A STRUCTURAL, BONDING, AND PROPERTIES STUDY OF THE ORDERED ROCK SALT STRUCTURES, Li$_2$MO$_3$ ($M = \text{Ru, Ir, Pt}$)

Dissertation

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ABSTRACT

The ordered rock salt structures of Li$_2$MO$_3$ have become of interest in recent years due to their potential applications as lithium ion battery and as pH sensing materials. Included in this class are the structures of Li$_2$IrO$_3$ and Li$_2$PtO$_3$ that can be derived from the well-known Li-ion battery cathode material, LiCoO$_2$, via ordering of Li$^+$ and Ir$^{4+}$/Pt$^{4+}$. The additional cation ordering lowers the symmetry from rhombohedral (R$3m$) to monoclinic (C$2/m$). Unlike Li$_2$RuO$_3$ no evidence for further distortion of the structure driven by formation of metal–metal bonds. Thermal analysis studies coupled with both ex-situ and in-situ X-ray diffraction measurements show that these compounds are stable up to temperatures approaching 1375 K in O$_2$, N$_2$, and air, but decompose at much lower temperatures in forming gas (5% H$_2$:95% N$_2$) due to reduction of the transition metal to its elemental form. Li$_2$IrO$_3$ undergoes a slightly more complicated decomposition in reducing atmospheres, which appears to involve loss of oxygen prior to collapse of the layered Li$_2$IrO$_3$ structure. Electrical measurements, UV–visible reflectance spectroscopy and electronic band structure calculations show that Li$_2$IrO$_3$ is metallic, while Li$_2$PtO$_3$ is a semiconductor, with a band gap of 2.3 eV.

Further analysis of faulting in Li$_2$IrO$_3$ and Li$_2$PtO$_3$ systems is presented, the degree of which is dependent on the heating temperatures used. Faulting analysis was carried out using Rietveld refinements as well as refinements using the software FAULTS based on powder X-ray diffraction (PXRD). Additionally, PXRD and selected area electron diffraction simulations were carried out using DIFFaX that are subsequently compared to experimental results. FAULTS analysis yields $\alpha_{12}$ values, transition probabilities, of
66.2%, 87.3%, and 94.7% for LIO-750, LIO-900, and LIO-1050, respectively, while they are 74.8%, 85.8%, and 96.8% for LPO-750, LPO-900, and LPO-1050, respectively.

Density functional theory (DFT) calculations and lattice energy calculations were also performed with manganese, tin, zirconium and lead being placed in the Li$_2$MnO$_3$, Li$_2$SnO$_3$, and Li$_2$ZrO$_3$ structure types. These results indicate that ionically, the Li$_2$ZrO$_3$ structure is the most stable. Upon considering covalent interactions the layered structures of Li$_2$MnO$_3$ and Li$_2$SnO$_3$ become more stable for both Sn and Mn, but not for Zr. Thus these results are consistent with expectations. Additionally, DFT calculations substantiate the occurrence of Ru-Ru dimerization in Li$_2$RuO$_3$, while also predicting the as yet unseen metal-metal bonding in Li$_2$IrO$_3$ and the theoretical Li$_2$OsO$_3$ and Li$_2$ReO$_3$ structures.
DEDICATION

Dedicated to

my loving and always supportive wife, Chrissy and our beautiful daughter Josephine.
AKNOWLEDGMENTS

One does not complete a body of work such as this without the help of others. Thus, it is appropriate to acknowledge their contribution to my scientific and professional development. Firstly, I need to thank my research advisor Prof. Pat Woodward for his patience and trust in my abilities. He provided the space and time needed to come to my own conclusions, which is so vital in developing confidence in one's own research abilities. I also need to thank my materials science advisor Prof. Henk Verweij, who showed me that one must focus on the small problems that ultimately affect the big picture. Due to their work and tutelage I believe I have become a researcher and steward of science for which they can be proud.

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To put it more simply, THANK YOU ALL!
VITA

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract ................................................................................................................................. ii</td>
</tr>
<tr>
<td>Dedication .............................................................................................................................. iv</td>
</tr>
<tr>
<td>Acknowledgments ...................................................................................................................... v</td>
</tr>
<tr>
<td>Vita ........................................................................................................................................ vii</td>
</tr>
<tr>
<td>List of Tables ......................................................................................................................... xi</td>
</tr>
<tr>
<td>List of Figures ....................................................................................................................... xiii</td>
</tr>
<tr>
<td>List of Symbols ...................................................................................................................... xix</td>
</tr>
</tbody>
</table>

## Chapters

Chapter 1 An Introduction to Alkali Platinum Group Metal oxides ........................................ 1

1.1 Background .......................................................................................................................... 1

1.2 Crystal Structure of Alkali Platinum Group Metal Oxides ................................................ 4

1.2.1 Crystal Structure of $A_2MO_3$ Structures ................................................................. 6

1.2.2 Crystal Structure of $A_8MO_6$ .................................................................................. 11

1.2.3 Crystal Structure of $A_3MO_4$ ............................................................ .......................... 13

1.2.4 Other APGMO Crystal Structures ............................................................................ 14

1.3 Electrochemical Properties of Alkali Platinum Group Metal Oxides ............................... 17

1.3.1 Electronic Conductivity of APGMO Structures ......................................................... 18

1.3.2 Experimental Delitiation of $A_2MO_3$ and Electrical Properties of the Delithiated Structures .......................... 20

1.4 Magnetic Properties of Alkali Platinum Group Metal Oxides ........................................ 24

1.4.1 Curie-Weiss Paramagnetism of $Li_2MO_3$ (M=Ru,Ir) ................................................. 24

1.4.2 Antiferromagnetic Ordering of $Li_3RuO_4$ ................................................................. 27
1.5 Conclusions ........................................................................................................29
1.6 References ..........................................................................................................30

Chapter 2 Structure and Properties of Ordered Li₂IrO₃ and Li₂PtO₃ .......................33
  2.1 Introduction .......................................................................................................33
  2.2 Experimental ....................................................................................................35
  2.3 Results and Discussion .....................................................................................38
    2.3.1 Structural Characterization .......................................................................38
    2.3.2 Thermal Stability .......................................................................................44
    2.3.3 Electronic Structure Calculations .............................................................49
    2.3.4 Optical Properties ......................................................................................50
    2.3.5 Electrical Measurements ..........................................................................52
  2.4 Conclusions ......................................................................................................54
  2.5 References .......................................................................................................55

Chapter 3 Control and Analysis of Faulting in Li₂IrO₃ and Li₂PtO₃ .........................57
  3.1 Introduction .......................................................................................................57
    3.1.1 History of Faulting Analysis .....................................................................59
    3.1.2 Methods of Faulting Analysis ..................................................................62
  3.2 Experimental ....................................................................................................65
  3.3 Results ...............................................................................................................67
    3.3.1 Rietveld Refinements ..............................................................................67
    3.3.2 Faulting Confirmation and Analysis .........................................................77
  3.4 Discussion .........................................................................................................89
  3.5 Conclusions .....................................................................................................92
  3.6 References .......................................................................................................94

Chapter 4 A computational Study of Bonding in Li₂MO₃ Ordered Rock Salt Structures ........................................................................................................97
  4.1 Introduction .....................................................................................................97
LIST OF TABLES

Table 1.1: Lattice parameters of various APGMOs [2]. .......................................... 2
Table 1.2: Structural parameters for $\beta$-Li$_2$SnO$_3$ (a), Li$_2$RuO$_3$ (b), and Li$_2$IrO$_3$
(c) with space group $C2/c$ (15). ................................................................. 10
Table 1.3: Electronic conductivity of the mixed metal oxides of the platinum
metals and the electronic configuration of the platinum group
metals [20]. ........................................................................................................ 19
Table 1.4: Structural parameters for Li$_2$MO$_3$ ($M =$ Ir, Pt) - $C2/m$ .................... 42
Table 1.5: Bond lengths and bond valence values for Li$_2$IrO$_3$ and Li$_2$PtO$_3$. ......... 43
Table 1.6: Structural parameters obtained via Rietveld refinement for Li$_2$MO$_3$
($M =$ Ir, Pt) prepared at 750 °C, 900 °C, and 1050 °C, respectively. ................. 72
Table 1.7: Structural parameters obtained via FAULTS refinement for Li$_2$IrO$_3$
and Li$_2$PtO$_3$ prepared at 750 °C, 900 °C, and 1050 °C, respectively. FAULTS is incapable of calculating estimated standard deviations, as such they are not provided. ................................................................. 88
Table 1.8: Symmetry and compositional variations in Li$_2$MnO$_3$, $\beta$-Li$_2$SnO$_3$, and Li$_2$ZrO$_3$ ................................................................. 102
Table 1.9: Metals possessing Li$_2$MnO$_3$, $\beta$-Li$_2$SnO$_3$, and Li$_2$ZrO$_3$ structure
types. *The Li$_2$MoO$_3$ system is so highly faulted it is reported with the
LiCoO$_2$ structure type. .................................................................................. 103
Table 1.10: Potential parameters utilized for the lattice energy calculations
(GULP) ........................................................................................................... 109
Table 1.11: Lattice energies per formula unit for Li$_2$MnO$_3$, $\beta$-Li$_2$SnO$_3$, and
Li$_2$ZrO$_3$ structure types with Mn, Sn, and Zr metals via GULP
calculations. .................................................................................................. 110
Table 1.12: Total electronic energies per formula unit for Li$_2$MnO$_3$, $\beta$-Li$_2$SnO$_3$,
and Li$_2$ZrO$_3$ structure types for Mn, Sn, Zr, and Pb metals obtained
from CASTEP calculations. $\Delta$ Energy is the difference between the
respective structure type and the highest energy structure type. ........... 112
Table 4.6: Total electronic energies per formula unit obtained via CASTEP calculations using $P_{2}/m$ and $C_{2}/m$ symmetries and the energy differences ($E_{P_{2}/m} - E_{C_{2}/m}$).

Table 4.7: Metal-metal distances obtained via CASTEP calculations using $P_{2}/m$ and $C_{2}/m$ symmetries along with average metal-metal distances and average metal-oxygen distances. The most stable symmetries are shaded.
LIST OF FIGURES

Figure 1.1: Structural comparisons for ordered rock salt structures from MgO (a), with $Fm\overline{3}m$ symmetry, to LiCoO$_2$ (b), with $R\overline{3}m$ symmetry, to Li$_2$RuO$_3$ (c), with $C2/m$ symmetry. Note that in all cases the average oxidation state of the metal sites remains +2............................................. 3

Figure 1.2: The $A_2MO_3$ structure type is represented depicting the alternating layers of pure $A$ and $AM_2$ using Li$_2$RuO$_3$ (a). Additionally, structure of a single $AM_2$ is also presented (b)............................................. 5

Figure 1.3: Li$_2$MnO$_3$ (a) and $\beta$-Li$_2$SnO$_3$ (b) are shown parallel to the Li$_M^2$ layer normal. .................................................................................................................. 7

Figure 1.4: Qualitative energy-level diagram for the t$_2$ manifold of Ru$^{4+}$ (4d$^4$) ions in Li$_2$RuO$_3$ [8] reproduced by permission of Elsevier. ................. 8

Figure 1.5: An ab plane projection of Li$_8$IrO$_6$ mixed layer, $A_2M$, including MO$_6$ octahedra (a) and a projection depicting the tetrahedral coordination of lithium within the pure lithium layer (b). ..................... 12

Figure 1.6: The structure of Li$_3$RuO$_4$ is presented showing the layering (a) as well as the bc plane projection of a LiRu mixed metal layer, including RuO$_6$ octahedra (b) [24].............................................................. 13

Figure 1.7: Perspective of the corner sharing RuO$_5$ bipyramids for Na$_2$RuO$_4$. ............ 16

Figure 1.8: Structure of NaRh$_2$O$_4$ (a) along with the double chain along the b-axis (b). .................................................................................................................. 18

Figure 1.9: The XRD patterns for Li$_{2-x}$RuO$_3$ deintercalated by electrochemical means (a) and chemical means (b) [6],[9] reproduced by permission of Elsevier.................................................................. 21

Figure 1.10: Charge and discharge curves of the cell, Li/Li$_2$RuO$_3$, with a current density of 0.1 mA/cm$^2$ and cut off voltages of 3.0 and 4.0 V [9] reproduced by permission of Elsevier......................................................... 22
Figure 1.11: Specific capacities of Li/LiCoO$_2$ and Li/Li$_2$PtO$_3$ cell; comparison of (a) gravimetric capacity, and (b) volumetric capacity [5] reproduced by permission of Elsevier................................................................. 23

