}\text{Ir}_x\text{O}_{5+\delta} \) family [29] where the charge difference is 2 or greater. Additionally, ordering is known to occur based solely on difference in ionic radii of the B cations in several \( A_2B^{4+}B'^{4+}\text{O}_6 \) \((A^{2+} = \text{Ba, Sr}; B^{4+} = \text{Ce, Tb, Pr}; B'^{4+} = \text{Ir, Pt})\) double perovskites [44,45,9]. The B-site ionic radii differences, based on Shannon radii [46], in these compounds range from 0.245 to 0.14 Å which encloses the value 0.175 Å for Ir(IV) and In(III) well. Both In and Ir are also known to order with other similarly sized ions as seen in \( \text{Ba}_2\text{InOsO}_6 \) and \( \text{Ba}_2\text{ScIrO}_6 \) [47,48]. Based on these examples, it is reasonable to expect In and Ir to order in a perovskite structure; the fact that they do not suggests there is a unique characteristic about the In/Ir pair.
3.3 Electronic Properties

3.3.1 Transport Characterization

High-temperature electrical resistivity and Seebeck data are shown in Figure 3.9 for Ba$_{2-x}$La$_x$InIrO$_6$ ($x = 0–1$) and BaLaIn$_{1-y}$Ca$_y$IrO$_6$ ($y = 0–0.75$) and estimated band gaps are listed in Table 3.2. Semiconductor behavior is observed for all compositions of both systems based on the trends seen in the $\rho(T)$ data. For Ba$_{2-x}$La$_x$InIrO$_6$, there seems to be no apparent trend or large changes in the resistivity behavior as the La content is changed. Analysis of the band gaps shows a slight increase in the values from $x = 0$ to 0.2, followed by a sudden drop at $x = 0.5$ and a subsequent increase as La content is increased beyond 0.5. The increasing trends in the band gaps for $x = 0–0.2$ and $x = 0.5–1$ can be attributed to the increase in orbital overlap as the crystal structure contracts. The sudden drop is likely due to the structure transition from the 6H structure, where the Ir environment is more localized, to the disordered perovskite structure where there is increased long-range connectivity between IrO$_6$ octahedra.

The data for BaLaIn$_{1-y}$Ca$_y$IrO$_6$, display a much clearer trend where the resistivity and band gaps increase with increasing Ca content. This increase is unexpected considering the expansion of the unit cell and the associated decrease in metal-oxygen orbital overlap as Ca is substituted into the structure. Since the $B$-site ordering increases with increasing $y$, the trend is likely due to the loss of connectivity between the IrO$_6$ octahedra caused by their growing isolation from one another.
Figure 3.9. High temperature resistivity ($\rho$) and Seebeck coefficient plots for (a,b) Ba$_{2-x}$La$_x$InIrO$_6$ ($x = 0$–1.0) and (c,d) BaLaIn$_{1-y}$Ca$_y$IrO$_6$ ($y = 0$–0.75).

<p>| Table 3.2. Calculated band gaps for Ba$_{2-x}$La$_x$InIrO$<em>6$ and BaLaIn$</em>{1-y}$Ca$_y$IrO$<em>6$. |
|---------------------------------|---------------------------------|-----------------|-----------------|
| **Ba$</em>{2-x}$La$_x$InIrO$<em>6$** | $E_g$ (eV) | **BaLaIn$</em>{1-y}$Ca$_y$IrO$_6$** | $E_g$ (eV) |</p>
<table>
<thead>
<tr>
<th>$x$</th>
<th>$E_g$ (eV)</th>
<th>$y$</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.450(11)</td>
<td>0</td>
<td>0.356(3)</td>
</tr>
<tr>
<td>0.2</td>
<td>0.496(7)</td>
<td>0.25</td>
<td>0.456(4)</td>
</tr>
<tr>
<td>0.5</td>
<td>0.335(3)</td>
<td>0.5</td>
<td>0.516(5)</td>
</tr>
<tr>
<td>0.8</td>
<td>0.336(3)</td>
<td>0.75</td>
<td>0.563(6)</td>
</tr>
<tr>
<td>1.0</td>
<td>0.356(3)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The Seebeck behavior (Figure 3.9) for Ba$_{2.5}$La$_x$InIrO$_6$ is similar to that seen in the Ba$_{2.5}$Ir$_x$O$_{5+y}$, in which a negative to positive sign change occurs, suggesting that both hole and electron charge carriers are present and their relative dominance is temperature dependent. As the La content increases and the Ir is reduced from 5+ to 4+, this transition is suppressed and the system eventually becomes p-type throughout the temperature range at $x = 1$. Unlike the resistivity data, there is no dramatic change around $x = 0.5$, suggesting the crystal structure has limited influence on the behavior. The data for BaLaIn$_{1.5}$Ca$_y$IrO$_6$ shows p-type character initially, but transitions to n-type when $y > 0.25$, indicating that the electrons take over as the dominant charge carrier. Increasing the Ca content further caused the Seebeck behavior to grow more negative and increasingly temperature dependent.

### 3.3.2 Magnetism

The magnetization as a function of temperature, $M(T)$, was measured for all samples of both systems in a field, $H$, of 0.1 T. No non-linearity in $M(H)$ was observed, meaning the susceptibility, $\chi(T)$, can be expressed as $M/H$. After subtraction of the core diamagnetic component, a positive constant representing the Van Vleck susceptibility was subtracted from $\chi(T)$ to obtain a linear $1/\chi(T)$, from which an effective moment, $\mu_{\text{eff}}$, was obtained using a least-squares fit in the region 100–300 K. These data are plotted in Figure 3.10 as $\mu(T)_{\text{eff}} = \chi(T)T \cdot 3k_B/N_A\mu_B^2$, and the near constant values above 100 K demonstrate the validity of the effective moment approximation. The data below 60 K for $x = 0.8$ and 1.0 are consistent with the onset of ferromagnetic correlations, while below 20 K, antiferromagnetic correlations dominate.
Figure 3.10. $\mu(T)_{\text{eff}}$ plots for (a) $\text{Ba}_{2-x}\text{La}_x\text{InIrO}_6$ and (b) $\text{BaLa}_{1-y}\text{Ca}_y\text{IrO}_6$. The temperature independence of the data above 100 K suggests Curie-Weiss behavior.
The ferromagnetic correlations in both systems are suppressed as Ir(IV) is oxidized to Ir(V) while the antiferromagnetic correlations in Ba$_{2-x}$La$_x$InIrO$_6$ are persistent even at the lowest La concentrations. Thus, the low temperature behavior is suggestive of antiferromagnetic nearest-neighbor interactions, and ferromagnetic next nearest-neighbor interactions, the latter of which only appear with high concentrations of Ir(IV). In BaLaIn$_{1-y}$Ca$_y$IrO$_6$, these cooperative correlations are suppressed much faster with Ir oxidation than in Ba$_{2-x}$La$_x$InIrO$_6$. This can be attributed to the increasing isolation of the IrO$_6$ octahedra leading to fewer Ir-O-Ir superexchanges. In Figure 3.10a are shown $\mu(T)_{\text{eff}}$ data for Ba$_{2-x}$La$_x$InIrO$_6$, with $0 \leq x \leq 1.0$ and we see that $\mu_{\text{eff}}$ ranges from 0.38 $\mu_B$ for $x = 0$ (nominal Ir(V) ox. state) to 0.81 $\mu_B$ for $x = 1.0$ (nominal Ir(IV) ox. state). In Figure 3.10b are shown $\mu(T)_{\text{eff}}$ data for BaLaIn$_{1-y}$Ca$_y$IrO$_6$ for $0 \leq y \leq 1.0$ and we see similar values of $\mu(T)_{\text{eff}}$ for $T > 100$ K. In Figure 3.11 is shown the fit value of $\mu_{\text{eff}}$ vs. the nominal Ir oxidation state state for both compound series. We see that, even for nominal oxidation state near 4.0, both compound series exhibit $\mu_{\text{eff}}$ values significantly less than the value 1.73 $\mu_B$ expected for an $s = \frac{1}{2}$ free spin. With increasing oxidation state, the moment decreases even further.

As mentioned earlier, values of $\mu_{\text{eff}}$ much less than the nominal values are not uncommon in iridates and have been observed in SrIrO$_3$ (0.117 $\mu_B$) [49], 5M BaIrO$_3$ (0.215 $\mu_B$) [50], 6M BaIrO$_3$ (0.276 $\mu_B$) [27], 9M BaIrO$_3$ (0.13 $\mu_B$) [2], Sr$_2$IrO$_4$ (0.33–0.50 $\mu_B$) [25,51], Ba$_2$IrO$_4$ (0.18 $\mu_B$) [52], Ba$_3$ZnIr$_2$O$_9$ (0.26 $\mu_B$) [13], Ba$_3$TiIr$_2$O$_9$ (0.28 $\mu_B$) [13], Ba$_3$CeIr$_2$O$_9$ (0.31 $\mu_B$) [53], Y$_2$Ir$_2$O$_7$ (0.54 $\mu_B$) [54], Sr$_3$Ir$_2$O$_7$ (0.69 $\mu_B$) [26], and Sr$_2$TiIrO$_6$ (0.699 $\mu_B$) [23]. Among these compounds, resistivity has been measured for SrIrO$_3$, all above mentioned polymorphs of BaIrO$_3$, Sr$_2$IrO$_4$, Ba$_2$IrO$_4$, Y$_2$Ir$_2$O$_7$ and Sr$_3$Ir$_2$O$_7$ and each exhibits either metallic (SrIrO$_3$, 5M
and 6M BaIrO$_3$), small gap semiconducting (9M BaIrO$_3$, Sr$_2$IrO$_4$, Ba$_2$IrO$_4$) or variable range hopping behavior (Y$_2$Ir$_2$O$_7$). Indeed, for the systems studied here, we observe small gap semiconducting behavior for temperatures above 300K, where the moments are well-developed. It is also worth noting that the Seebeck effect data in the same temperature region, do not resemble that expected for medium-size bandgap semiconductor (0.5–1.0 eV). These results indicate that in the present systems, like several of the small-$\mu_{\text{eff}}$ compounds listed above, the delocalization of Ir valence electrons is responsible for moment reduction.

![Graph](image)

**Figure 3.11.** A plot of $\mu_{\text{eff}}$ as a function of Ir oxidation state for Ba$_{2-x}$La$_x$InIrO$_6$ (triangles) and BaLaIn$_{1-y}$Ca$_y$IrO$_6$ (squares). The dashed line is the trend the expected $\mu_{\text{eff}}$ values should follow when considering spin-orbit coupling effects.

It should be noted that sizeable effective moments of 0.38 and 0.59 $\mu_B$ are observed for BaInIrO$_6$ and BaLaCaIrO$_6$, respectively, both of which should have a formal oxidation state
corresponding to Ir(V) which should be non-magnetic. Other examples of non-zero $\mu_{\text{eff}}$ values for Ir(V) have been reported in literature [1,23,55–57]. These were attributed to either the weakening of SOC interactions through structural distortion or the presence of a small amount of Ir(IV) due to oxygen vacancies, which are common in perovskites. It is also a possibility that BaInIrO$_6$ and BaLaCaIrO$_6$ possess a small amount of Ir(VI) due to the presence of electropositive ions (i.e. Ba$^{2+}$ and Ca$^{2+}$) which are known to stabilize higher Ir oxidation states [23,29,58].

3.4 Conclusions

The Ba$_{2-x}$La$_x$InIrO$_6$ ($x = 0–1$) solid solution was found to transition from the 6M polytype structure to a disordered distorted perovskite structure with the $Pbnm$ space group. Based on our neutron diffraction refinements, BaLaInIrO$_6$ showed little tendency toward $B$-site ordering and the octahedra tilted along all three axes with the Glazer tilt scheme $a^*a^*c^*$. The BaLaIn$_{1-y}$Ca$_y$IrO$_6$ ($y = 0–1$) system retained a perovskite structure throughout the entire series, transitioning gradually from a disordered and orthorhombically-distorted form to an ordered cubic form. Both systems were found to be semiconducting with transitions in the dominant charge carrier. The resistivity of the Ba$_{2-x}$La$_x$InIrO$_6$ series was observed to increase with increasing La content and was largely affected by the structure transition, characterized by a large drop in the band gap at $x = 0.5$. There was not an abrupt change observed in the Seebeck behavior. The gradual n-type to p-type transition with temperature was suppressed with increased Ir(IV) concentration. For the BaLaIn$_{1-y}$Ca$_y$IrO$_6$ series, increasing the Ir(V) concentration via Ca substitution was found to both increase the resistivity as well as cause the
electrons to become the dominant charge carriers. The increasing resistivity is likely caused by the greater separation of the Ir ions due to ordering on the B-site. Curie-Weiss behavior was observed above 100 K in magnetic susceptibility data for both Ba$_{2-x}$La$_x$InIrO$_6$ and BaLaIn$_{1-y}$Ca$_y$IrO$_6$. For both systems, the trends in the $\mu_{\text{eff}}$ values going from Ir(IV) to Ir(V) did not correlate well with the predicted nominal values. In both series, the $\mu_{\text{eff}}$ values for compounds with Ir oxidation state closer to 4 tended to be too low, whereas those with oxidation state close to 5 tended to be too high. Other iridates similar to this work’s compounds, where Ir(IV) is the only magnetic ion and $\mu_{\text{eff}}$ is much lower than predicted, were also found to be quite conductive suggesting the lower values are caused by electron delocalization.

3.5 Methods and Materials

Black polycrystalline samples were prepared by mixing and grinding stoichiometric amounts of BaCO$_3$ (Cerac, 99.9%), La$_2$O$_3$ (Stanford Materials, 99.999%), IrO$_2$, CaCO$_3$ (Mallinckrodt, 99.8%) and In$_2$O$_3$ (Stanford Materials, 99.99%) using an agate mortar and pestle. The carbonates and La$_2$O$_3$ were dried overnight at 120 °C and 850 °C, respectively. IrO$_2$ was obtained by decomposing IrCl$_3$ (Alfa Aesar, 99.9%) at 750 °C under air flow for 12 h. The samples were then pelletized and sintered at 1200 °C for 36 h with intermittent grinding.

Initial XRD characterization of the samples was performed using a Rigaku Miniflex II diffractometer with Cu Kα radiation and a graphite monochromator. Single-crystal Si sample holders were used to maximize peak intensity and aid detection of minor impurities in the XRD patterns. A fixed-time scan was employed with collection parameters of a 2θ range of 10-70° with a step size of 0.02° and a dwell time of 2.0 s. Lattice parameters for all samples were
extracted using the Le Bail method [59] on the GSAS software with EXPGUI user interface [60,61]. Room-temperature (298 K) time-of-flight neutron diffraction data for BaLaInIrO$_6$ were collected at Oak Ridge National Laboratory on the POWGEN (BL-11A) beam line using center wavelength of 1.33 Å. Approximately 1 g of the sample was loaded into a 6 mm vanadium sample can and data was collected over about 3 h. Structure refinement was performed using the Rietveld method [62] on the GSAS software with EXPGUI user interface [60,61]. Crystal structures were generated using the VESTA software [63]. Seebeck and resistivity measurements were performed at high temperatures (300–800 K) on an ULVAC-RIKO ZEM 3 under a static helium atmosphere. Low-temperature (5–300 K) magnetization measurements were obtained using a Quantum Design MPMS.

3.6 References


[48] W.T. Fu, D.J.W. Ijdo, Re-examination of the structure of Ba$_2$MIrO$_6$ (M=La, Y): space
101


[58] D.-Y. Jung, G. Demazeau, J. Etourneau, M.A. Subramanian, Preparation and characterization of new perovskites containing Ir(VI) and Ir(V) [BaM$_{0.50}$Ir$_{0.50}$O$_{2.75}$ and BaM$_{0.25}$Ir$_{0.75}$O$_3$ (M = Li or Na)], Mater. Res. Bull. 30 (1995) 113–123. doi:10.1016/0025-5408(94)00115-4.


Chapter 4: Structure Determination and Magnetic Characterization of $A_{1+x}Rh_{2-x}O_4$ ($A^{2+} = \text{Co, Ni, Cu}$) Spinels

Abstract

Three members of the spinel family $A_{1+x}Rh_{2-x}O_4$ ($A^{2+} = \text{Co, Ni, Cu}$) were prepared and their structures characterized using X-ray and neutron diffraction and CoRh$_2$O$_4$ and CuRh$_2$O$_4$ was successfully prepared stoichiometrically while attempts to prepare NiRh$_2$O$_4$ resulted in a spinel phase with a large unreacted Rh$_2$O$_3$ impurity. Instead, a pure spinel phase was obtained by substituting a small amount of Ni for Rh resulting in the novel composition Ni$_{1.25}$Rh$_{1.75}$O$_4$. CoRh$_2$O$_4$ was found to have a normal cubic spinel structure ($Fd\bar{3}m$) whereas CuRh$_2$O$_4$ and Ni$_{1.25}$Rh$_{1.75}$O$_4$ crystallized in tetragonally distorted spinel structures ($I\bar{4}_1/amd$) due to Jahn-Teller effects. The magnetic behavior of each spinel was also characterized using magnetic susceptibility measurements. Antiferromagnetic behavior was observed in $\chi(T)$ data for CoRh$_2$O$_4$ ($T_N = 24.9(1) \, \text{K}$, $\mu_{\text{eff}} = 4.42(1) \, \mu_B$) and CuRh$_2$O$_4$ ($T_N = 24(1) \, \text{K}$, $\mu_{\text{eff}} = 1.97(1) \, \mu_B$). Their magnetic structures were determined, for the first time, to be an antiferromagnetic $A$-type and an $ab$-plane helical structure, respectively. A divergence in ZFC and FC $\chi(T)$ data was observed for Ni$_{1.25}$Rh$_{1.75}$O$_4$ as well as a lack of long-range ordering in low temperature neutron data both of which suggest spin-glasslike behavior.
Publications based on this chapter:

[1] L. Ge, J. Flynn, J.A.M. Paddison, M.B. Stone, S. Cadler, A.P. Ramirez, M.A. Subramanian, M. Mourigal, Spin order and dynamics in the perfect and distorted diamond-lattice Heisenberg antiferromagnets CoRh$_2$O$_4$ and CuRh$_2$O$_4$. (In preparation)

4.1 Motivation for Study

The spinel family \((AB_2X_4)\) is known for having many different properties and has been widely used as a host for interesting or unusual magnetic behavior. Due to the spatial arrangement of the \(A\)- and \(B\)-sites, spinels often display frustrated magnetic properties such as spin glasses or unusual magnetic structures [1–3]. For instance, \(\text{CuIr}_2\text{S}_4\) has been reported to have spin glass magnetism [4] and behavior of \(\text{FeSc}_2\text{S}_4\) has been described as somewhere between a spin-orbital liquid and an antiferromagnet [5–7]. The spinel structure is typically very rigid and is not as susceptible to distortion away from cubic symmetry or site vacancies compared to the perovskite structure. Nevertheless, there are a few reported examples of spinels that are tetragonally distorted due to Jahn-Teller effects such as \(\text{MnCr}_2\text{Mn}_2\text{O}_4\) [8] and a couple \(AB_2\text{O}_4\) families \((A^{2+} = \text{Ni, Cu}; B^{3+} = \text{Cr, Rh})\) [9–11]. Since \(\text{Rh}^{3+}\) is diamagnetic, the \(\text{ARh}_2\text{O}_4\) spinel family are candidates for interesting magnetism as spinels with only \(A-A\) magnetic interactions are not very common.

This work aims to characterize and compare members \(\text{ARh}_2\text{O}_4\) that have both Jahn-Teller active \((\text{Ni}^{2+}, \text{Cu}^{2+})\) and inactive \((\text{Co}^{2+})\) ions in the \(A\) site. Although all three of these compounds are known, little has been reported beyond basic structural and magnetic information. For instance, each member is reported to show antiferromagnetic character [11] but as \(\text{NiRh}_2\text{O}_4\) and \(\text{CuRh}_2\text{O}_4\) are tetragonally distorted, it is unknown what effect this distortion may have on the \(A-A\) interactions.
4.2 Structural Characterization

Rietveld refinements were performed for CoRh$_2$O$_4$, CuRh$_2$O$_4$, and Ni$_{1.25}$Rh$_{1.75}$O$_4$ using TOF neutron diffraction data. The refinement for CoRh$_2$O$_4$ (Figure 4.1) was done using the cubic spinel structure with space group $Fd\bar{3}m$ and structural parameters are summarized in Table 4.1. Asymmetric broadening on right side of every peak was observed likely caused by unrelieved thermal stress within the structure. This broadening was modeled by including a “strain phase” with the same symmetry as the main phase but with slightly smaller lattice parameters.

![Figure 4.1](image)

**Figure 4.1.** Time-of-flight neutron diffraction pattern for Co(Rh$_{1.90(1)}$Co$_{0.10(1)}$)O$_4$ with calculated intensities (red) and difference (blue) and background (green) curves. The magenta tick marks indicate the allowed reflections for $Fd\bar{3}m$ and the teal tick marks indicate the “strain phase” use to model the asymmetric broadening.
The results of this work’s CoRh$_2$O$_4$ refinement are consistent with previous reports [12,13] with two notable differences. First, the RhO$_6$ octahedral are less distorted in this work’s structure compared to previous reports. This results in shortened Co–O bonds which leads to better bond-valence sums (BVS) [14] of 1.79 for Co and 3.05 for Rh than previously reported. Second, the refinement resulted in a small degree of site mixing with 5.0(6)% of Co on the B-site and formally, a refined chemical formula of Co(Rh$_{1.90(1)}$Co$_{0.10(1)}$)O$_4$.

Table 4.1. Summarized crystallographic information CoRh$_{1.90(1)}$Co$_{0.10(1)}$O$_4$.

<table>
<thead>
<tr>
<th></th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occ.</th>
<th>$U_{iso}$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>8a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.0</td>
<td>0.0021(2)</td>
</tr>
<tr>
<td>Rh/Co</td>
<td>16d</td>
<td>5/8</td>
<td>5/8</td>
<td>5/8</td>
<td>0.95(1)/0.05(1)</td>
<td>0.0002(1)</td>
</tr>
<tr>
<td>O</td>
<td>32e</td>
<td>0.2601(1)</td>
<td>0.2601(1)</td>
<td>0.2601(1)</td>
<td>1.0</td>
<td>0.0023(1)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond Distances (Å)</th>
<th>Bond Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co–O</td>
<td>4×1.989(1)</td>
</tr>
<tr>
<td>Rh–O</td>
<td>6×2.044(1)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The Rh deficiency originates from the presence of a small Rh$_2$O$_3$ impurity phase. To maintain overall charge imbalance, either octahedral Co ions are 3+, i.e. Rh(III)$_{1.9}$Co(III)$_{0.1}$, or 5% of the Rh ions are 4+, i.e. Rh(III)$_{1.8}$Rh(IV)$_{0.1}$Co(II)$_{0.1}$. One way to determine the oxidation states would be to compare the theoretical bond distances for each case to the values determined from the refinement; however, the average ionic radii on the B-site for the two extreme cases mentioned above are too similar (0.662 vs. 0.666 Å) to favor one case over the other.

Although NiRh$_2$O$_4$ has been previously reported and characterized by XRD [15], our attempts to prepare it were unsuccessful as a significant amount of Rh$_2$O$_3$ remained unreacted.
Pure samples were obtained by instead substituting about 12.5% of the Rh for Ni resulting in a nominal formula of NiRh$_{1.75}$Ni$_{0.25}$O$_4$. The reason why preparing pure NiRh$_2$O$_4$ was so difficult is not immediately clear. The only other reported preparations of NiRh$_2$O$_4$ mention the use of carbonates in the solid state reactions [11,16]. Since carbonates tend to be more reactive than their counterparts, it’s possible that the combination of NiO and Rh$_2$O$_3$ is not reactive enough to complete the reaction.

![Figure 4.2](image-url)

**Figure 4.2.** Time-of-flight neutron diffraction pattern for NiRh$_{1.86(1)}$Ni$_{0.14(1)}$O$_4$ with calculated intensities (red) and difference (blue) and background (green) curves. The magenta tick marks indicate the allowed reflections for $I\bar{4}/amd$ and the teal tick marks indicate the “strain phase” used to model the asymmetric broadening.

NiRh$_2$O$_4$ crystalizes in a lower-symmetry structure compared to CoRh$_2$O$_4$ due to a Jahn-Teller distortion caused by the lifting of degeneracy in the Ni$^{2+}$ $t_2$ orbitals [11,15,16]. Rietveld refinement of the diffraction data (Figure 4.2) gave refined formula of NiRh$_{1.86(1)}$Ni$_{0.14(1)}$O$_4$ and
a structure model comparable to NiRh$_2$O$_4$ [15] with $I\bar{4}_{1}$/amd symmetry but slightly smaller lattice parameters. Other crystallographic data is summarized in Table 4.2. Asymmetric broadening was also observed in the neutron data but unlike CoRh$_2$O$_4$, the broadening appears sporadic, occurring on different sides of different peaks or, occasionally, not at all. Taking an approach similar to that used for CoRh$_2$O$_4$, this unusual broadening could be modeled using a less tetragonally distorted “strain phase”.

| Table 4.2. Summarized crystallographic information for NiRh$_{1.86(1)}$Ni$_{0.14(1)}$O$_4$. |
|---------------------------------|--------|--------|--------|--------|--------|
| Site   | x     | y      | z      | Occupancy |
| Ni     | 4a    | 0      | 3/4    | 1/8     | 1.0    |
| Rh/Ni  | 8d    | 0      | 0      | 1/2     | 0.93(1)/0.07(1) |
| O      | 16h   | 0      | 0.0133(1) | 0.2655(1) | 1.0    |

| Anisotropic atomic displacement parameters (Å$^2$) |
|---------------------------------|--------|--------|--------|--------|--------|--------|
| U$_{11}$ | U$_{22}$ | U$_{33}$ | U$_{12}$ | U$_{13}$ | U$_{23}$ |
| Ni     | 0.0061(2) | 0.0061(2) | 0.0041(3) | 0.0     | 0.0     | 0.0     |
| Rh/Ni  | 0.0027(4) | 0.0016(4) | 0.0011(3) | 0.0     | 0.0     | 0.0008(2) |
| O      | 0.0054(3) | 0.0041(3) | 0.0042(3) | 0.0     | 0.0     | -0.0005(2) |

<table>
<thead>
<tr>
<th>Bond Distances (Å)</th>
<th>Bond Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni–O</td>
<td>4×1.975(1)</td>
</tr>
<tr>
<td>Equatorial B–O</td>
<td>4×2.039(1)</td>
</tr>
<tr>
<td>Axial B–O</td>
<td>2×2.033(1)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Similar to CoRh$_{1.90}$Co$_{0.10}$O$_4$, the Ni substitution into the B-site causes a charge imbalance that must be compensated. Since there two oxidation states for Ni (2+/3+) and Rh (3+/4+) that are typically observed in oxides, this can be done in a few ways assuming only
Ni(II) is found in the tetrahedral sites. The Ni oxidation state can be all 2+, Ni(Ni(II)$_{0.07}$Rh(IV)$_{0.07}$Rh(III)$_{0.84}$)$_2$O$_4$, or all 3+, Ni(Ni(III)$_{0.07}$Rh(III)$_{0.93}$)$_2$O$_4$. The average ionic radii on the $B$-site for the extreme cases are 0.664 Å and 0.662 Å, respectively. Since these values are smaller than the Rh$^{3+}$ radius (0.665 Å), it is not possible to reliably establish which oxidation states are present using lattice parameters or bond distances.