Figure 1.12: Magnetization curves of the paramagnetic Li$_2$MO$_3$ ($M$ = Ru and Ir) [35] reproduced by permission of Elsevier................................................................. 25

Figure 1.13: Mössbauer spectroscopy at 4.1 K for 1% Fe doped Li$_2$RuO$_3$ [35] reproduced by permission of Elsevier................................................................. 25

Figure 1.14: Temperature dependence of zero field cooled and field cooled molar magnetic susceptibility and reciprocal susceptibility (insert) of Li$_3$RuO$_4$ measured in an applied field of Oe [24] reproduced by permission of The Royal Society of Chemistry. ................................................................. 28

Figure 2.1: The Li$_2$MO$_3$ structure shows the characteristic layering (a), as well as the Li$M_2$ layer with corresponding oxygen atoms (b). ................................................. 34

Figure 2.2: Powder X-ray diffraction pattern and Rietveld refinement for (a) Li$_2$RuO$_3$ (b) Li$_2$IrO$_3$ (c) Li$_2$PtO$_3$: observed (•), calculated (red), and difference (green) profiles. Tick marks indicate the Bragg reflection positions................................................................. 40

Figure 2.3: TGA for Li$_2$MO$_3$ ($M$ = Ru, Ir, Pt) in O$_2$, air, N$_2$, and H$_2$:N$_2$ (5:95). The horizontal dashed lines represent the calculated weight percent for potential decomposition products................................................................. 45

Figure 2.4: In-situ Powder X-ray diffraction patterns of Li$_2$IrO$_3$ in forming gas (H$_2$:N$_2$, 5:95) from 300 to 675 K with 5 K increments................................................................. 47

Figure 2.5: Unit cell volume evolution of Li$_2$IrO$_3$ and the refined phase fractions of Ir and Li$_2$O during reduction in forming gas (H$_2$:N$_2$, 5:95) as obtained from the Rietveld refinements................................................................. 48

Figure 2.6: The electronic density of states (DOS) plots for Li$_2$MO$_3$ ($M$ = Ir, Pt). The d-orbital contribution can be completely attributed to the platinum group metal, while the p-orbital contribution comes predominantly from oxygen. The horizontal dashed line depicts the Fermi energy................................................................. 49

Figure 2.7: Plot of UV-Vis diffuse reflectance spectra converted to absorbance using the Kubelka-Munk function for Li$_2$IrO$_3$ and Li$_2$PtO$_3$................................................................. 51

Figure 2.8: Impedance Spectra from 0 to $10^7$ Hz for Li$_2$PtO$_3$ from 400 to 800 K.................................................................................................................................. 51
Figure 2.9: Conductivity plot, $\log(\sigma) = f(10^3/T)$, of $\text{Li}_2\text{MO}_3$ ($M = \text{Ir}, \text{Pt}$) with corresponding linear fits (line) for the semi-conducting $\text{Li}_2\text{PtO}_3$ used to determine the reported activation energies........................................53

Figure 3.1: The structure of $\text{Li}_2\text{MnO}_3$ is shown depicting both the layering (a) and the stacking of successive layers (b) for ideal un-faulted system. For clarity pure lithium and oxygen layers are omitted in (b)...........................................................................................................................58

Figure 3.2: Examples of stacking faults observed in ordered rock salt $A_2\text{MO}_3$ ($C2/m$) (based on figure originally published in [1]). The arrows indicate the shift in lithium progression through successive layers, thereby representing stacking faults.................................................................62

Figure 3.3: Simulated X-ray diffraction patterns for ordered rock salt structures of $\text{Li}_2\text{MnO}_3$ ($C2/m$), $\text{Li}(\text{Li}_{1/3}\text{Mn}_{2/3})\text{O}_2$ ($R\bar{3}m$), and the unordered rock salt structure $\text{Li}_2\text{Mn}_{1/3}\text{O}$ ($F\bar{m}3m$). (Lattice parameters based on $\text{Li}_2\text{MnO}_3$ unit cell [1].).................................................................................................64

Figure 3.4: HRTEM image of $\text{Li}_2\text{IrO}_3$ prepared at $750^\circ\mathrm{C}$ (LIO-750), viewed down the [1 0 0] axis. The arrows are used to identify faulting. ..........68

Figure 3.5: Powder X-ray diffraction pattern and Rietveld refinement for $\text{Li}_2\text{IrO}_3$ (a) and $\text{Li}_2\text{PtO}_3$ (b) prepared at $750^\circ\mathrm{C}$: observed ($\bullet$), calculated (red), and difference (green) profiles. Tick markers indicate the Bragg reflection positions. ...............................................................69

Figure 3.6: Powder X-ray diffraction pattern and Rietveld refinement for $\text{Li}_2\text{IrO}_3$ (a) and $\text{Li}_2\text{PtO}_3$ (b) prepared at $900^\circ\mathrm{C}$: observed ($\bullet$), calculated (red), and difference (green) profiles. Tick markers indicate the Bragg reflection positions. ........................................................................70

Figure 3.7: Powder X-ray diffraction pattern and Rietveld refinement for $\text{Li}_2\text{IrO}_3$ (a) and $\text{Li}_2\text{PtO}_3$ (b) prepared at $1050^\circ\mathrm{C}$: observed ($\bullet$), calculated (red), and difference (green) profiles. Tick markers indicate the Bragg reflection positions. ........................................................................71

Figure 3.8: Simulated PXRD patterns for $\text{Li}_2\text{IrO}_3$ with iridium occupancies on the iridium site ranging from 66.7% (fully disordered $\text{LiM}_2$ layers) to 100% (fully ordered $\text{LiM}_2$ layers), the remaining balance is occupied by lithium........................................................................................................75
Figure 3.9: DIFFaX simulated PXRD patterns for Li$_2$IrO$_3$ with faulting ranging from 33.3% Ideal (fully faulted) to 100% Ideal (fully ordered) ................................................................. 76

Figure 3.10: DIFFaX simulated (blue) and experimental (red) PXRD patterns comparisons for Li$_2$IrO$_3$ (a) and Li$_2$PtO$_3$ (b) ................................................................. 79

Figure 3.11: Simulated SAED patterns for Li$_2$IrO$_3$ with $\alpha_{12}$ percentages of 100% (a), 82% (b), 58% (c) and 33% (d) produced using DIFFaX along [1 1 0] based on C2/m symmetry. Note that for hkl with $h-k=3n$ no streaking is observed ................................................................. 81

Figure 3.12: SAED patterns for Li$_2$IrO$_3$ (a) and Li$_2$PtO$_3$ (b) prepared at 750 °C along [1 1 0]. Streaking is observed in [0 0 1]* direction for $h-k \neq 3n$ reflections ................................................................. 82

Figure 3.13: SAED patterns for a given sample of Li$_2$IrO$_3$ prepared at 900 °C both highly faulted crystals (a) and less faulted crystals (b) are observed ................................................................. 83

Figure 3.14: Powder X-ray diffraction pattern and Faults refinement for Li$_2$IrO$_3$ (a) and Li$_2$PtO$_3$ (b) prepared at 750 °C: observed (•), calculated (red), and difference (green) profiles. Tick markers indicate the Bragg reflection positions ................................................................. 85

Figure 3.15: Powder X-ray diffraction pattern and Rietveld refinement for Li$_2$IrO$_3$ (a) and Li$_2$PtO$_3$ (b) prepared at 900 °C: observed (•), calculated (red), and difference (green) profiles. Tick markers indicate the Bragg reflection positions ................................................................. 86

Figure 3.16: Powder X-ray diffraction pattern and Rietveld refinement for Li$_2$IrO$_3$ (a) and Li$_2$PtO$_3$ (b) prepared at 1050 °C: observed (•), calculated (red), and difference (green) profiles. Tick markers indicate the Bragg reflection positions ................................................................. 87

Figure 3.17: A plot of OP(Rietveld) derived from $\alpha_{12}$ (%) layer transition probability versus OP(Faults) derived from $M$ occupancy ($M=Ir, Pt$) obtained from refinements is presented. Calibration curve obtained via Rietveld refinement of DIFFaX simulations ................................................................. 93

Figure 4.1: Li$_2$MnO$_3$ structure showing the layered arrangement alternating between pure lithium and mixed metal, LiMn$_2$, layers (a), the linear lithium channels through the LiMn$_2$ layers (b) and stacking
of the LiMn$_2$ layers themselves, with oxygen and pure lithium layers omitted for clarity (c). ................................................................. 99

**Figure 4.2:** $\beta$-Li$_2$SnO$_3$ structure showing the layered arrangement alternating between pure lithium and mixed metal, LiSn$_2$, layers (a), the undulating, zig-zaging, lithium channels through the LiSn$_2$ layers (b) and stacking of the LiSn$_2$ layers themselves, with oxygen and pure lithium layers omitted for clarity (c). ................................................................. 100

**Figure 4.3:** Li$_2$ZrO$_3$ structure showing the layered arrangement solely composed of mixed metal, Li$_2$Zr, layers (a), the edge sharing ZrO$_6$ octahedra passing through the Li$_2$Zr layers (b) and stacking of the Li$_2$Zr layers themselves, with oxygen layers omitted for clarity (c). ...... 101

**Figure 4.4:** Plots of $M^{4+}$ Ionic radii versus d-electron count for the metals observed to occur in the Li$_2$MO$_3$ ordered rock salt structure. ................................................................. 104

**Figure 4.5:** Plot of $M^{4+}$ Ionic radii versus electronegativity (Pauling) for the metals observed to occur in the Li$_2$MnO$_3$, $\beta$-Li$_2$SnO$_3$, and Li$_2$ZrO$_3$ structure types. ................................................................. 104

**Figure 4.6:** LiRu$_2$ layer of Li$_2$RuO$_3$ C2/m symmetry (a) and P2$_1$/m symmetry (b). ......................................................................................................................... 106

**Figure 4.7:** Energy level diagram for Ru$^{4+}$-Ru$^{4+}$ dimers, where the electrons and there spins are presented by arrows. ................................................................. 107

**Figure 4.8:** Lattice energy per formula unit incorporating Mn, Sn, and Zr into Li$_2$MnO$_3$, Li$_2$SnO$_3$, and Li$_2$ZrO$_3$ structure types. ................................................................. 110

**Figure 4.9:** Total energy calculations incorporating Mn, Sn, Zr and Pb into the Li$_2$MnO$_3$, Li$_2$SnO$_3$, and Li$_2$ZrO$_3$ structure types. $\Delta$ Energy is the difference between the respective structure type and the highest energy structure type per formula unit.................................................. 112

**Figure 4.10:** Plot of energy difference per formula unit between P2$_1$/m and C2/m ($E_{P21/m}$-$E_{C2/m}$) versus respective group number. ........................................... 116

**Figure 4.11:** Plot of $M^{4+}$-$M^{4+}$ distances versus respective group number.............. 117

**Figure 4.12:** Experimental and simulated powder X-ray diffraction patterns for Li$_2$RuO$_3$ (a) and Li$_2$IrO$_3$ (b). Simulated patterns generated from C2/m and P2$_1$/m structures obtained with CASTEP geometry optimizations. Arrows indicate peaks associated with P2$_1$/m superstructure................................................................. 119
Figure 4.13: Plot of average $M^{t+} - M^{t+}$ distances versus average $M^{t+} - O$ distances for the most stable geometry optimized Li$_2$MO$_3$ structures.
## LIST OF SYMBOLS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
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<td>Density of States</td>
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</tr>
<tr>
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<td>electron-volts</td>
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<td>General Utility Lattice Program</td>
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<td>High resolution transmission electron microscopy</td>
</tr>
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<td>$M_{occ}$</td>
<td>Fractional occupancy of $M1$ site with $M$, balance of lithium</td>
</tr>
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<td>Mössbauer spectroscopy</td>
</tr>
<tr>
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<td>Nuclear magnetic resonance</td>
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<tr>
<td>PXRD</td>
<td>Powder X-ray Diffraction</td>
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<td>SAED</td>
<td>Selected Area Electron Diffraction</td>
</tr>
<tr>
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<td>Super conducting quantum interference device</td>
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<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
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<tr>
<td>$Z$</td>
<td>Formula units per cell</td>
</tr>
<tr>
<td>$\alpha_{ij}$</td>
<td>Transition vector probability between layers $i$ and $j$</td>
</tr>
</tbody>
</table>
CHAPTER 1

AN INTRODUCTION TO ALKALI PLATINUM GROUP METAL OXIDES

1.1 Background

The occurrence of alkali platinum group metal oxides (APGMOs) was first observed in 1953 during a study of the conductivity of molten salts [1]. In this study Li₂O was melted in platinum crucibles to determine its conductivity, but at elevated temperatures the lithium oxide readily reacted with the platinum. The initial assumption was that a lithium-platinum alloy was produced. Subsequent studies performed by Scheer et al. later determined the product to be the ordered rock salt structure of Li₂PtO₃, the first anhydrous platinum group metal oxide [2]. In addition to Li₂PtO₃, a number of other APGMOs were described during the initial work of Scheer and are presented with their lattice constants in Table 1.1. The structures presented in Table 1.1 are presented as monoclinic, but at the time these structures were also reported to potentially be pseudo-orthorhombic with a unit cell three times as large as the monoclinic unit cells presented.


<table>
<thead>
<tr>
<th></th>
<th>Na$_2$PtO$_3$</th>
<th>Na$_2$IrO$_3$</th>
<th>NaRhO$_2$</th>
<th>Li$_2$PtO$_3$</th>
<th>Li$_2$RhO$_3$</th>
<th>LiRhO$_2$</th>
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<td>a (Å)</td>
<td>5.39</td>
<td>5.39</td>
<td>5.34</td>
<td>5.17</td>
<td>5.12</td>
<td>5.23</td>
</tr>
<tr>
<td>b (Å)</td>
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<td>9.33</td>
<td>9.22</td>
<td>8.96</td>
<td>8.87</td>
<td>9.07</td>
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<tr>
<td>c$_{rh}$ (Å)</td>
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<td>31.11</td>
<td>28.86</td>
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<tr>
<td>c$_{mo}$ (Å)</td>
<td>10.71</td>
<td>10.68</td>
<td>10.32</td>
<td>9.77</td>
<td>9.73</td>
<td>9.66</td>
</tr>
<tr>
<td>β</td>
<td>99.67°</td>
<td>99.68°</td>
<td>99.73°</td>
<td>100.17°</td>
<td>100.10°</td>
<td>100.37°</td>
</tr>
</tbody>
</table>

$rh$ = orthorhombic; $mo$ = monoclinic

Table 1.1: Lattice parameters of various APGMOs [2].

At this early stage in the history of APGMOs the space groups and the debate between pseudo-orthorhombic and truly orthorhombic was left undetermined. Despite lacking a space group assignment, it was clear that these structures were ordered rock salt in nature possessing a cubic close packing of oxygen ions with the metals filling the octahedra interstitial positions. Also in this study was the first report of Na$_x$Pd$_3$O$_4$ and Na$_x$Pt$_3$O$_4$ where the palladium and platinum structures were reported to be cubic ($a = 5.67$ and $5.64$ Å, respectively). However rather than the palladium and platinum occupying octahedra sites they are now observed to occur at the center of a square planar Pdo$_4$ and PtO$_4$ groups, which likely results from the transition to the 2+ oxidation state. Details on the exact sodium content were not reported, yet based on more recent work the structures were likely near stoichiometric NaPt$_3$O$_4$ and NaPd$_3$O$_4$, ($x = 1$) [3].

Ultimately, the correct crystal system of the Li$_2$PtO$_3$ type structures was determined to be monoclinic. Using high resolution X-ray diffraction (XRD) Kobayashi was able to
Figure 1.1: Structural comparisons for ordered rock salt structures from MgO (a), with \textit{Fm\overline{3}m} symmetry, to LiCoO$_2$ (b), with \textit{R\overline{3}m} symmetry, to Li$_2$RuO$_3$ (c), with \textit{C\overline{2}/m} symmetry. Note that in all cases the average oxidation state of the metal sites remains +2.
observe a shoulder on a peak centered between 93° and 97° 2θ [4]. The shoulder can only be observed at very high resolution and only if the crystal system is monoclinic. However, these structures are still derived from the rock salt structure.

1.2 **Crystal Structure of Alkali Platinum Group Metal Oxides**

A majority of APGMOs contain a layered structure that can be derived from the rock salt structure, as shown in Figure 1.1. The APGMOs are most easily derived from the ordered rock salt structure of LiCoO₂, Figure 1.1b, examples include the well known lithium ion cathode materials LiCoO₂ and LiNiO₂. These structures all possess cubic close packing of oxygen ions as well as cation layers that alternate between pure Li⁺ or Na⁺ and layers with varying transition metal composition.

The APGMO structures, contain cation layers that alternate between alkali metal (A = Li, Na) layers and mixed cation layer composed of A and the platinum group metal, M. The composition of the mixed layers depends on the system; currently known compositions of mixed metal layers include AM₂, AM, and A₂M for the A₂MO₃, A₃MO₄, and A₈MO₆ systems respectively, to be discussed in greater detail below. The difference between these structures occurs due to a change in composition of the mixed metal layers and in a change in the relative position of the mixed metal layers with respect to each other. It is via these changes that all the APGMOs form their varying structures. Additionally, coordination of the platinum group metals in these structures is typically
Figure 1.2: The $A_2MO_3$ structure type is represented depicting the alternating layers of pure $A$ and $AM_2$ using $Li_2RuO_3$ (a). Additionally, structure of a single $AM_2$ is also presented (b).
octahedral, $MO_6$. It is this octahedral coordination that is most commonly observed in the mixed layered structures. Other systems exist for APGMOs that contain both square planar coordination and trigonal bipyramidal coordination, to be discussed below.

### 1.2.1 Crystal Structure of $A_2MO_3$ Structures

The $A_2MO_3$ structures are composed of pure alkali metal layers ($A = Li, Na$) and mixed metal layers of $AM_2$ these layers are separated by cubic close packing oxygen layers, shown in Figure 1.2a for Li$_2$RuO$_3$ [6]. The mixed metal layers are what truly make this system interesting and an example of such a layer, from Li$_2$RuO$_3$, is presented in Figure 1.2b. The $AM_2$ layers are composed of edge sharing $MO_6$ octahedra that are arranged in a 2-dimensional hexagonal network. The centers of these resulting hexagons contain a single $A^+$ ion.

The APGMO systems that have been reported to have this structure include: Li$_2$RuO$_3$ [6]-[9], Li$_2$RhO$_3$ [2], Li$_2$PdO$_3$ [10], Li$_2$IrO$_3$ [4],[10],[11], Li$_2$PtO$_3$ [2],[5],[10], Na$_2$RuO$_3$ [12],[13], Na$_2$PdO$_3$ [14], Na$_2$IrO$_3$ [2],[10],[15], and Na$_2$PtO$_3$ [2],[15]-[17]. Li$_2$RhO$_3$ and Li$_2$PdO$_3$ have only been reported once and in each case with little supporting evidence, likely due to the unstable +4 oxidation state of rhodium and palladium. Most of the previously mentioned systems have been determined using either X-ray or neutron structure refinements, while only unit cell parameters were reported for Li$_2$RhO$_3$ and Li$_2$PdO$_3$ and was reported to be isostructural with the $A_2MO_3$ structures.
The $A_2MO_3$ structures are composed of layers and it is the variation in position of the mixed metal layers with respect to the neighboring mixed metal layers that allows for variation in the crystal structure. Two such structures are known to exist, the $\text{Li}_2\text{MnO}_3$ structure [18] and the $\beta$-$\text{Li}_2\text{SnO}_3$ structure [19]. The mixed metal layers, LiMn$_2$, of the $\text{Li}_2\text{MnO}_3$ structure stack in along $[1/2 0 1/2]$ with $C2/c$ symmetry, producing a linear chain of Li$^+$ sites between successive LiMn$_2$ layers, seen in Figure 1.3a. On the other hand, the mixed metal layers, LiSn$_2$, of the $\beta$-$\text{Li}_2\text{SnO}_3$ structure stack along $[0 \pm 1/6 1/2]$ with $P2_1/m$ symmetry, resulting in an undulating chain of Li$^+$ sites between successive layers parallel to the c-axis, seen in Figure 1.3b. These Li$^+$ chains or channels may prove to be of central importance when considering ionic conductivity in polycrystalline samples. Therefore, it is vital to understand the exact stacking sequence of the given structures.
Figure 1.4: Qualitative energy-level diagram for the $t_2$ manifold of Ru$^{4+}$ (4d$^4$) ions in Li$_2$RuO$_3$ [8] reproduced by permission of Elsevier.

The crystal structure and stacking sequence in Li$_2$RuO$_3$ is agreed upon in the literature to be isostructural with Li$_2$MnO$_3$ rather than $\beta$-Li$_2$SnO$_3$, thus having the [1/2 0 1/2] shift between mixed layers [8], [9]. James and coworkers attributed this preferred structure of Li$_2$RuO$_3$, and subsequently other $A_2MO_3$ systems, to long range orbital interaction from the ruthenium atoms in the layers above and below a given layer. Figure 1.4 depicts the orbital splitting which results from the short range octahedra environment as well as a long range trigonal distortion (splitting) that occurs at a given ruthenium site. James argues that the partial occupancy of the a$_1$ orbital allows for Ru-Ru interaction to occur perpendicularly to the mixed metal layers. Thus inter-layer interactions drive the formation of these structures rather than intra-layer interactions as intra-layer interactions are equivalent between these two structure types. It is mentioned that while these inter-layer interactions maybe weak as a result of being separated by an additional lithium layer, they are strong enough to stabilize the Li$_2$RuO$_3$ into its given structure.
There is not the same level of agreement in the literature concerning the structure of Li$_2$IrO$_3$ as there is for Li$_2$RuO$_3$. James and coworkers state that Li$_2$IrO$_3$ possess the $\beta$-Li$_2$SnO$_3$ structure and justify this using the same analysis as was used for Li$_2$RuO$_3$ [8]. In the case of Li$_2$IrO$_3$ the a$_1$ orbital, as depicted in Figure 1.4, would be filled thereby preventing the structure from having the long range interaction seen in Li$_2$RuO$_3$. These results are said to verify the $\beta$-Li$_2$SnO$_3$ structure of Li$_2$IrO$_3$ as reported by Lazarev and coworkers [20], but their results do not describe the structural parameters or the stacking sequence. The system as described by Lazarev and coworkers simply describes the unit cell parameters, but since both proposed structures are of C2/c (15) symmetry with similar lattice parameters, a unit cell refinement is not sufficient. The Na$_2$PtO$_3$ structure was also described to be $\beta$-Li$_2$SnO$_3$ by James based on orbital analysis and work by Scheer [2]. Scheer and coworkers described the unit cell parameters of Na$_2$PtO$_3$ and do not mention the layer stacking or structural similarity to $\beta$-Li$_2$SnO$_3$, so there was limited experimental evidence that the stacking found in Na$_2$PtO$_3$ is of the $\beta$-Li$_2$SnO$_3$ type.

The structural parameters for $\beta$-Li$_2$SnO$_3$, Li$_2$RuO$_3$, and Li$_2$IrO$_3$ are reported in Table 1.2. The structural parameters seem to indicate that Li$_2$IrO$_3$ does not possess the $\beta$-Li$_2$SnO$_3$ structure, but rather possess the Li$_2$MnO$_3$ structure type. The explanation for the Li$_2$IrO$_3$ structure to possess the $\beta$-Li$_2$SnO$_3$ structure seems insufficient since the correct structure is that of Li$_2$MnO$_3$ as such a better understanding of these varying systems needs to be obtained in order to explain the structural characteristics of these $A_2MO_3$ systems.
Table 1.2: Structural parameters for $\beta$-Li$_2$SnO$_3$ (a), Li$_2$RuO$_3$ (b), and Li$_2$IrO$_3$ (c) with space group $C2/c$ (15).
1.2.2 Crystal Structure of $A_8MO_6$

Only four structures of the composition $A_8MO_6$ have been produced: Li$_8$RuO$_6$ [22], Li$_8$IrO$_6$ [23], Li$_8$PtO$_6$ [23], and Na$_8$PtO$_6$ [16]. Based on single crystal X-ray diffraction Li$_8$IrO$_6$ and Li$_8$PtO$_6$ were found to have a symmetry of R3 with $a = 5.4151(6)$ Å and $c = 15.058(4)$ Å and $a = 5.4146(2)$ Å and $c = 15.014(1)$ Å, respectively [23]. An example of a mixed metal layer for a given $A_8MO_6$ structure, Li$_8$IrO$_6$, composed of $A_2M$, is provided in Figure 1.5a. It is very clear from Figure 1.5 that the MO$_6$ octahedra in the $A_8MO_6$ systems are isolated. The result of this is loss of interactions between the platinum group metal centers, such as magnetic ordering and electronic conductivity. Also the isolated octahedra are surrounded by AO$_6$ octahedra, thus any structural stability the system has, would be lost upon any substantial degree of ion extraction such as de-lithiation. Additionally, the mixed layers stack in an ABC type sequence in the $c$-direction, consistent of cubic close packing of the oxygen ions. However unlike the $A_2MO_3$ systems the lithium sites in the pure lithium layer do not occupy octahedral sites, rather they occupy the tetrahedral sites, as seen in Figure 1.5b. As there are twice as many tetrahedral sites compared to octahedral sites these lithium layers results in the addition of 6 $A$ ions rather than the 3 expected based on octahedral coordination.