The tetrahedral sites are elongated along the $c$ axis with O-Ni-O bond angles of 104.0(1)$^\circ$ and 112.3(1)$^\circ$ due to Jahn-Teller distortion produced by the degeneracy in the Ni $t_2$ orbitals. The tetrahedral distortion displaces the oxygens that, in turn, leads to distortion of the octahedral sites. The BVS values for Ni, Rh, and O sites were calculated to be 1.68, 3.10, and 1.96, respectively. The composition was refined to be NiRh$_{1.86(1)}$Ni$_{0.14(1)}$O$_4$ which indicates that not all of the nominal Ni content was successfully substituted into the octahedral sites. Variable temperature neutron diffraction data for Ni$_{1.25}$Rh$_{1.75}$O$_4$ show that the tetragonally distorted spinel structure is present down to 4 K. Refinements of the lattice parameters shows the distortion increases as temperature decreases and the structure contracts, indicated by the increased separation of $a$ and $c$ (Figure 4.3).
The structure of CuRh$_2$O$_4$ is similar to NiRh$_2$O$_4$ in that it is distorted by a Jahn-Teller effect but in the opposite direction. The Jahn-Teller effects in NiRh$_2$O$_4$ result in cooperative elongation of the unit cell along the $c$ axis with respect to the cubic spinel unit cell whereas the
distortion seen in CuRh$_2$O$_4$ is compression. The CuRh$_2$O$_4$ structure has been described by both x-ray [12,17] and neutron diffraction [18] as a tetragonally distorted spinel at room temperature but transitions to the cubic form at 600 °C [18]. There has been some debate over whether the correct room temperature space group is $I4_1/amd$ or $I4_2d$. The room temperature neutron diffraction pattern for our sample of CuRh$_2$O$_4$ is shown in Figure 4.4.

![CuRh$_2$O$_4$ Neutron Diffraction Pattern](image)

Figure 4.4. Time-of-flight neutron diffraction pattern for CuRh$_2$O$_4$ with calculated intensities (red) and difference (blue) and background (green) curves. The magenta tick marks indicate the allowed reflections for $I4_1/amd$ and the teal tick marks indicate the “strain phase” used to model the asymmetric broadening.

Based on the Rietveld refinement, it was concluded that the appropriate room-temperature space group is $I4_1/amd$, consistent with the most recent studies [10,18]. The refined atomic parameters are summarized in Table 4.3. Similar to CoRh$_2$O$_4$ and Ni$_{1.25}$Rh$_{1.75}$O$_4$, 
asymmetric broadening was also observed in the neutron data for CuRh$_2$O$_4$. The broadening was irregular similar to Ni$_{1.25}$Rh$_{1.75}$O$_4$ and could be modeled using a more tetragonally distorted “strain phase”.

Table 4.3. Summarized crystallographic information for CuRh$_2$O$_4$.

<table>
<thead>
<tr>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
<th>$U_{\text{iso}}$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>8e</td>
<td>0</td>
<td>3/4</td>
<td>1.0</td>
<td>0.0017(2)</td>
</tr>
<tr>
<td>Rh</td>
<td>8d</td>
<td>0</td>
<td>0</td>
<td>1/2</td>
<td>0.0005(1)</td>
</tr>
<tr>
<td>O</td>
<td>16h</td>
<td>0</td>
<td>0.0334(1)</td>
<td>0.2430(1)</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Anisotropic atomic displacement parameters (Å$^2$)

<table>
<thead>
<tr>
<th></th>
<th>$U_{11}$</th>
<th>$U_{22}$</th>
<th>$U_{33}$</th>
<th>$U_{12}$</th>
<th>$U_{13}$</th>
<th>$U_{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>0.0021(2)</td>
<td>0.0010(2)</td>
<td>0.0022(2)</td>
<td>0.0</td>
<td>0.0</td>
<td>-0.0002(1)</td>
</tr>
</tbody>
</table>

Bond Distances (Å) | Bond Angles (°)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance</th>
<th>Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu–O</td>
<td>2×1.942(1)</td>
<td>O–Cu–O 2×128.8(2)</td>
</tr>
<tr>
<td>“</td>
<td>2×2.029(1)</td>
<td>“        2×102.6(1)</td>
</tr>
<tr>
<td>Equatorial Rh–O</td>
<td>4×2.044(1)</td>
<td>O–Rh–O 3×84.62(5)</td>
</tr>
<tr>
<td>Axial Rh–O</td>
<td>2×2.042(1)</td>
<td>“        3×95.38(5)</td>
</tr>
</tbody>
</table>

Unlike CoRh$_2$O$_4$ and Ni$_{1.25}$Rh$_{1.75}$O$_4$, no evidence for site mixing was observed indicating a stoichiometric formula. Bond valence sums of 3.05 for Rh, 1.97 for O and 1.79 for Cu, were found to be consistent with literature values [18]. The Rh octahedral are distorted with O-Rh-O bond angles of 95.38(4)° and 84.62(5)°. In turn, the Cu tetrahedral are flattened with two distinct O-Cu-O bond angles of 128.8(2)° and 102.6(1)°. The refined crystal structure also indicates Cu is displaced off of the ideal 4$a$ site and instead randomly sits on the 8$e$ site which is split along the c axis. This displacement is not observed in any reported structure for CuRh$_2$O$_4$, however, fitting the above data with Cu on the ideal 4$a$ site resulted in a largely
anisotropic thermal ellipsoid with a very high $U_{33}$ value suggesting the Cu was not present on that site. Displacing the Cu to the $8e$ site, which is split along the $c$ axis, resulted in a more spherical ellipsoid. The typical explanation for an ion to displace from the ideal site to compensate for being underbonded [19]. In this case, the displacement only improved the Cu BVS by 0.004 which is essentially negligible and makes the reason for the displacement unclear.

It is interesting to compare the three structures since CoRh$_2$O$_4$ is a cubic spinel while the other two are both tetragonally distorted but in opposite directions. Figure 4.5 illustrates the splitting caused on the $t_2$ and $e$ orbitals by Jahn-Teller elongation and compression.

---

**Figure 4.5.** Orbital diagrams illustrating of the splitting of the $t_2$ and $e$ orbitals (center) caused by Jahn-Teller elongation (left) and compression (right).
The compression brings the O ions closer to the $xy$ plane causing the $d_{x^2-y^2}$ and $d_{xy}$ orbitals to increase in energy while the rest of the orbitals decrease to compensate. Conversely, elongation moves the anions closer to the $z$ axis which increases the energy of the $d_{z^2}$, $d_{xz}$ and $d_{yz}$ orbitals. The specific distortions in the Ni and Cu tetrahedra can be rationalized by examining the stabilization energy (SE) caused of the two distortions (shown in Figure 4.6). For Ni$^{2+}$, the elongation gives the best SE value of $-0.67\Delta_{JT}$, where $\Delta_{JT}$ is the Jahn-Teller splitting energy. Cu$^{2+}$, on the other hand, is best stabilized by compression which gives an SE value of $-0.67\Delta_{JT}$ as well.

**Figure 4.6.** Schematic showing the different stabilization energies (SE) for Ni$^{2+}$ and Cu$^{2+}$ produced by Jahn-Teller compression and elongation. The values $m$ and $n$ are the number of electrons in the lower and upper orbitals, respectively. The grey dotted line represents the relative position of the unsplit $t_2$ orbitals.
4.3 Magnetic Characterization

4.3.1 CoRh$_2$O$_4$

The $1/\chi(T)$ data for CoRh$_2$O$_4$ (Figure 4.7) shows antiferromagnetic (AFM) behavior with a $T_N$ of 25 K. Above 50 K, $1/\chi(T)$ is linear indicating Curie-Weiss behavior and fitting yields values of 4.43(1) $\mu_B$ and $-34.4(1)$ K for the magnetic moment ($\mu_{\text{eff}}$) and Weiss constant ($\theta$), respectively. These results are consistent with previous studies on CoRh$_2$O$_4$ [11,20]. The magnetic moment is quite large compared to the theoretical spin-only value of 3.87 $\mu_B$ for a tetrahedrally coordinated $d^7$ ion. This discrepancy is common in Co-containing oxides and is likely caused by an unquenched orbital contribution to the moment. The ratio $f = |\theta|/T_N$ can give an indication of how frustrated a magnetic system is. The further this ratio is from 1, the stronger the frustration is with $f > 10$ indicating a strongly frustrated system [21]. The $f$ value calculated for CoRh$_2$O$_4$ is 1.4 suggesting a very low degree of frustration. Large peak intensity changes were observed in the neutron diffraction pattern for CoRh$_2$O$_4$ upon cooling from 40 K to 4 K and the development of new reflections forbidden by the nuclear space group symmetry (Figure 4.8). As indicated by the temperature-dependence of the integrated Bragg intensity (Figure 4.8 inset), these peaks were associated with the development of long-range magnetic order beginning at $T_N = 24.88(9)$ K, which correlates well with the behavior and value seen in the susceptibility data. The magnetic Bragg peaks were indexed to the magnetic space group $I4_1'/a'm'd$ which has a magnetic propagation vector $\mathbf{k} = (0, 0, 0)$ with respect to the conventional unit cell. Refinement of the diffraction data ($R_{wp} = 8.11\%$; $R_{mag} = 7.62\%$) yields an ordered magnetic moment of 3.11(5) $\mu_B$, which is close to the expected value of 3.0 $\mu_B$ for a spin-3/2 ion.
Figure 4.7. $1/\chi(T)$ plot for CoRh$_2$O$_4$ shows antiferromagnetic (AFM) behavior ($T_N = 25$ K) with the red line showing the fit to the Curie-Weiss Law. Inset shows close-up view of the AFM transition.