Na$_8$PtO$_6$ was determined to be tetragonal with $a = 7.965$ Å and $c = 4.053$ Å [16]. The Na$_8$PtO$_6$ structure possesses chains of corner sharing PtO$_6$ octahedra that run parallel to the $c$-axis, while the sodium ions are located in highly distorted octahedral environments with Na-O bond lengths from 1.80 Å to 2.97 Å. It is also worth noting that the platinum
Figure 1.5: An $ab$ plane projection of Li$_8$IrO$_6$ mixed layer, $A_2M$, including $MO_6$ octahedra (a) and a projection depicting the tetrahedral coordination of lithium within the pure lithium layer (b).
Figure 1.6: The structure of Li$_3$RuO$_4$ is presented showing the layering (a) as well as the $bc$ plane projection of a LiRu mixed metal layer, including RuO$_6$ octahedra (b) [24].

sites are reported to be half occupied in order to retain stoichiometry. The Li$_8$RuO$_6$ structure is reported to be tetragonal with $a = 5.372$ Å and $c = 14.88$ Å by Shaplygin and coworkers [22]. However seeing as only lattice parameters have been reported for this system, these results should be taken with caution.

1.2.3 Crystal Structure of A$_3$MO$_4$

The A$_3$MO$_4$ structure has only been observed for one APGMO system, Li$_3$RuO$_4$ [24]. This structure type requires the platinum group metal to possess a +5 oxidation state, which is not likely for platinum group metals other than ruthenium and the likely reason for the observation of only one A$_3$MO$_4$ structure for APGMOs. The structure of the mixed metal layer for Li$_3$RuO$_4$, composed of LiRu, is depicted in Figure 1.6. These mixed metal layers are composed of undulating chains of edge sharing RuO$_6$ octahedra.
that stack in a chain over chain type manner between the mixed metal layers. This system has a unit cell of $P2/\alpha$ symmetry with $a = 5.1057(1)$ Å, $b = 5.8545(1)$ Å, $c = 5.1062(1)$ Å, and $\beta = 110.039(1)^\circ$ [24]. The structural parameters were determined via refinement of neutron powder diffraction data.

1.2.4 Other APGMO Crystal Structures

1.2.4.1 NaRhO$_2$ and LiRhO$_2$

NaRhO$_2$ and LiRhO$_2$ structural parameters have been reported by Hoppe and coworkers. These structures have been reported to possess unit cells of $R\bar{3}m$ symmetry with $a = 3.0971(4)$ Å and $c = 15.528(3)$ Å for NaRhO$_2$ [25] and $a = 3.02$ Å and $c = 14.3$ Å for LiRhO$_2$ [26]. These structures are isostructural with the previously discuss LiCoO$_2$ structure type. LiRhO$_2$ has also been reported to possess $Fd\bar{3}m$ symmetry with $a = 8.4127(6)$ Å for LiRhO$_2$ [27]. The $Fd\bar{3}m$ structure contains a 3-dimensional network of edge sharing octahedra while retaining an ordered rock salt structure. However, unlike previous structures this system does not possess pure lithium layers rather all cation layers are fifty percent Li and fifty percent Rh, resulting in the observed 3-dimensional network, not a 2-dimensional hexagonal network. Previous work by Lazarev also stated that NaRhO$_2$ was rhombohedral with similar unit cell dimensions, but also stated that LiRhO$_2$ was also rhombohedral with $a = 2.643$ Å and $c = 14.213$ Å [20]. The peaks as listed by Lazarev and coworkers are pretty similar to those reported by Hoppe and thus these structures are likely identical, with slight variations in unit cell refinement.
1.2.4.2 **Na₂PdO₂ and Na₂PtO₂**

The structure of Na₂PtO₂ has been reported by Urland and coworkers to be of *Immm* symmetry with \( a = 4.585 \, \text{Å} \), \( b = 3.119 \, \text{Å} \) and \( c = 9.588 \, \text{Å} \) [17], the structural parameters were also determined by performing refinements of XRD data. Structural parameters have not been determined for Li₂PdO₂, but the unit cell parameters are reported to be \( a = 3.077 \, \text{Å} \), \( b = 10.359 \, \text{Å} \) and \( c = 8.351 \, \text{Å} \) all within an orthorhombic system [14]. Very little has been reported on these structures other than their unit cells and structural parameters in the case of Na₂PtO₂.

1.2.4.3 **Na₄IrO₄ and Na₄PtO₄**

The Na₄IrO₄ structure was prepared by an “exchange reaction,” using Li₂IrO₃ and Na₂O as reagents, in a silver ampoule at 800°C for 71 days [28]. Mader and coworkers report the structure to be tetragonal, *I4/m*, with \( a = 7.1670(4) \, \text{Å} \) and \( c = 4.7132(4) \, \text{Å} \). The Na₄IrO₄ structure contains square planar IrO₄ groups, rather than the IrO₆ octahedral groups that have been seen previously seen in most of our APGMOs. The only report of the Na₄PtO₄ structure is from Hauck and solely reports the structure to be cubic with \( a = 4.52 \, \text{Å} \) [16].

1.2.4.4 **NaPt₃O₄ and Na₂Pd₃O₄**

The NaPt₃O₄ structure contains layers of PtO₄ square planar groups and a symmetry of *Pm3n* with \( a = 5.6868(2) \, \text{Å} \) [29]. The Na₂Pd₃O₄ structure was first reported to occur by McDaniel [15] and later confirmed by Lazarev and coworkers [20], and the structural
parameters were first reported by Wilhelm and Hoppe [30]. The structure of Na$_2$Pd$_3$O$_4$ is composed of Pd$_3$O$_4$ double-layers that are normal to [0 0 1]. These layers are then connected via trigonal prismatic coordination by sodium. The driving force to form square planar PtO$_4$ and PdO$_4$ groups is likely caused by the +2 oxidation states, as the d$^8$ configuration for these metals will prefer a square planar environment rather than an octahedral coordination.

1.2.4.5 Na$_2$RuO$_4$ and NaRh$_2$O$_4$

The Na$_2$RuO$_4$ structure was prepared using traditional solid state techniques and contains a new structure type composed of chains of RuO$_5$ trigonal bipyramids [31]. The connectivity of the chains can be visualized in Figure 1.7. Structural parameters have
been determined and the monoclinic unit cell has a symmetry of $P2_1/n$ with $a = 10.7098(1)$ Å, $b = 7.0356(1)$ Å, $c = 10.9253(2)$ Å, and $\beta = 119.67(1)^\circ$. Similar results were also reported by Mogare and coworkers for the Na$_2$RuO$_4$ structure [13].

The NaRh$_2$O$_4$ structure also has an unusual alignment of the metal oxide polyhedra. The NaRh$_2$O$_4$ structure belongs to the space group $Pnma$ with $a = 2.0026(4)$ Å, $b = 3.0461(2)$ Å, and $c = 10.7268(5)$ Å [32]. The structure contains double chains of octahedra that are edge sharing and are two octahedra wide. These chains are then connected to each other via a corner sharing oxygen. The result of these bands, double chains, is the presence or highly ordered channels of Na$^+$ ions. The structure can be viewed in Figure 1.8. The mixed valent nature of this system, Rh$^{3+}$ and Rh$^{4+}$, results in metallic conductivity, which is lost upon replacing Na$^+$ with Ca$^{2+}$ causing all the rhodium sites to be in the 3+ oxidation state [32].

### 1.3 Electrochemical Properties of Alkali Platinum Group Metal Oxides

Materials such as LiCoO$_2$ and LiNiO$_2$ are currently used as lithium ion conductors [33]. The structural similarities between the APGMOs and the LiMO$_2$ systems results in the logical extension into investigations both of the electronic and ionic conductivity of the APGMOs. The ionic conductivity can also be considered in parallel with de-lithiation as it is affected by ionic conductivity.
1.3.1 Electronic Conductivity of APGMO Structures

James and coworkers predict the conductivity of a number of $A_2MO_3$ structures using a simple semi-empirical band model [8]. It is this model that generated the band model presented in Figure 1.4. The cutting of the $a_1$ band is said to be the cause of the metallic conductivity observed in Li$_2$RuO$_3$ [20]. Table 1.3 presents the nature of electrical conductivity in a number of APGMO systems. The semi-empirical band model was also used to validate the metallic conductivity of Li$_2$IrO$_3$ and the semiconducting character of Na$_2$PtO$_3$ [8].

**Figure 1.8:** Structure of NaRh$_2$O$_4$ (a) along with the double chain along the $b$-axis (b).
Table 1.3: Electronic conductivity of the mixed metal oxides of the platinum metals and the electronic configuration of the platinum group metals [20].

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formal oxidation state</th>
<th>Electronic configuration</th>
<th>Nature of the electrical conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiRhO$_3$</td>
<td>+3</td>
<td>d$^6$</td>
<td>Semiconducting</td>
</tr>
<tr>
<td>NaRhO$_3$</td>
<td>+3</td>
<td>d$^6$</td>
<td>Semiconducting</td>
</tr>
<tr>
<td>Na$_2$PtO$_3$</td>
<td>+4</td>
<td>d$^6$</td>
<td>Semiconducting</td>
</tr>
<tr>
<td>Na$_2$Pd$_3$O$_4$</td>
<td>+2</td>
<td>d$^8$</td>
<td>Semiconducting</td>
</tr>
<tr>
<td>Li$_2$RuO$_3$</td>
<td>+4</td>
<td>d$^4$</td>
<td>Metallic</td>
</tr>
<tr>
<td>Li$_2$IrCl$_3$</td>
<td>+4</td>
<td>d$^5$</td>
<td>Metallic</td>
</tr>
<tr>
<td>Na$_2$IrO$_3$</td>
<td>+4</td>
<td>d$^5$</td>
<td>Metallic</td>
</tr>
</tbody>
</table>

The metallic character of Li$_2$RuO$_3$ as reported by both James and Lazarev is contradicted by Kobayashi and coworkers [9], who state that Li$_2$RuO$_3$ is semiconducting. The semiconducting character obtained by Kobayashi could have been based on grain boundary interactions rather than the property of the bulk material. However, as the percent theoretical density was not given the actual cause for this deviation is not clear. In the case the grain boundary interactions were dominant a metallic system may appear to be a semi-conductor. Kobayashi and coworkers also determined the electrical conductivity of the de-lithiated species Li$_{1.3}$RuO$_3$ and Li$_{1.6}$RuO$_3$ to both be semiconducting, but once again theoretical densities were not provided.
1.3.2 Experimental Delitiation of $A_2MO_3$ and Electrical Properties of the Delithiated Structures

Two methods of de-lithiation have been employed by Kobayashi and coworkers: electrochemically [9] and chemically using I$_2$ in CH$_3$CN [6]. The electrochemical method starts with a pellet consisting of approximately 100 mg of Li$_2$RuO$_3$, 10 mg acetylene black, and 0.1 mg Teflon powder while the lithium counter electrode is made of lithium metal foil. The two electrodes were separated by a micro-porous poly-propylene sheet. The chemical method uses a chemical treatment of I$_2$ at room temperature for 14 days. After the reaction the products were washed and filtered using CH$_3$CN.

The two different methods of de-lithiation result in slightly different ratios within the single phase products. The electrochemical method produces Li$_{1.4}$RuO$_3$ and Li$_{0.9}$RuO$_3$, while the chemical method produces Li$_{1.3}$RuO$_3$ and Li$_{1.0}$RuO$_3$. The XRD patterns for the varying structures are depicted in Figure 1.9, where Figure 1.9a also depicts the multiphase regions. Structural parameters for the single phase regions have also been determined.

The Li$_{1.4}$RuO$_3$ structure is reported to have $C2/c$ symmetry with $a = 4.9398(6)$ Å, $b = 8.6271(10)$ Å, $c = 9.9353(8)$ Å and $\beta = 99.262(9)^o$ and Li$_{0.9}$RuO$_3$ is reported to have $R3$ symmetry with $a = 5.1016(5)$ Å and $c = 14.0301(17)$ Å [9]. Structural parameters are very similar for Li$_{1.4}$RuO$_3$ and Li$_2$RuO$_3$ thereby indicating that the overall structure is retained upon de-lithiation, which is ideal when considering use in lithium ion batteries.
Figure 1.9: The XRD patterns for Li$_{2-x}$RuO$_3$ deintercalated by electrochemical means (a) and chemical means (b) [6],[9] reproduced by permission of Elsevier.
The charge and discharge characteristics of Li$_2$RuO$_3$ were studied and show no significant degradation after ten cycles, as seen in Figure 1.10. Also seen is the similarity in the charge and discharge curves which indicates a low overvoltage for the electrode process. The plateaus observed at 3.4 and 3.6 V are indicative of the multiphasic reactions. The lattice parameters experience no change even after the tenth cycle. The highly reversible system is a result of the tightly composed mixed layers of LiRu$_2$.

Similar charge-discharge analyses have been performed for Li$_2$IrO$_3$ and Li$_2$PtO$_3$ [4],[5],[34]. The Li$_2$IrO$_3$ system shows an excellent cycle retention rate of 98.7% in the 25$^{th}$ cycle within the voltage range of 3.0-4.2 V with a current density of
0.5 mA cm$^{-2}$ with a discharge capacity of 97 mA h g$^{-1}$ [34]. The mechanism of de-lithiation for Li$_2$IrO$_3$ differs from that of Li$_2$RuO$_3$ in that the ruthenium structure cycles through a monoclinic phase ($C2/c$) to a rhombohedral phase ($R3$), while the Li$_{2-x}$IrO$_3$ phase passes directly to an orthorhombic phase as the lithium composition approaches one. The mechanism of de-lithiation along with a varying degree of ordering found within the LiIr$_2$ layer itself variations in effects upon charge-discharge cycling are observed [34].

The interest in Li$_2$PtO$_3$ is based on its ability to act as a 4 V electrode and remain stable for at least 50 cycles. Also of interest is that Li$_2$PtO$_3$ has a larger volumetric capacity compared to LiCoO$_2$ as seen in Figure 1.11. In Figure 1.11 it is seen that the gravimetric
capacity of Li$_2$PtO$_3$ is not significant, but its volumetric capacity is noticeably larger than that of LiCoO$_2$ [5]. Thus in applications were space is more of an issue than weight, such as in solid state microbatteries, a material such as this may be preferred.

1.4 **Magnetic Properties of Alkali Platinum Group Metal Oxides**

The APGMOs all have potentially interesting magnetic properties due to their varying numbers of d-electrons. The number of d-electrons varies from 6 in the case of Pt$^{4+}$ down to 3 in the case of Ru$^{5+}$. A large majority of these structures possess MO$_6$ octahedra, in varying arrangements including hexagonally connected octahedra and undulating chains of edge sharing octahedra, as discussed previously. The occurrence of these octahedra causes an octahedral crystal field splitting that results in splitting the d-orbitals thereby generating sets of e$_g$ and t$_{2g}$ orbitals, while the connectivity of the MO$_6$ octahedra may potentially lead to varying degrees of magnetic interaction.

1.4.1 **Curie-Weiss Paramagnetism of Li$_2$MO$_3$ (M=Ru,Ir)**

Li$_2$RuO$_3$ and Li$_2$IrO$_3$ are both Curie-Weiss paramagnetic [4],[6]. Figure 1.12 presents the magnetization curves of these structures, which clearly indicates that Li$_2$IrO$_3$ is paramagnetic down to 5 K. Li$_2$RuO$_3$ is also paramagnetic yet a cusp is located near 63 K, potentially due to magnetic ordering [35].
Figure 1.12: Magnetization curves of the paramagnetic Li$_2$MO$_3$ ($M$ = Ru and Ir) [35] reproduced by permission of Elsevier.

Figure 1.13: Mössbauer spectroscopy at 4.1 K for 1% Fe doped Li$_2$RuO$_3$ [35] reproduced by permission of Elsevier.
Using Mössbauer spectroscopy (MS), Felner and coworkers investigated ruthenium’s magnetic environment by placing iron atoms at 1% of the ruthenium sites. If iron is in an antiferromagnetic (AFM) environment its nuclei will experience a magnetic hyperfine field which will result in a sextet in the MS spectra. In the absence of an AFM environment there will be no splitting due to a magnetic hyperfine field thereby resulting in a singlet. The singlet observed in Figure 1.13 indicates that the system in still paramagnetic even down to 4.1 K. As a result the cusp at 63 K cannot be due to AFM ordering.

Based on the magnetic measurements the number of unpaired electrons can be determined based on plots of $1/\chi$ (inverse magnetic susceptibility) versus temperature. The slope of the paramagnetic region is equivalent to $1/C$, where $C$ is the curie constant. Using this method the effective moments for Li$_2$RuO$_3$ have been reported to range from $1.83\mu_B$ to $2.68\mu_B$, which corresponds to 1.09 unpaired electrons to 2.00 unpaired electrons per Ru atom [6],[8],[35]. One reason for the variation in the number of unpaired electrons could be a result of the experimental methods used. James and coworkers employed a method that uses a Faraday balance to determine the magnetic moment, while Felner et al. and Kobayashi et al. performed their experiments using a superconducting quantum interference device (SQUID) magnetometer [8],[9],[35]. Yet despite using the same experimental method Kobayashi and Felner arrive at different values, 1.36 and 2.00 unpaired electrons respectively. In an octahedral environment one would expect Ru$^{4+}$ to be low spin and possess 2 unpaired electrons, which is presented by
James et al., yet the number of unpaired electrons located on the ruthenium centers is still not resolved.

The magnetic properties of the Li$_2$IrO$_3$ structure are much less debated in the literature with effective moments of 1.73$\mu_B$ to 1.9$\mu_B$ being reported, thereby indicating the presence of 1.0 to 1.15 unpaired electrons [6],[35]. A lone unpaired electron is expected from a d$^5$ metal in a low spin octahedral environment such as Ir$^{4+}$, thus theoretical expectations are in agreement with the experimental results.

1.4.2 Antiferromagnetic Ordering of Li$_3$RuO$_4$

As discussed previously, the undulating chains of Li$_3$RuO$_4$ are composed of edge sharing octahedra. A result of the edge sharing in Li$_3$RuO$_4$ is the AFM ordering that occurs at $\sim$50 K [24]. The plot of magnetic susceptibility versus temperature clearly shows a maximum at approximately 50 K, as seen in Figure 1.14.

There are 3 potential methods of AFM ordering in this structure: intra-chain, ordering, inter-chain ordering, and layers of chains ordering. Based on the lack of magnetic Bragg scattering in low temperature neutron diffraction experiments long range magnetic ordering can be ruled out [24]. The lack of long range ordering indicates intra-chain ordering is likely, with negligible interaction occurring between chains and between successive layers.
The Curie constant, as determined from the inverse susceptibility plot seen in the Figure 1.14 insert, is 1.7605(5) cm$^3$ K mol$^{-1}$ [24]. The Curie constant is in agreement with the calculated spin only Curie constant for a 4d $t_{2g}^3$ metal such as Ru$^{5+}$ in an octahedral environment, 1.875 cm$^3$ K mol$^{-1}$. The slight variation from the calculated value is expected since a tendency towards spin-orbit coupling prevents the system from being spin-only. The spin orbit coupling will result in a decreased Curie constant, which is observed. Also from the inverse susceptibility plot, a Weiss constant, $\theta$, of -137 K is observed, a clear indication of antiferromagnetic interactions [24].
1.5 Conclusions

The APGMOs may possess a large number of possible structure types, but they do tend to form $A_2MO_3$ type structures, that can be derived from a rock salt type ordering more readily than others. Structures that have the $A_2MO_3$ ratio include the following: $Li_2RuO_3$, $Li_2PdO_3$, $Li_2IrO_3$, $Li_2PtO_3$, $Na_2RuO_3$, $Na_2IrO_3$, and $Na_2PtO_3$. The $A_2MO_3$ structures may contain one of two possible structures that differ only in the stacking of the $AM_2$ mixed layers, which form a hexagonal network of edge sharing $MO_6$ octahedra. Either the $\beta$-$Li_2SnO_3$ or the $Li_2MnO_3$ structure may occur with a mixed layer shift of $[0, \pm1/6, 1/2]$ and $[1/2, 0, 1/2]$, respectively. Other APGMO structures possess structural similarities to that of the $A_2MO_3$ such as $A_3MO_4$ and $A_8MO_6$ which contain undulating chains of edge sharing octahedra and isolated octahedra within the mixed metal layers respectively. A number of other structures have also been synthesized from various combinations of the alkali and platinum group metals.

Due to the connectivity of the $MO_6$ octahedra in a number of these structures, $A_2MO_3$, in particular, metallic conductivity may occur. The only $A_2MO_3$ system that does not possess metallic conductivity is $Na_2PtO_3$. Structures that do possess this metallic character include $Li_2IrO_3$ and $Na_2IrO_3$, while the metallic or semi-conducting character of $Li_2RuO_3$ character is still unclear. The de-lithiation of the $Li_2MO_3$ structures indicates their potential use as lithium ion batteries. All of the systems investigated, $Li_2RuO_3$, $Li_2IrO_3$, and $Li_2PtO_3$, have good charge-discharge cycling characteristics. The mechanism of de-lithiation appears to differ between $Li_2RuO_3$, $Li_2IrO_3$, and $Li_2PtO_3$
structures, but the reversibility of the charging and discharging deviates minimally between the structures. Of particular interest is the large volume capacity of the Li$_2$PtO$_3$ system, 764 mAh/cc, which is larger than that of LiCoO$_2$. The reason for the improved volume capacity of Li$_2$PtO$_3$ is not clear, but may involve the increased ratio of lithium to transition metal.

A result of these APGMOs containing platinum group metals that have d-electrons is the potential for interesting magnetic phenomenon to occur. No magnetic ordering is observed to occur in either Li$_2$IrO$_3$ or Li$_2$RuO$_3$, but a cusp in the magnetization at ~63 K for Li$_2$RuO$_3$ and experiments based on Li$_2$(Mn$_{1-x}$Ru$_x$)O$_3$ indicate that Li$_2$RuO$_3$ is on the verge of antiferromagnetically ordering. One structure that is seen to have AFM ordering is Li$_3$RuO$_4$, where the chains of edge sharing octahedra align in an AFM fashion. In Li$_3$RuO$_4$ there appears to be no long range ordering between the chains or sheets of plains present in the structure.

1.6 References


CHAPTER 2

STRUCTURE AND PROPERTIES OF ORDERED Li$_2$IrO$_3$

AND Li$_2$PtO$_3$


2.1 Introduction

Solid state $p_H$ sensors are highly desirable due to their stability at high temperatures, high pressures, and potential use in non-aqueous environments. Transition metal oxides such as RuO$_2$, IrO$_2$, and PtO$_2$ have been investigated as solid state $p_H$ sensing materials since the mid 1980s [1], [2], with IrO$_2$ showing the most promise. The use of a lithium carbonate melt process to produce solid state iridium oxide $p_H$ sensors has been shown to produce sensors that are more stable and reproducible than other techniques used to produce iridium oxide based $p_H$ sensors [3].
Figure 2.1: The Li$_2$MO$_3$ structure shows the characteristic layering (a), as well as the LiM$_2$ layer with corresponding oxygen atoms (b).

Carbonate melt based sensors are produced via oxidation of an iridium wire in molten lithium carbonate [3]-[5]. The phases responsible and the mechanism behind the $p_H$ sensitivity of these systems are not well understood, despite their current use in commercial applications. Thus, knowledge of the structure and properties of phases produced via reactions between lithium carbonate and both Ir and Pt, are vital to further improving these sensors.

The stable phases obtained using traditional solid state reactions between Li$_2$CO$_3$ and the platinum group metals ($M$ = Ru, Ir, Pt) include Li$_2$RuO$_3$[6]-[8], Li$_2$IrO$_3$ [9] and Li$_2$PtO$_3$ [10]. Of these phases the ruthenate has been most extensively studied. There are relatively few reports of other ternary oxide phases forming, only Li$_3$RuO$_4$ [11], Li$_8$IrO$_6$ [12], Li$_8$PtO$_6$ [12] and Li$_{0.64}$Pt$_3$O$_4$ [13] have been reported. The structure of Li$_2$MO$_3$ can be described as an ordered variant of the rock salt structure containing cation layers that alternate between pure lithium layers and mixed metal layers, LiM$_2$. 