Figure 4.8. Rietveld refinement on CoRh$_2$O$_4$ powder neutron diffraction data collected at $T = 4$ K. Contribution from nuclear peaks (blue ticks), magnetic peaks (red ticks) and Al can (gray ticks) are considered. The inset shows the temperature dependence of the second magnetic peak intensity (highlighted with asterisk).
Figure 4.9. Unit cells displaying (a) the nearest neighbor interactions ($J$) and (b) the $A$-type antiferromagnetic magnetic structure (red and yellow arrows) of CoRh$_2$O$_4$.

The magnetic structure (Figure 4.9b) is an $A$-type AFM structure where there are ferromagnetic intraplanar ordering with antiferromagnetic interplanar ordering. Other examples of oxides with this magnetic structure include many manganate perovskites [22–24] and Na$_x$CoO$_2$ layered structures [25,26]. The $A$-site exchange mechanism for a spinel was first introduced by Blasse [11] who proposed a $A$-$O$-$B$-$O$-$A$ exchange interaction (Figure 4.10). He proposed that a direct $A$-$A$ exchange or a traditional $A$-$O$-$A$ superexchange were unlikely as the exchange distances required for those interactions in the spinel are too long. Blasse demonstrated that substituting Al for Rh in CoRh$_2$O$_4$ and decreasing the orbital overlap in the O-$B$-$O$ interaction caused $T_N$ to decrease indicating a weakening of the AFM interactions. This superexchange can explain the CoRh$_2$O$_4$ magnetic structure as shown in Figure 4.10. The empty Rh$^{3+}$ $e_g$ orbitals allows for direct interaction between the O electrons which results in ant-aligned electron spins in Co.
Figure 4.10. Schematics showing (top) the relative position of one Co-O-Rh-O-Co superexchange pathways (green lines) within CoRh$_2$O$_4$ and (bottom) illustrating how the superexchange results in AFM ordering.

4.3.2 \textit{Ni$_{1.25}$Rh$_{1.75}$O$_4$}

The high temperature region of $1/\chi(T)$ for Ni$_{1.25}$Rh$_{1.75}$O$_4$ was slightly non-linear and was corrected for by subtracting a temperature-independent paramagnetism term ($\chi_0$) from the
susceptibility. This method is common when dealing with magnetism for 4\textit{d} and 5\textit{d} transition metals (TMs) [27–32]. The $\chi_0$ value used for Ni$_{1.25}$Rh$_{1.75}$O$_4$ was $1.5 \times 10^{-3}$ emu/mol which is comparable to values reported for other rhodate compounds in literature. The $1/(\chi(T) - \chi_0)$ data (Figure 4.11) shows show paramagnetic behavior above 90 K and fitting gives $\mu_{\text{eff}}$ and $\theta$ values of 2.77(1) $\mu_B$/f.u. and 34.5(1) K, respectively.

![Figure 4.11](image)

**Figure 4.11.** $1/(\chi(T) - \chi_0)$ plot for Ni$_{1.25}$Rh$_{1.75}$O$_4$ with the fit to Curie-Weiss behavior (red line) above 90 K. Upward deviation from CW below suggests AFM correlations. Inset shows close-up view reveals of large divergence between field-cooled (FC) and zero field-cooled (ZFC) data typical of spin-glass behavior. $T_g$ is the spin-glass transition temperature.

As discussed above, the Ni substitution on $B$-site creates a charge imbalance that can be compensated via two possible mixtures of valence states: Ni(II)[Ni(III)$_{0.07}$Rh(III)$_{0.93}$]$_2$O$_4$ or Ni(II)[Ni(II)$_{0.07}$Rh(IV)$_{0.07}$Rh(III)$_{0.86}$]$_2$O$_4$. These creates a range of 2.97–3.19 $\mu_B$/f.u. for a
predicted theoretical spin-only moment which is slightly above the experimental $\mu_{\text{eff}}$ value of 2.77(1) $\mu_B$. Below 90 K, $1/(\chi(T) - \chi_0)$ begins to deviate upward indicating the presence of AFM correlations which conflicts with the positive $\theta$ value that suggests ferromagnetic (FM) correlations. A possible explanation for the discrepancy is that the introduction of magnetic Ni ions on to $B$-site interrupts the Ni-O-Rh-O-Ni superexchange and creates a competition between AFM and FM interactions. Both Ni$^{2+}$ and Ni$^{3+}$ have occupied $e_g$ orbitals. This adds an additional electron to the superexchange at the $B$-site and results in ferromagnetically aligned Ni ions on the $A$-site (Figure 4.12).

Figure 4.12. Superexchange mechanisms in Ni$_{1.25}$Rh$_{1.75}$O$_4$. Rh on the $B$-site allows for an antiferromagnetic $A$-$A$ interaction between the Ni ions. Substituting Ni for Rh interrupts the exchange and results in ferromagnetic $A$-$A$ and antiferromagnetic $A$-$B$ interactions.
Examination of the region below 10 K shows what seems to be an AFM-like transition at ~7.5 K. Comparing the field-cooled (FC) and zero field-cooled (ZFC) data (Figure 4.11 inset) reveals a large divergence in $\chi(T)$ beginning at ~8.2 K. This feature is typically an indication of spin-glass behavior. Analysis of the low temperature neutron diffraction data (4–200 K) shows no observable changes in any of the peak intensities (Figure 4.13) signifying a lack of long-range magnetic ordering present down to 4 K. This observation, in conjunction with the divergence of the ZFC and FC $\chi(T)$ data, is strong evidence that $\text{Ni}_{1.25}\text{Rh}_{1.75}\text{O}_4$ is a spin-glass material. This behavior is likely caused by a combination of the Jahn-Teller distortion and the disruption of the superexchange by the presence of the magnetic Ni ions in the $B$ site.

Figure 4.13. Variable temperature neutron diffraction data (4–200 K) for $\text{Ni}_{1.25}\text{Rh}_{1.75}\text{O}_4$. The lack of new peaks or intensity changes indicates there is no long-range magnetic ordering.
4.3.3 CuRh$_2$O$_4$

The examination of the $1/\chi(T)$ data for CuRh$_2$O$_4$ reveals AFM transition was observed at $T_N = 24.5$ K (Figure 4.14). Similar to Ni$_{1.25}$Rh$_{1.75}$O$_4$, a non-linear trend in the high temperature data was observed and corrected for using a $\chi_0$ term of $3 \times 10^{-4}$ emu/mol that is comparable to values reports in literature [32,33]. The CW modeling above $\sim$140 K gave values of $1.94(1) \mu_B$ and $-108(1)$ K for $\mu_{\text{eff}}$ and $\theta$, respectively. The $\mu_{\text{eff}}$ value is slightly above the theoretical spin-only moment of 1.73 $\mu_B$ for $S = 1/2$ but compares well experimental values reported for CuRh$_2$O$_4$ in literature [11,32]. The moment is likely greater due to incompletely quenched orbital contribution similar to CoRh$_2$O$_4$.

![Figure 4.14](image.png)

Figure 4.14. $1/(\chi(T) - \chi_0)$ plot for CuRh$_2$O$_4$ shows AFM behavior ($T_N = 24.5$ K) with the red line showing the fit to the Curie-Weiss Law. Inset shows close-up view of the AFM transition with an upward trend beginning at $\sim$11 K.
The value obtained for $\theta$ is negative and correlates well with the observed AFM behavior; however, it is rather large compared to the value for $T_N$. Calculating $f$ gives a value of 4.5 suggesting a moderate degree of frustration. Below 140 K, there is an upward deviation from the CW behavior similar to Ni$_{1.25}$Rh$_{1.75}$O$_4$ suggesting the beginning of AFM correlations. An upturn in the $\chi(T)$ data was observed below $T_N$ beginning at $\sim$12 K. Similar behavior is reported in literature but the cause is unclear. A possible explanation is the presence of impurity spins either within CuRh$_2$O$_4$ or as an impurity that was too dilute to be detected by X-ray or neutron diffraction.

![Figure 4.15. Rietveld refinement on CuRh$_2$O$_4$ powder neutron diffraction data at $T = 4$ K. Contribution from nuclear peaks (blue ticks) and magnetic peaks (red ticks) are considered. The inset shows the temperature dependence of the second magnetic peak intensity (highlighted with asterisk).](image-url)
Low temperature neutron diffraction data reveal the emergence of new diffraction peaks upon cooling from 40 K to 4 K (Figure 4.15) that, like CoRh$_2$O$_4$, are not allowed by the nuclear structure. The temperature dependence of the peak intensity (Figure 4.15 inset) suggests that these new peaks are associated with long-range AFM ordering with $T_N = 24(1)$ K which correlates well with the value seen in the $\chi(T)$ data. The magnetic peaks were indexed to the magnetic space group $I\bar{4}1221'$ and Rietveld refinements ($R_{wp} = 6.53\%$; $R_{mag} = 18.8\%$) revealed the magnetic structure to be an $ab$-helix type structure with $\mu_{ord} = 0.56(6) \mu_B$ (Figure 4.16b). The propagation vector was found to be $k = (0, 0, 0.790(4))$ which signifies a 108° rotation of the magnetic moments within the $ab$ plane as you move from layer to layer of Cu ions along the $c$ axis.

**Figure 4.16.** Unit cells displaying (a) the nearest neighbor interactions ($J_n$) with different colors to distinguish the different orders of neighbors and (b) the incommensurate helical magnetic structure (red arrows) of CuRh$_2$O$_4$. The gray rings serve as a guide to the eye for the propagation and orientation of the magnetic moments.
Helical magnetic structures are somewhat uncommon but they are often seen in barium hexaferrites such as BaFe$_{12}$O$_{19}$ and Ba$_2$Mg$_2$Fe$_{12}$O$_{12}$ [34–36]. The divergence from the A-type magnetic structure seen in CoRh$_2$O$_4$ is undoubtedly linked to the compression of the tetrahedral site by the Jahn-Teller effect that changes the overlap between the Cu and O orbitals, disrupting the superexchange.

4.4 Conclusions

CoRh$_2$O$_4$, CuRh$_2$O$_4$ and the novel composition Ni$_{1.25}$Rh$_{1.75}$O$_4$ were successfully prepared using standard solid state methods. X-ray and neutron diffraction refinements confirmed the reported cubic and tetragonal spinel structures for CoRh$_2$O$_4$ and CuRh$_2$O$_4$ while Ni$_{1.25}$Rh$_{1.75}$O$_4$ was observed to have a tetragonal spinel structure similar to NiRh$_2$O$_4$. The distortions in both CuRh$_2$O$_4$ and Ni$_{1.25}$Rh$_{1.75}$O$_4$ are caused by Jahn-Teller effects though they are distorted in opposite directions due to differences in the filling of the $t_2$ orbitals. In CuRh$_2$O$_4$, the Cu was found to sit on the 8e site rather than the ideal 4a site despite a negligible difference in the BVS. No site displacements were seen in CoRh$_2$O$_4$ and Ni$_{1.25}$Rh$_{1.75}$O$_4$.

Antiferromagnetic transitions were observed in both CoRh$_2$O$_4$ ($T_N = 24.9(1)$ K) and CuRh$_2$O$_4$ ($T_N = 24(1)$ K) and Curie-Weiss behavior in the high temperature region. The extracted $\mu_{\text{eff}}$ values for both compounds were larger (4.43(1) and 1.94(1) $\mu_B$, respectively) than their expected spin-only values (3.87 and 1.73 $\mu_B$, respectively) due to an unquenched orbital contribution. The $\theta$ value for CuRh$_2$O$_4$ was found to be larger than $T_N$ indicating there may be magnetic frustration present in the lattice. CoRh$_2$O$_4$ was determined, via low temperature neutron refinements, to have an A-type AFM structure, which agrees well with a
Co-O-Rh-O-Co superexchange mechanism. The low temperature data for CuRh$_2$O$_4$ gave an *ab-*
plane helix magnetic structure. There is no reason Cu should not follow the same superexchange
as in CoRh$_2$O$_4$ which suggests the differences in magnetic structure is linked to lattice
compression from the Jahn-Teller effect. This distortion changes the bond angles of the CuO$_4$
tetrahedra, which will affect the overlap between Cu *d* and O *p* orbitals and disrupt the
superexchange.

The magnetic behavior of Ni$_{1.25}$Rh$_{1.75}$O$_4$ is more complex compared to its Co and Cu
analogs. Paramagnetic behavior was observed above 90 K and fitting the region gave $\mu_{\text{eff}}$ and
$\theta$ values of 2.77(1) $\mu_B$/f.u. and 34.5(1) K, respectively. The magnetic moment is a bit lower
than the range of spin-only values based on the possible mixture of Rh and Ni oxidation states.
Below 90 K, antiferromagnetic correlations begin to dominate as indicated by deviation from
Curie-Weiss behavior. Conversely, the positive value for $\theta$ suggests the presence of
ferromagnetic interactions. A case for competing ferromagnetic and antiferromagnetic
correlations can be made based on how the Ni substitution affects the Ni-O-Rh-O-Ni
superexchange. A divergence in the ZFC and FC $\chi(T)$ data (~8.5 K) in addition to the lack of
evidence for long-range ordering in our low temperature neutron diffraction studies indicates
that Ni$_{1.25}$Rh$_{1.75}$O$_4$ is a spin-glass material.

### 4.5 Methods and Materials

Black, polycrystalline samples were prepared by intimately mixing and grinding
stoichiometric amounts of CoCO$_3$ (Baker Adamson, 99.9%), CuO (Aldrich, 99.99%), NiO$_2$
(Baker Adamson, 99.9%) and Rh$_2$O$_3$ in an agate mortar. The Rh$_2$O$_3$ was obtained by
decomposing RhCl$_3$ (Johnson Matthey, 99.9\%) at 850 °C for 12 h under air flow. For CoRh$_2$O$_4$ and CuRh$_2$O$_4$, the samples were pelletized and sintered at 900-950 °C for 36 h (CuRh$_2$O$_4$) and 900-1000 °C for 36 h (CoRh$_2$O$_4$) with intermittent grinding. For Ni$_{1.25}$Rh$_{1.75}$O$_4$, samples were heated as loose powders at 1075 °C under O$_2$ flow for 48 h with intermittent grinding.

Initial (XRD) characterization of the samples was done on a Rigaku Miniflex II diffractometer using Cu Kα radiation and a graphite monochromator. Single-crystal Si sample holder were used to maximize peak intensity and aid detection of minor impurities. A fixed time scan was used with collection parameters of a 2θ range of 10-70° with a step size of 0.02° and a dwell time of 2.0 s. Room-temperature (298 K) time-of-flight neutron diffraction data for all samples were collected at Oak Ridge National Laboratory on the POWGEN (BL-11A) beamline using center wavelength of 1.33 Å. Approximately 2 g of sample was loaded into 6 mm vanadium sample cans and data was collected over about 3 hours.

Structure refinement was performed using the Rietveld method [37] on the GSAS software with EXPGUI user interface [38,39]. Low temperature (4–200 K) neutron diffraction data was collected at Oak Ridge National Laboratory using the HB2A and SEQUOIA beamlines. Crystal structures were generated using VESTA and PyMol software [40,41]. The magnetic space groups for CoRh$_2$O$_4$ and CuRh$_2$O$_4$ were determined using Isodistort [42] and low temperature nuclear structures were refined using the Rietveld method [37] on the Fullprof suite [43]. Low-temperature (5–300 K) magnetization measurements were obtained using a Quantum Design MPMS.
4.6 References


General Conclusions and Future Work

This dissertation presented and discussed the preparation and characterization of both novel and previously known materials. We demonstrated that the series $\text{Ba}_2\text{In}_{2-x}\text{Ir}_x\text{O}_{5+\delta}$ ($x = 0–1.4, 2$) undergoes a series of structural transitions spanning several perovskite-related structures leading to several novel compositions included $\text{Ba}_2\text{In}_{1.62}\text{Ir}_{0.38}\text{O}_{5.49}$ which was shown to contain a relatively large amount of Ir(VI) (~50%). This was the first time Ir(VI) was stabilized without the aid of an oxygen-rich atmosphere or flux methods. In addition to novel compositions, $\text{Ba}_2\text{InIrO}_6$ was found to crystallize as a monoclinic distortion of the previously reported 6H structure with a different ordering on the In and Ir ions. This serves as a great example about how there is still more to learn even about compounds we already know about.