34
(Figure 2.1). These phases are structurally and compositionally related to LiCoO$_2$ currently used as the cathode in lithium ion batteries.

The relative simplicity of the Li$_2$O–IrO$_2$ phase diagram suggests that Li$_2$IrO$_3$ may play a key role in the production and/or operation of miniaturized $p_H$ sensors produced via the lithium carbonate melt oxidation of iridium wires. Despite the technological importance of this material a number of questions regarding its structure, chemical stability and physical properties remain unanswered. To address this deficiency we report here a systematic study of the structural, thermal, optical, and electrical properties of highly ordered Li$_2$IrO$_3$ and Li$_2$PtO$_3$. These are compared and contrasted with Li$_2$RuO$_3$.

### 2.2 Experimental

Li$_2$MO$_3$ ($M =$ Ru, Ir, Pt) were prepared using stoichiometric mixtures of Li$_2$CO$_3$ (J.T. Baker, 99.2%) and either Ru (~325 mesh, Cerac, 99.95%), Ir (~325 mesh, Alfa Aesar, 99.9%) or Pt (~325 mesh, Alfa Aesar, 99.9+%). For all syntheses 5% excess Li$_2$CO$_3$ was added to compensate for high temperature lithium volatility. The starting materials were mixed under isopropanol using an agate mortar and pestle, and placed in high density alumina crucibles (Coorstek, 99.8%). The mixtures were then heated in air at a rate of 10 K/min to the initial target temperature of 1025 K and held at that temperature for 12 h before cooling back to room temperature at a rate of 10 K/min. Successive heating cycles were performed by increasing the annealing temperature in 50 K steps, up to 1325 K where pure ordered phases were obtained. Attempts to streamline the synthesis by
pre-reacting the starting materials at 1025 K followed by heating directly to 1325 K lead to premature decomposition rather than the formation of highly ordered structures.

Powder X-ray diffraction (PXRD) data were collected in Bragg-Brentano geometry using a Bruker D8 Advance X-ray powder diffractometer (40 kV, 50 mA, sealed Cu X-ray tube). This instrument is equipped with an incident beam Ge 111 monochromator, selecting only CuKα₁ radiation (λ = 1.5406 Å), and a Braun linear position sensitive detector. The data were collected over the angular range 10° < 2θ < 100° with a step size of 0.014265° and a counting time of 1 sec per step. Structural refinements were completed using the Rietveld method as incorporated in the software package TOPAS Academic [14], [15].

Thermo-gravimetric analyses (TGAs) were performed using a Perkin Elmer TGA 7 with TAC 7/DS Thermal Analysis Instrument Controller. Approximately 50 mg of sample was placed in a platinum boat for each analysis. The samples were heated to 1575 K with a heating rate of 10 K/min. A gas flow rate of 40 mL/min was used for reagent grade O₂, Air, N₂, and forming gas (5:95, H₂:N₂).

High temperature in-situ PXRD measurements in forming gas (5:95, H₂:N₂) were made using an Anton Paar HTK 1200 furnace in conjunction with the Bruker D8 Advance. The samples were heated to 673 K with a ramp rate set to 1 K/min and then held at constant temperature for each measurement. The in-situ PXRD data were collected over the angular range 17.5° < 2θ < 47.5° with a step size of 0.072978° and a counting time of 0.5 sec per step. The lattice parameters from the in-situ PXRD experiments were
determined using Rietveld refinements. Due to the limited angular range over which the high temperature data were collected the atomic parameters were constrained to be equal to their room temperature values.

UV-Visible diffuse reflectance data were collected on polycrystalline samples using a Perkin-Elmer Lambda 20 scanning double-beam spectrometer equipped with a 50-mm Labsphere integrating sphere over the spectral range 400-1100 nm (3.1-1.1 eV). The Kubelka-Munk function was used to convert the diffuse reflectance data into absorption data. The band gap energies reported were determined using Shapiro’s method of extrapolating the onset of absorption to the wavelength axis [16].

Electronic structure calculations were performed using the Cambridge Serial Total Energy Package (CASTEP) [17]. CASTEP is a first principles density functional theory (DFT) plane wave pseudo-potential simulation code. The calculations were performed in the frame of the Generalized Gradient Approximation (GGA) as derived by Perdew and Wang (PW-91) for the exchange and correlation effects [18],[19]. A Gaussian smearing scheme of 0.05 eV was employed when drawing the density of states (DOS) plots.

Alternating current (AC) electrical measurements were performed using a Solartron SI 1260 Impedance/Gain-Phase Analyzer scanning from $10^7$ Hz and 1 Hz, over the temperature range 300-800 K. Compact pellet samples were prepared using uniaxial pressing (230 MPa) followed by heating at 1300-1400 K for 4 h. The circular pellets were sanded to obtain a smooth surface before making electrical contacts with silver paint, (Ted Pella, Leitsilber 200) connected via gold mesh contacts. The material that was
removed from the pellet during sanding was analyzed using PXRD on a zero-background sample holder to verify that sintering did not alter the phase purity.

2.3 Results and Discussion

2.3.1 Structural Characterization

There is some debate in the literature regarding the proper choice of unit cell and space group symmetry of the Li$_2$MO$_3$ phases. Li$_2$IrO$_3$ has been reported using $C2/c$ ($Z = 8$) symmetry [9], as has Li$_2$RuO$_3$ [6]-[8], while Li$_2$PtO$_3$ has been reported to possess $P3_1$ ($Z = 6$) [20] and $C2/m$ ($Z = 4$) symmetry [21]. A recent neutron diffraction study on Li$_2$RuO$_3$ reported $C2/m$ symmetry ($Z = 4$) at 600 K [22], and $P2_1/m$ symmetry ($Z = 4$) at room temperature [22],

A closer look shows that the $C2/m$ and $C2/c$ descriptions are only subtly different. However, consideration of symmetry relationships shows that the $C2/m$ description is much more likely to be correct. Starting from the LiCoO$_2$ structure and removing the 3-fold axis of the $R3m$ space group results in a monoclinic unit cell with $C2/m$ symmetry, and $a$, $c$ and $\beta$ parameters that closely match the $C2/m$ descriptions of Li$_2$RuO$_3$ and Li$_2$PtO$_3$, and a $b$-axis that is 1/3 of the value reported for the Li$_2$MO$_3$ compositions. By replacing every third transition metal ion with Li$^+$ the $b$-axis is tripled leading directly to the $C2/m$ description of Li$_2$RuO$_3$ and Li$_2$PtO$_3$. The symmetry of the room temperature structure of Li$_2$RuO$_3$ is further lowered to $P2_1/m$ through the formation of Ru–Ru pairs. This is presumably an electronic distortion driven by metal-metal bonding interactions.
To confirm the structural details of the Li$_2$MO$_3$ phases, Rietveld refinements were carried out using the PXRD data. The Rietveld fits to the PXRD patterns are presented in Figure 2.2. The results of the structural refinements for Li$_2$RuO$_3$ are in good agreement with the previously reported Li$_2$RuO$_3$ with $P2_1/m$ symmetry [22], while Li$_2$IrO$_3$ and Li$_2$PtO$_3$ are in good agreement with the isostructural Li$_2$MnO$_3$ possessing $C2/m$ symmetry [23].
Figure 2.2: Powder X-ray diffraction pattern and Rietveld refinement for (a) Li$_2$RuO$_3$ (b) Li$_2$IrO$_3$ (c) Li$_2$PtO$_3$: observed (●), calculated (red), and difference (green) profiles. Tick marks indicate the Bragg reflection positions.
The structural parameters obtained from the refinements of Li$_2$IrO$_3$ and Li$_2$PtO$_3$ are reported in Table 2.1. The accuracies of the refined structures are supported by the bond valence analyses presented in Table 2.2. The bond valence sums for the respective cations and anions are in good agreement with the expected oxidation states. This shows that even the light atom positions are determined with a reasonable degree of accuracy.

As seen in Figure 2.2, we were not able to completely model the profiles of a number of peaks in the 2θ region between 19° and 33°. The asymmetry of these peaks originates from the presence of stacking faults associated with shifts between successive Li$M_2$ layers as previously observed for disordered Li$_2$MnO$_3$ [23] and Li$_2$PtO$_3$ [21], causing the classic Warren lineshape seen in Figure 2.2 [24]. To partially account for the presence of stacking faults we have refined the cation site occupancies in the Li$M_2$ layers, within the constraint that the Li$_2$MO$_3$ stoichiometry is maintained. While this approach adequately accounts for changes in intensity of these peaks, it does nothing to improve the fit of the peak profiles. Thus, it should be stressed that the disorder associated with the site occupancy values in Table 2.1 appears to be largely due to faults in stacking of highly ordered layers rather than random Li/$M$ disorder. It should also be noted that concentration of stacking faults (as assessed by the peak broadening) looks to be smaller than most previous descriptions of these materials in the literature.

As noted above attractive Ru–Ru interactions in Li$_2$RuO$_3$ are reported to lower the symmetry from C2/m to P2$_1$/m. Because the two space groups have different systematic
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<th>B_{iso}/Å²</th>
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Table 2.1: Structural parameters for Li₂MO₃ (M = Ir, Pt) - C2/m
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<td>2.17(2)</td>
<td>x2</td>
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<td></td>
<td>2.35(4)</td>
<td>x2</td>
<td>0.092(2)</td>
<td>x2</td>
<td>2.23(4)</td>
<td>x2</td>
<td>0.127(2)</td>
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<tr>
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<td>1.170(6)</td>
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<td>BVS</td>
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<td>1.050(6)</td>
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<td>x1</td>
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Bond valence values for a given site were determined using the most abundant element, as such Li1 from Table 2.

**Table 2.2:** Bond lengths and bond valence values for Li$_2$IrO$_3$ and Li$_2$PtO$_3$.
absences this distortion should give rise to additional reflections in the diffraction pattern. Such peaks can be observed at \( \sim 19.0^\circ \ (1 \ 0 \ 1) \) and \( \sim 30.3^\circ \ (1 \ 0 \ 2) \) as well as shoulders on more intense peaks near \( \sim 21.9 \ (1 \ 0 \ 0) \) and \( \sim 27.9^\circ \ (1 \ 2 \ 1) \) in the PXRD patterns of Li\(_2\)RuO\(_3\) (Figure 2.2a). These peaks only appear for Li\(_2\)RuO\(_3\) systems that show moderate to low degrees of faulting. No evidence of these extra peaks can be found in the PXRD patterns for Li\(_2\)IrO\(_3\) and Li\(_2\)PtO\(_3\) (Figures 2.2b and 2.2c). Apparently increasing the d-orbital electron count from four (Ru\(^{4+}\)) to five (Ir\(^{4+}\)) or six (Pt\(^{4+}\)) destabilizes the electronic interactions responsible for this distortion.

### 2.3.2 Thermal Stability

The thermal stabilities of Li\(_2\)RuO\(_3\), Li\(_2\)IrO\(_3\), and Li\(_2\)PtO\(_3\), at elevated temperatures are of interest for high temperature \( p_H \) sensing applications. Thus, thermal gravimetric analysis (TGA) was performed in O\(_2\), air, N\(_2\) and H\(_2\):N\(_2\) (5:95). Plots of the TGA results are presented in Figure 2.3. The compounds have similar stabilities in O\(_2\), air and N\(_2\). Under these non-reducing atmospheres they are stable, as determined by the onset of weight loss, up to \( \sim 1525 \) K, \( \sim 1475 \) K, and \( \sim 1375 \) K for Li\(_2\)RuO\(_3\), Li\(_2\)IrO\(_3\), and Li\(_2\)PtO\(_3\), respectively. The increasing thermal stability upon going from Pt to Ir to Ru correlates with the decrease in noble character of the metallic element. We also note a small weight loss beginning at \( \sim 475 \) K of 0.49%; 0.60%, and 0.18% for Li\(_2\)RuO\(_3\), Li\(_2\)IrO\(_3\), and Li\(_2\)PtO\(_3\), respectively. The origin of this feature is not certain, but it may be caused by the loss of water.
Figure 2.3: TGA for Li$_2$MO$_3$ ($M = $ Ru, Ir, Pt) in O$_2$, air, N$_2$, and H$_2$:N$_2$ (5:95). The horizontal dashed lines represent the calculated weight percent for potential decomposition products.
All three phases show reduced thermal stability in forming gas, H\textsubscript{2}:N\textsubscript{2} (5:95). Li\textsubscript{2}PtO\textsubscript{3} and Li\textsubscript{2}RuO\textsubscript{3} lose weight in two steps. The first weight loss takes place over the temperature range of 800-1000 K. \textit{Ex-situ} PXRD measurements of quenched samples show that this step corresponds to reduction of the platinum group metal to its elemental state accompanied by exsolution of lithium oxide. The upper set of dashed lines in Figure 2.3 show the theoretical weight loss corresponding to the decomposition reaction:

\[ \text{Li}_2\text{MO}_3(s) \rightarrow \text{Li}_2\text{O}(s) + \text{M}(s) + \text{O}_2(g) \]

The differences between the calculated and observed mass losses likely result from a fractional amount of Li\textsubscript{2}O decomposition and/or volatilization prior to reaching the observed plateau. Further heating leads to complete loss of Li\textsubscript{2}O (see lower set of dashed lines), as seen in Figure 2.3.

The TGA of Li\textsubscript{2}IrO\textsubscript{3} in forming gas differs from those of Li\textsubscript{2}PtO\textsubscript{3} and Li\textsubscript{2}RuO\textsubscript{3}. An additional weight loss begins around 475 K, reaching a plateau at ~94 wt%. This feature suggests formation of an intermediate phase along the decomposition pathway. To better understand this behavior \textit{in-situ} PXRD experiments were performed. Notwithstanding the inevitable temperature and heating rate differences between the two measurements a cursory look at the \textit{in-situ} PXRD data (Figure 2.4) indicates that Li\textsubscript{2}IrO\textsubscript{3} decomposes into Ir and a Li\textsubscript{2}O like phase. The PXRD patterns above 550 K are dominated by the diffraction peaks of metallic iridium. In addition there are a couple of weak peaks that cannot be unambiguously identified. Nevertheless, on cooling the peak at 32.1° shifts to ~33.6° which is exactly where the strongest peak for Li\textsubscript{2}O, the (1 1 1) peak, is expected. Thus we conclude that the weak peaks seen in Figure 2.4 originate from Li-containing phases.
Figure 2.4: *In-situ* Powder X-ray diffraction patterns of Li$_2$IrO$_3$ in forming gas (H$_2$:N$_2$, 5:95) from 300 to 675 K with 5 K increments.
Figure 2.5: Unit cell volume evolution of Li$_2$IrO$_3$ and the refined phase fractions of Ir and Li$_2$O during reduction in forming gas (H$_2$:N$_2$, 5:95) as obtained from the Rietveld refinements.

Upon closer inspection shifts in the positions of several diffraction peaks for Li$_2$IrO$_3$ are observed. Figure 2.4 shows the unit cell volume of the Li$_2$IrO$_3$ phase as determined from the in-situ PXRD data. There is an abrupt increase of ~1% in the unit cell volume that precedes the decomposition. Loss of oxygen and the corresponding reduction of Ir$^{4+}$ would be expected to both increase the unit cell volume and trigger a weight loss. However, a 6% weight loss corresponds to loss of one oxygen ion per formula unit and it is difficult to imagine how Li$_2$IrO$_3$ could accommodate such a degree of oxygen loss while maintaining its structural integrity. Further study is needed to fully understand the thermal decomposition of Li$_2$IrO$_3$, but it does not appear as though a structurally distinct intermediate phase exists.
Figure 2.6: The electronic density of states (DOS) plots for Li$_2$MO$_3$ ($M$ = Ir, Pt). The d-orbital contribution can be completely attributed to the platinum group metal, while the p-orbital contribution comes predominantly from oxygen. The horizontal dashed line depicts the Fermi energy.

2.3.3 Electronic Structure Calculations

To better understand the properties of the Li$_2$MO$_3$ phases electronic band structure calculations were performed on the structures obtained for Li$_2$IrO$_3$ and Li$_2$PtO$_3$. The electronic structure of Li$_2$RuO$_3$ is complicated by the symmetry lowering distortion of the Ru-sublattice. A full computational study of this distortion is in progress and will be published elsewhere. Electronic density of states (DOS) plots for Li$_2$IrO$_3$ and Li$_2$PtO$_3$ are presented in Figure 2.6. The octahedral coordination of Ir$^{4+}$ and Pt$^{4+}$ splits the d-orbitals into $t_{2g}$ ($\pi^*$) and $e_g$ ($\sigma^*$) states. The 2D edge-sharing connectivity of the MO$_6$ octahedra in Li$_2$MO$_3$ broadens the antibonding M–O levels into bands. The $t_{2g}$ ($\pi^*$) states are 5/6 and
completely filled in Li$_2$IrO$_3$ and Li$_2$PtO$_3$, respectively. The Fermi level cuts through the $t_{2g}$ ($\pi^*$) band in Li$_2$IrO$_3$, suggesting metallic character. The electronic structure of Li$_2$PtO$_3$ is clearly that of a semiconductor with a gap of 2.32 eV between the filled $t_{2g}$ ($\pi^*$) and empty $e_g$ ($\sigma^*$) bands. These results agree with expectations based on a simple consideration of the d-orbital filling.

Upon moving from Ir to Pt there is a decrease in the energy separation of the bands which are nominally labeled as O 2p bands and the $t_{2g}$ ($\pi^*$) states. (The lower energy “O 2p” bands are actually $M$–O 2p bonding gradually giving way to nonbonding O 2p bands as the energy increases.) This is a reflection of the increasingly covalent character of the $M$–O bonds. While these two sets of bands are separated in Li$_2$IrO$_3$, the gap has completely collapsed for Li$_2$PtO$_3$. Another measure of the bond covalency is seen in the fact that the O 2p orbitals and the Pt 5d orbitals contribute almost equally to both the bonding states ($-5$ to $-7$ eV) and antibonding states ($>-2$ eV). Thus the Pt–O bonding in Li$_2$PtO$_3$ is almost fully covalent. The increased covalency correlates well with the thermal stability observed in oxidizing and inert atmospheres.

2.3.4 Optical Properties

The UV-Visible diffuse reflectance spectra for Li$_2$IrO$_3$ and Li$_2$PtO$_3$ are presented in Figure 2.7. The Li$_2$IrO$_3$ is strongly absorbing in the visible spectrum and hence black in appearance. Li$_2$PtO$_3$ is bright yellow and only begins to strongly absorb at wavelengths
Figure 2.7: Plot of UV-Vis diffuse reflectance spectra converted to absorbance using the Kubelka-Munk function for Li$_2$IrO$_3$ and Li$_2$PtO$_3$.

Figure 2.8: Impedance Spectra from 0 to $10^7$ Hz for Li$_2$PtO$_3$ from 400 to 800 K.
<500 nm. By extrapolating the absorbance in the UV-Visible spectrum to zero absorbance a band gap of 2.3 eV for Li₂PtO₃ is obtained. This value is in excellent agreement with the calculated band gap of 2.32 eV.

### 2.3.5 Electrical Measurements

The electrochemical impedance spectroscopy measurements for Li₂PtO₃ are shown in Figure 2.8. Because the measurements were made on a polycrystalline pellet of limited density, 63.1% theoretical, our interpretation is limited to qualitative features.

The impedance of the Li₂PtO₃ sample decreases rapidly with increasing temperature, indicating activated carrier transport. The conductivities determined upon extrapolation to a frequency of 0 Hz were used to construct an Arrhenius plot (Figure 2.9), from which an activation energy of, 0.92(5) eV was extracted. The difference between this value and the optical band gap (2.3 eV) is not immediately obvious. It is worth noting, the activation energy reported here is almost twice the value of 0.49 eV previously reported for Li₂PtO₃ [20]. The origin of this discrepancy is not clear, but X-ray patterns suggest that the earlier studies were carried out on a sample with a higher degree of stacking faults. It appears that the conductivities of these systems are dependent on the method of preparation and the degree of stacking fault disorder present.

Figure 2.9 also presents the temperature dependence of Li₂IrO₃ conductivities determined upon extrapolation to a frequency of 0 Hz. Although the measured conductivities for these two compounds are not as high as might be expected for a
Figure 2.9: Conductivity plot, $\log(\sigma) = f(10^3/T)$, of $\text{Li}_2\text{MO}_3$ ($M = \text{Ir, Pt}$) with corresponding linear fits (line) for the semi-conducting $\text{Li}_2\text{PtO}_3$ used to determine the reported activation energies.

metallic conductor, $\text{Li}_2\text{IrO}_3$ shows little temperature dependence. This behavior, taken together with the electronic structure calculations suggest this phase is in fact a metallic conductor. The relatively low absolute conductivity observed for $\text{Li}_2\text{IrO}_3$ is likely a result of the combined effects of incomplete sintering of the pellets and the anisotropic nature of the electronic structure.

Given the structural similarities to well known $\text{Li}^+$-ion conductors, such as $\text{LiCoO}_2$, we considered the possibility that $\text{Li}^+$ conduction may be contributing to the total conductivity, of the semiconducting $\text{Li}_2\text{PtO}_3$. If the ionic conductivity was a significant portion of the total conductivity the resistance should increase as one proceeds to higher frequencies due to the inability of the ions to respond to high frequency changes in field,
but this is not observed. Therefore, it is reasonable to assume that electronic conductivity dominates any contribution from ionic conductivity to the total conductivity.

2.4 Conclusions

The Li$_2$MO$_3$ ($M =$ Ru, Ir, Pt) systems are thermally stable against reduction in air, O$_2$, and N$_2$ below 1375 °K, which is an attractive feature for sensor operation over a wide range of temperatures. The thermal stability is significantly reduced in forming gas (N$_2$:H$_2$), where Li$_2$RuO$_3$ and Li$_2$PtO$_3$ are stable up to ~850 K, while Li$_2$IrO$_3$ is stable to ~450 K. Thermal analysis coupled with ex-situ and in-situ diffraction measurements show that Li$_2$MO$_3$ compounds decompose through reduction of the platinum group metal cation to its elemental state combined with exsolution of Li$_2$O. Li$_2$IrO$_3$ undergoes a slightly more complicated decomposition which appears to involve loss of oxygen prior to collapse of the layered Li$_2$IrO$_3$ structure.

Optical measurements, electronic structure calculations, and impedance measurements indicate that Li$_2$IrO$_3$ is a metallic conductor, while Li$_2$PtO$_3$ is a semiconductor. Relatively high electronic conductivity is a prerequisite for a material to effectively function as a $p_H$ sensing material. Thus Li$_2$PtO$_3$ is unlikely to behave favorably for this application. In contrast the formation of metallic Li$_2$IrO$_3$ is observed when iridium metal is reacted with either a stoichiometric amount or even a large excess of Li$_2$CO$_3$. This may help to explain why pH sensors made from lithium carbonate melt oxidation of Ir wires are superior to sensors produced from a similar treatment of platinum.
2.5 References


CHAPTER 3

CONTROL AND ANALYSIS OF FAULTING IN Li$_2$IrO$_3$ AND Li$_2$PtO$_3$

3.1 Introduction

Imperfections invariably influence the mechanical, electrical, physical, and chemical properties of polycrystalline systems, the extent of which is determined by the type of imperfection as well as the number of imperfections present. A stacking fault is one such imperfection, which occurs within systems that consist of equidistant, parallel layers that allow for translations parallel to the layers and rotations about the layer normal. Systems that have been reported to possess such stacking faults include the ordered rock salt systems Li$_2$MnO$_3$, Li$_2$IrO$_3$, Li$_2$PtO$_3$, and Na$_2$PdO$_3$ [1]-[4]. An ideal un-faulted structure of this type is presented below in Figure 3.1, which clearly depicts both the layering (a) and the stacking between successive layers (b) for Li$_2$MnO$_3$. As seen in Figure 3.1b, the lithium sites in the LiMn$_2$ layer progress linearly through the structure resulting in a plane of lithium ions perpendicular to the LiMn$_2$ layers. When deviations from this linearity occur the result is a stacking fault.
Figure 3.1: The structure of Li$_2$MnO$_3$ is shown depicting both the layering (a) and the stacking of successive layers (b) for ideal un-faulted system. For clarity pure lithium and oxygen layers are omitted in (b).