For the novel solid solutions series $\text{Ba}_{2-x}\text{La}_x\text{InIrO}_6$ ($x = 0–1.0$) and $\text{BaLaIn}_{1-x}\text{Ca}_x\text{IrO}_6$ ($y = 0–1.0$), several changes in structure, magnetic moment, and charge transport were observed. The $\text{Ba}_{2-x}\text{La}_x\text{InIrO}_6$ series exhibits a transition from a 6M polytype to an orthorhombic perovskite structure with increased La content. The $\text{BaLaIn}_{1-x}\text{Ca}_x\text{IrO}_6$ series transitioned from a disordered orthorhombic perovskite to an ordered cubic perovskite with increased Ca content. Seebeck measurements for both systems showed that Ir(IV)-rich compounds tended to have a n-type conduction mechanism while Ir(V)-rich compounds appeared to be p-type. Both systems were found to be semiconducting and the magnitude of the resistivity is dependent on the crystal structure and Ir environment. Characterization of the magnetic behavior showed that while both systems exhibit paramagnetic behavior, their $\mu_{\text{eff}}$ values do not correlate well with moments expected for Ir(IV) and Ir(V). While this deviation appears to be somewhat common in conductive iridates, it would be interesting to study analogous Os and Re oxides to see if they
exhibit similar electronic behavior. Additionally, the inclination of In to share sites with Ir in \( \text{Ba}_2\text{In}_{2.3}\text{Ir}_x\text{O}_{5+x}, \text{Ba}_{2.3}\text{La}_x\text{InIrO}_6, \) and \( \text{BaLaIn}_{1.7}\text{Ca}_x\text{IrO}_6 \) indicates there is something special about the pairing. Ir is known to form ordered perovskites with metals similar in size to In\(^{3+}\) such as Y\(^{3+}\) and Sc\(^{3+}\). This suggests the behavior is linked to the fact that In possesses a full \( d \) shell. It would therefore be interesting to see if similar site sharing could be achieved by pairing Ir with other Group 13 elements such as Ga or Tl.

While \( \text{CoRh}_2\text{O}_4 \) and \( \text{CuRh}_2\text{O}_4 \) had been previously reported, we were the first to perform more detailed structural and magnetic characterization on them and the novel composition, \( \text{Ni}_{1.25}\text{Rh}_{1.75}\text{O}_4 \). Neutron and X-ray diffraction studies confirmed that \( \text{CoRh}_2\text{O}_4 \) crystallizes in a normal cubic spinel structure (\( \text{Fd}\overline{3}m \)). \( \text{CuRh}_2\text{O}_4 \) and \( \text{Ni}_{1.25}\text{Rh}_{1.75}\text{O}_4 \), were found to be tetragonally-distorted spinels (\( I_4/1/amd \)) due to cooperative Jahn-Teller compression and elongation, respectively. In terms of their magnetic behavior, antiferromagnetic behavior was observed for both \( \text{CoRh}_2\text{O}_4 (T_N = 24.9(1) \text{ K}, \mu_{\text{eff}} = 4.42(1) \mu_\text{B}) \) and \( \text{CuRh}_2\text{O}_4 (T_N = 24(1) \text{ K}, \mu_{\text{eff}} = 1.97(1) \mu_\text{B}) \) confirming previous literature reports. Their magnetic moments were a bit higher than predicted spin-only values due to unquenched orbital contributions. Additionally, the magnetic structures of \( \text{CoRh}_2\text{O}_4 \) and \( \text{CuRh}_2\text{O}_4 \) were determined, for the first time, to be an antiferromagnetic \( A \)-type and an \( ab \)-plane helical structure, respectively. For \( \text{Ni}_{1.25}\text{Rh}_{1.75}\text{O}_4 \), a divergence in ZFC and FC \( \chi(T) \) data was observed in addition to a lack of long-range ordering in low temperature neutron data both of which suggest this compound is a spin-glass. A possible competition between ferromagnetic and antiferromagnetic correlations was also observed for \( \text{Ni}_{1.25}\text{Rh}_{1.75}\text{O}_4 \). These magnetic behaviors are likely the result of superexchange disruption caused by the presence of a magnetic ion on the B-site. This hypothesis could be tested by
preparing other members of a general NiRh$_{2-x}$M$_x$O$_4$ spinel family to study how the behavior is affected by varying concentration of difference magnetic ions.

The investigations presented in this dissertation demonstrate that there is always more to learn and study even when dealing with previously known compounds or structures types that have been heavily studied like the perovskite and spinel structures. As researchers and scientists, it is our duty not only to seek out new ideas and technologies but to also to occasionally look back and find something that we missed the first time around.

"The worst thing you can ever do is think that you know enough."

– Arnold Schwarzenegger
Bibliography


Cussen, E.J., Sloan, J., Vente, J.F., Battle, P.D., Gibb, T.C., 15R SrMn$_{1.5}$Fe$_2$O$_{3-d}$ (x = 0.1); A New Perovskite Stacking Sequence, Inorg. Chem. 37 (1998) 6071–6077.


Davis, M.J., Smith, M.D., Stitzer, K.E., zur Loye, H.-C., High temperature flux growth, structural characterization, and magnetic properties of Ca$_{3.15}$Li$_{0.85}$Ir$_6$O$_{19}$, Sr$_3$LiIrO$_6$, Ca$_3$LiRuO$_6$ and Sr$_3$LiRuO$_6$, J. Alloys Compd. 351 (2003) 95–100. doi:10.1016/S0925-8388(02)01082-4.


Goodenough, J.B., Oxide-ion conduction in Ba₂In₂O₅ and Ba₂In₂MO₈ (M = Ce, Hf, or Zr), Solid State Ionics. 44 (1990) 21–31.


Jiang, P., Li, J., Ozarowski, A., Sleight, A.W., Subramanian, M.A., Intense Turquoise and Green Colors in Brownmillerite-Type Oxides Based on Mn$^{5+}$ in Ba$_2$In$_{2-x}$Mn$_x$O$_{5+}$, Inorg. Chem. 52 (2013) 1349–57. doi:10.1021/ic3030332.

Jung, D.-Y., Demazeau, G., Etourneau, J., Subramanian, M.A., Preparation and characterization of new perovskites containing Ir(VI) and Ir(V) [BaM$_{0.50}$Ir$_{0.50}$O$_{2.75}$ and BaM$_{0.25}$Ir$_{0.75}$O$_3$ (M = Li or Na)], Mater. Res. Bull. 30 (1995) 113–123. doi:10.1016/0025-5408(94)00115-4.


Kakinuma, K., Yamamura, H., Haneda, H., Atake, T., Oxide-ion conductivity of (Ba$_{1-\delta}$La$_{\delta}$)$_2$In$_2$O$_{5+\delta}$ system based on brownmillerite structure, Solid State Ionics. 140 (2001) 301–306. doi:10.1016/S0167-2738(01)00853-0.


Siegrist, T., Chamberland, B.L., The crystal structure of BaIrO₃, J. Less-Common Met. 170 (1990) 93–99.


Appendix A: Linear Magnetoresistance in BaIrO$_3$

Abstract

BaIrO$_3$ was found to exhibit non-saturating positive linear magnetoresistance (LMR), despite ferromagnetic order, which usually results in a negative saturating magnetoresistance. Based on other reports of positive LMR in literature, we believe the phenomenon in BaIrO$_3$ caused by quantum interference effects. The anomalous Hall effect was also observed and the sign of the charge carriers was found primarily positive based on experimental Hall coefficients with some fluctuations in carrier sign around $T_C$. This behavior may be attributed to either a depletion of carrier concentration due to the opening of the band gap or an anisotropic scattering time which has been observed in quasi-one-dimensionality of the 9M crystal structure.

A.1 Introduction

A.1.1 BaIrO$_3$

BaIrO$_3$ crystallizes at ambient temperature and pressure as a monoclinically distorted, quasi-one-dimensional 9R polytype structure (often called a “9M” polytype) with $C2/m$ symmetry. It can be described as a zigzag network of corner-sharing Ir$_3$O$_{12}$ trimers of face-sharing IrO$_6$ octahedra aligned roughly along the $c$ axis (Figure A.1a) [1]. In addition to the 9M polytype, two monoclinically distorted 5H and 6H polytypes (or “5M” and “6M”) have been stabilized [2,3]. The 5M polytype (Figure A.1b) forms at 3.0 GPa and is stable up to 5.0 GPa where the 6M polytype (Figure A.1c) forms and is stable up to 10.0 GPa [4]. Above 10 GPa, BaIrO$_3$ crystallizes as an ideal perovskite structure or 3C polytype. This transition series is
similar to that of BaRuO$_3$ which transitions according to a 9R-4H-6H-3C sequence with increasing pressure [5–7].

Figure A.1. Crystal structures of the (a) 9M, (b) 5M, and (c) 6M polymorphs of BaIrO$_3$ (Ba = green, Ir = brown, O = red).

The 9M phase of BaIrO$_3$ has been studied extensively in recent years and is theorized to be spin-orbit Mott insulator (SOMI) [8]. It is a weak ferromagnet with a saturated moment of only $\sim 0.04 \, \mu_B$ which was originally thought to be due to canted antiferromagnetic interactions [9]. However, more recent studies have argued the low moment is due to $d$-$p$ orbital hybridization and small exchange splitting [10]. Interestingly, the ferromagnetic transition is accompanied by a simultaneous anomaly in the electrical resistivity at the $T_C$ that is consistent with the formation of a charge density wave. Its magnetic behavior, electrical resistivity and thermopower have all been reported to have anisotropic properties due to the distinctive crystal structure [10,11].
A.1.2 Magnetoresistance

Magnetoresistance, often called “ordinary” magnetoresistance (OMR), was first reported by William Thomson in 1856 [12] and is a phenomenon that involves the change in the electrical resistivity upon application of a magnetic field ($H$). In OMR, when a conductive material is placed in a magnetic field that is perpendicular to the current flow ($I$) in the material, the trajectory of the charge carriers becomes curved. This increases the number of scattering events and causes an increase in the resistivity of the material ranging from a few percent to as high as 200% [13].

Magnetic order adds a layer of complexity and gives rise to several unique types of magnetoresistance. For example, “giant” magnetoresistance and “tunneling” magnetoresistance are the result of separating ferromagnetic thin films with either antiferromagnetic or insulating materials [14,15]. These effects have led to many advancements in spintronic devices such as memory storage [16] but the magnetoresistance in bulk ferromagnetic materials is different. While most materials have a positive magnetoresistance for reasons discussed above, ferromagnets exhibit negative magnetoresistance (NMR) due to ordering of electronic spin domains. The magnitude of the effect is typically $< 30\%$ and is most intense near the Curie temperature ($T_C$).

Bulk ferromagnets also exhibit “anisotropic” magnetoresistance (AMR) meaning the effect is different depending on whether $H$ is perpendicular ($\perp$) or parallel ($\parallel$) to $I$. AMR can be defined as $\Delta \rho_{\text{AMR}} = \rho_{\parallel} - \rho_{\perp}$ [17] and is a result of spin-orbit coupling (SOC). The magnitude of AMR will, therefore, vary from material to material depending on the strength of the SOC and orbital anisotropy [18].
The dependence of OMR on $H$ is typically quadratic (i.e. $H^2$) [19]; however, some materials display linear magnetoresistance (LMR) such as elemental bismuth [20]. LMR is somewhat uncommon but can occur in specific circumstances. The most common route to LMR is through disorder which causes fluctuations in carrier mobility. Disorder can also lead to positive LMR in ferromagnetic materials due to quantum interference effects [21]. The combination of ferromagnetic ordering and disorder leads to electron-electron interactions that cause their wavefunctions to interfere coherently. This theory has been previously proposed to explain the behavior observed in disordered paramagnetic metals [22].

### A.3 Characterization of BaIrO$_3$

#### A.3.1 Single Crystals

Single crystals of BaIrO$_3$ were prepared via a molten flux reaction of BaCl$_2$ and IrCl$_3$. The sizes of the crystals were varied and the crystal shapes tended to be anisotropic with dimensions of the larger ones being about 1 mm $\times$ 0.5 mm $\times$ 0.5 mm (Figure A.2). The anisotropic shape makes sense considering the length of the $c$ axis of the unit relative to the $a$ and $b$ axes. The purity and crystal structure of single crystals was confirmed using powder XRD diffraction.
Figure A.2. Photos of example BaIrO$_3$ single crystals showing (a) relative size and (b) close-up view of crystal shapes.

A.3.2 Electronic Properties

Resistivity ($\rho(T)$) data (Figure A.3) for BaIrO$_3$ shows semiconductor with an unusual bump in the data at $T_C \approx 160$ K.

Figure A.3. $\rho(T)$ plot for BaIrO$_3$ exhibiting an anomaly at $T_C \approx 160$ K. Inset is an overlay plot of $-d \log \rho / d (T^{-1})$ and $\Delta \rho / \rho_0(T)$. 

This feature has been reported in literature and attributed to the formation of a charge density wave and the opening of small band gap \cite{10,23}. The derivative of the resistivity, \(-d \log \rho / d(T^{-1})\), exhibits a negative intensity peak at \(T_C\) likely due to the onset of ferromagnetic order. Similar peaks are commonly observed in ferromagnets but are usually positive as ferromagnets are typically metallic conductors \cite{24}.

As mentioned earlier, BaIrO\(_3\) is known to exhibit weak ferromagnetism with a very small ordered moment of \(\sim 0.04 \mu_B/\text{Ir}\) \cite{10}. Thus, the magnetoresistance \((\Delta \rho / \rho_0)\) for BaIrO\(_3\) is expected to be negative. Contrary to this prediction, \(\Delta \rho / \rho_0\) was found to positive (Figure A.3 inset) exhibiting a peak at \(T_C\). There are examples of ferromagnet metals with peaks in \(\Delta \rho / \rho_0(T)\) near \(T_C\) in literature such as Pr\(_{0.5}\)Sr\(_{0.5}\)CoO\(_3\) and La\(_{0.7}\)Sr\(_{0.3}\)MO\(_3\) perovskites \cite{25,26}, however, the peaks for these compounds were all negative in sign.

![Figure A.4. Plots of \(\Delta \rho / \rho_0(H)\) BaIrO\(_3\) (a) near \(T_C \approx 160\) K and (b) well below \(T_C\).](image)
This suggests the $\Delta \rho/\rho_0(T)$ behavior is more complex. The field dependence of $\Delta \rho/\rho_0$ supports a more complex mechanism as positive LMR is observed in $\Delta \rho/\rho_0(H)$ within $\pm 30$ K of $T_C$ (Figure A.4). Hysteresis is observed in $\Delta \rho/\rho_0(H)$ well below $T_C$ due to ferromagnetic ordering.

In addition to the positive LMR, BaIrO$_3$ exhibits the anomalous Hall effect (AHE), where transverse resistivity ($\rho_{xy}$) has a dependence on the magnetization ($M$) in the sample, behavior common to ferromagnets. The relationship between AHE and the $H$-dependence of $\rho_{xy}$ can be expressed as $\rho_{xy} = R_H H + R_{AHE} M$ where $R_H$ and $R_{AHE}$ are the “normal” and anomalous Hall coefficients, respectively [27]. The $\rho_{xy}(H)$ data for BaIrO$_3$ are plotted in Figure A.5.

![Figure A.5](image)

**Figure A.5.** $\rho_{xy}(T)$ plot for BaIrO$_3$ for $T = 40–160$ K. The black arrow is a guide for the trend for decreasing $T$. The inset is a plot of $R_H(T)$ exhibiting a positive-negative-positive sign change near $T_C$. 
The AHE term dominates $\rho_{xy}$ at low $H$, meaning $R_H$ can be extracted increasing $H$ until $M$ is saturated effectively producing a constant AHE term. While the sign of $R_H$ is primarily positive and correlates well with previous thermopower studies on BaIrO$_3$ [11,23], there is a slight transition with decreasing temperature from positive to negative then back to positive around $T_C$ (Figure A.5 inset). This behavior may be attributed to either a depletion of carrier concentration due to the opening of the band gap, as observed in some transition metal dichalcogenides [28], or an anisotropic scattering time which has been observed in quasi-one-dimensional metals [29].

Positive LMR has also been observed in ferromagnets with strong disorder and low carrier densities [21] as well as in geometrically-constrained ferromagnetic thin films [30]. In both of these studies, the positive LMR is similar to BaIrO$_3$ and shows no indication of saturation even at high $T$, suggesting a similar mechanism for the LMR in all three systems. The models for both the thin film and low carrier density systems link the positive LMR to quantum interference effects. These models do not fit BaIrO$_3$ perfectly as our samples are single crystals, not thin films and our Hall measurements yield a relatively high carrier density on the order of $10^{22}$ cm$^{-3}$. We therefore speculate that the quasi-one-dimensional structure of BaIrO$_3$ makes it more susceptible to disorder and contributes to quantum interference effects.

A.4 Conclusions and Future Studies

Our studies show that BaIrO$_3$ exhibits an AHE and unexpected positive LMR, the latter of which we attribute to quantum interference effect. These properties arise in part due to the
large SOC, competing energy scales, and possibly the quasi-one-dimensionality of the 9M structure. Future studies on polycrystalline samples, which have a cleaner gap [31], may provide further insight into the effects of disorder, as well as into the significance of the quasi-one-dimensionality, which will no longer be in play.

One remaining mystery concerns $\Delta \rho / \rho_0(T)$, which appears near $T_C$, implying a relationship to the charge or magnetic order where the spin or charge fluctuations associated with the low-$T$ ordering might augment the quantum effects. Future studies that clarify the nature of the charge order in this system, and its relation to the magnetic order, may help us further comprehend the positive LMR in BaIrO$_3$.

### A.5 Methods and Materials

Single crystals of were prepared using IrCl$_3 \cdot x$H$_2$O in a BaCl$_2$ flux. which were ground together via mortar and pestle. The mixture was heated at 1000–1025 °C for 3 h in an alumina crucible and then cooled at a rate of 2 °C/h to 900 °C, then allowed to cool to room temperature. The excess BaCl$_2$ was dissolved by submerging in an ultrasonic water bath and the BaIrO$_3$ crystals were then filtered, collected, and dried. Silver epoxy was used for current/voltage contacts and were applied directly to the single crystals. All transport measurements were performed in a commercial cryostat in a standard DC four-probe configuration with the current, $I$, parallel to the $c$ axis.
A.6 References