Recent efforts to produce solid state $p_H$ sensors have presented evidence that the level of faulting present in Li$_2$IrO$_3$ is directly related to the extent of proton uptake upon exposure to 5 molar HNO$_3$ [5]. It is believed that similar dependencies will be observed when studying the affect of faulting on extraction and insertion of lithium into Li$_2$MnO$_3$, Li$_2$RuO$_3$, Li$_2$IrO$_3$, and Li$_2$PtO$_3$, as lithium ion battery materials [6]-[16]. The importance of controlling, characterizing, and quantifying the extent of faulting is clear and will be presented here, however, in order to accomplish this, one must understand the nature of faulting.
3.1.1 History of Faulting Analysis

One of the first analyses of stacking faults was reported by B. E. Warren in 1941 in heat treated carbon black, graphite, with additional analysis being performed by Bacon and Wilson [17]-[19]. Warren described a "saw-tooth" appearance, now known as Warren fall, or Warren profile, occurring in powder X-ray diffraction patterns for the two-dimensional grating reflections, \((h\,k\,0)\) reflections, while the Warren fall was not observed for \((0\,0\,l)\) reflections. The \((h\,k\,l)\) reflections were non-existent. As a result the \((0\,0\,l)\) reflections behaved as if they were within a perfect crystal, while the \((h\,k\,0)\) reflections rose rapidly upon approaching the point of reflection with a displacement of \(0.32/L\), where \(L\) is the square root of the crystal area for a given \((h\,k\,0)\) reflection [20]. Besides subtle peak displacement, the \((h\,k\,0)\) reflections also experience broadening with a peak's width being proportional to \(1.75/L\). Such are the results of systems that are faulted in random directions and magnitude.

In the case of faulting in specific directions and specific magnitudes additional effects are observed, such as in the well studied hexagonal close-packed \((ABAB)\) and the face-centered cubic \((ABCABC)\) structures [21]-[24]. In these structures the close-packed lattice is retained while specific layers can be replaced, as in the hexagonal close-packed lattice, or inserted, as in the face-centered cubic lattice. For example, a layer \(A\) can be replaced by a layer \(C\) in a hexagonal lattice. As a result the hexagonal series would contain a single fault \((\perp)\) as well as three consecutive layers of the cubic type, \((ABC)\).

\[
\ldots A B A B (A \perp B C B C B C B C B \ldots)
\]
In the case of inserting a layer $A$ between layers $B$ and $C$, within a *face-centered cubic* lattice results in the formation of two hexagonal triplets, $(ABA)$ and $(ACA)$, as well as two faults [20].

$$\ldots A B C (A B \perp (A) C \perp A) B C A B C \ldots$$

The affect of such stacking faults are observed in the diffraction patterns. In order to understand these effects the structure factors of layer $A$ ($F_A$), $B$ ($F_B$) and $C$ ($F_C$) must be considered. The layers are described based on a hexagonal lattice with layer $A$ containing an atom with a scattering factor $f$ at the corner of the unit cell, while the atom's of layer $B$ and layer $C$ are translated by the lattice vectors $(2a/3) + (b/3)$ and $(a/3) + (2b/3)$, respectively [20]. The resulting structure factors are

$$F_A = f$$

(3.1)

$$F_B = f \exp \left[ -2\pi i \left( \frac{2h}{3} + \frac{k}{3} \right) \right] = f \exp \left[ 2\pi i \left( \frac{h-k}{3} \right) \right]$$

(3.2)

$$F_C = F_B^* = f \exp \left[ -2\pi i \left( \frac{h}{3} + \frac{2k}{3} \right) \right] = f \exp \left[ 2\pi i \left( \frac{k-h}{3} \right) \right]$$

(3.3)

for layer $A$, layer $B$, and layer $C$. Consequently, the structure factors for layer $A$, layer $B$, or layer $C$ are $f$ for any $hk$ such that $h-k = 3n$, when $n$ is nonzero. Now in addition to the $(00l)$ reflections being unaffected by faulting, as previously shown for randomly faulted systems, it is now shown that faulting in close packed lattices it is more general, with $(hkl)$ being unaffected for all $h-k = 3n$. When $h-k \neq 3n$ distortions are observed that are proportional to the degree of faulting present within a given crystal. The result is the occurrence of rows of reflections in reciprocal space that alternate between an unaffected row followed by two distorted rows, for $h-k = 3n$ and $3n\pm1$, respectively.
As mentioned previously, stacking faults have been observed in ordered rock salt structures including Li$_2$MnO$_3$ [1], Li$_2$IrO$_3$ [2], and Li$_2$PtO$_3$ [3]. These structures all possess the Li$_2$MnO$_3$ structure type, which is composed of hexagonally ordered Li$_M$$_2$ ($M = $ Mn, Ir, Pt) mixed metal layers separated by a sequence of oxygen, pure lithium, and oxygen layers while retaining an $ABC$ stacking sequence. The stacking of the Li$_M$$_2$ layers occurs in such a manner that planes of lithium occur perpendicular to the layering with a linear progression of lithium sites. The resulting structure and proposed layer faults, or transitions, are presented in Figure 3.2.

In order to account for the three potential arrangements of Li in the Li$_M$$_2$ layers an additional descriptor, $i$, is required. As a result nine layer types are observed ($A_i$, $B_i$, and $C_i$, where $i = $ 1, 2, and 3), as previously derived for Li$_2$MnO$_3$ [1]. An ideal structure is retained when successive layer transitions of $a/3$ are maintained between consecutive Li$_M$$_2$ layers, resulting in an $A_1B_1C_1$ repeat unit. Additionally, recall that the structure retains an overall $ABC$ stacking sequence including the oxygen and lithium layers. The faulting is the result of ordering present in the Li$_M$$_2$ layers along with deviations from the standard layer transition. The faults occur via translation and rotations ($\pm 120^\circ$) as indicated via the arrows shown in Figure 3.2 [1], which destroys the uniform lithium plane and propagation. The arrows indicate the direction of lithium propagation before and after faulting. Translations maintain the direction of lithium propagation following a fault. Thus, a translation fault occurring after $A_1B_1C_1$ possesses an $A_2B_2C_2$ repeat. Rotational faults actually change the direction of lithium propagation with a $-120^\circ$ fault and $+120^\circ$ fault possessing $A_3B_2C_1$ and $A_2B_3C_1$ repeat following a fault from $A_1B_1C_1$. 

61
Figure 3.2: Examples of stacking faults observed in ordered rock salt \( A_2MO_3 \) \((C2/m)\) (based on figure originally published in [1]). The arrows indicate the shift in lithium progression through successive layers, thereby representing stacking faults.

3.1.2 Methods of Faulting Analysis

Transition Probability Simulation and Refinement

In order to quantitatively analyze faulting, efforts have been directed to create software that is capable of simulating and refining powder X-ray diffraction patterns, such as DIFFaX [25] and FAULTS [26]. Both DIFFaX and FAULTS require the structure to be defined in such a way that the \(c\)-axis is perpendicular to the proposed faulting direction; resulting in a new \textit{idealized} unit cell being constructed. The result is a hexagonal unit cell with \(a_{\text{hex}} = a_{C2/m}\) and \(c_{\text{hex}}\) equivalent to that of three times the \(\text{LiM}_2\) layer spacing. In order to generate the stacking sequence observed in the \(\text{Li}_2\text{MnO}_3\) structure type, which
possesses $C2/m$ symmetry, transition vectors are generated such that a stacking sequence of $A_1B_1C_1$ is observed. The transition vectors are defined such that a transition from one mixed metal layer to the next via the $[ \frac{1}{3} 0 1 ]$ vector, which occurs with a probability of $\alpha_{12}$. When the $[ \frac{1}{3} 0 1 ]$ transition vector probability is less than 1.0, ($\alpha_{12} < 1.0$), faulting is observed. The transition vectors resulting in faulting are $[ \frac{2}{3} \frac{2}{3} 1 ]$ and $[ 0 \frac{1}{3} 1 ]$, which occur with probabilities of $\alpha_{13}$ and $\alpha_{14}$, respectively. These faulting vectors correspond to the ±120° rotations where $\alpha_{13} = \alpha_{14} = (1-\alpha_{12})/2$. As a result determining an appropriate $\alpha_{12}$ to model a specific diffraction patterns allows one to quantify the degree of faulting present in a given system. Details of the respective transition vectors are provided in Appendix A in the respective input files for DIFFaX and FAULTS.

DIFFaX is capable of simulating powder X-ray diffraction patterns while varying the transition probabilities. Rather than simply simulating diffraction patterns as a function of faulting, FAULTS refines diffraction patterns with the transition probabilities as a parameter that can be refined. Traditional Rietveld refinements are incapable of accounting for the affects of faulting as the only take into account unit cells repeated infinitely in all directions [27]. However as shown below Rietveld methods can be used to quantify the degree of faulting by refining site occupancies.

**Rock Salt Ordering and Site Occupancy Refinement**

A stacking fault occurring in the Li₂MnO₃ structure type results in lithium occupying manganese sites and manganese occupying the lithium sites. One may attempt to account
Simulated X-ray diffraction patterns for ordered rock salt structures of Li$_2$MnO$_3$ (C2/m), Li(Li$_{1/3}$Mn$_{2/3}$)O$_2$ (R3m), and the unordered rock salt structure Li$_{2/3}$Mn$_{1/3}$O (Fm3m). (Lattice parameters based on Li$_2$MnO$_3$ unit cell [1].)

Figure 3.3: Simulated X-ray diffraction patterns for ordered rock salt structures of Li$_2$MnO$_3$ (C2/m), Li(Li$_{1/3}$Mn$_{2/3}$)O$_2$ (R3m), and the unordered rock salt structure Li$_{2/3}$Mn$_{1/3}$O (Fm3m). (Lattice parameters based on Li$_2$MnO$_3$ unit cell [1].)

for this by refining the site occupancies of lithium and platinum group metals in the LiM$_2$ layers. To understand this, one needs to consider the effects of rock salt ordering

Figure 3.3 shows simulated powder X-ray diffraction patterns for the ordered rock salt structure Li$_2$MnO$_3$ (C2/m), Li(Li$_{1/3}$Mn$_{2/3}$)O$_2$ (R3m), and Li$_{2/3}$Mn$_{1/3}$O (Fm3m). When LiMn$_2$ mixed metal layer is disordered the result is the formation of the higher symmetry structure Li(Li$_{1/3}$Mn$_{2/3}$)O$_2$ (R3m). Additionally the peaks occurring between ~18.9° and ~37.5° 2θ are lost; these lost peaks are indicative of coherent ordering of mixed metal
layers. When further cation disorder is extended to include the pure lithium cation layers the still higher symmetry structure of Li$_{2/3}$Mn$_{1/3}$O ($Fm3m$) is formed. The resulting structure of $Fm3m$ symmetry no longer possesses the intense peaks occurring at $\sim$$18.4^\circ$, $\sim$$35.2^\circ$, and $\sim$$37.0^\circ$, which were indicative of layered ordering, as they are now systematically absent. The remaining peaks occurring at $\sim$$43.0^\circ$, $\sim$$75.0^\circ$, and $\sim$$79.0^\circ$ are consistent with the rock salt sub-cell and are present under all three conditions. Thus, one may attempt to account for coherent ordering of mixed metal layers (faulting) and layer ordering by refining the site occupancies in a similar manner. However as faulting only results when Li$M_2$ layers are disordered, the lithium in lithium layers for Li$_2$$MO_3$ will have fixed site occupancies of 1.0 that are not refined.

In order to address the issue of faulting and methods of quantification the methods mentioned have been used to analyze faulting observed Li$_2$IrO$_3$ and Li$_2$PtO$_3$ prepared using three different sets of conditions. The results shed light on the ability to control the degree of faulting present in layered rock salt ordered structures and shed light on methods of quantifying the degree of faulting.

### 3.2 Experimental

Li$_2$IrO$_3$ and Li$_2$PtO$_3$ were prepared using stoichiometric mixtures of Li$_2$CO$_3$ (J.T. Baker, 99.2%) as well as Ir (~325 mesh, Alfa Aesar, 99.9%) and Pt (~325 mesh, Alfa Aesar, 99.9+%), respectively. For all syntheses 5% excess Li$_2$CO$_3$ was added to compensate for high temperature lithium volatility. The starting materials were mixed under isopropanol using an agate mortar and pestle, and placed in high density alumina crucibles (Coorstek,
99.8%). The mixtures were then heated in air at a rate of 10 °C/min to the initial target temperature of 750 °C and held at that temperature for 12 h before cooling back to room temperature at a rate of 10 °C/min. Successive heating cycles were performed by increasing the annealing temperature in 50 °C steps, up to 900 °C and 1050 °C. The iridium and platinum systems are referred to as LIO-750, LIO-900, LIO-1050, LPO-750, LPO-900, and LPO-1050, where the number corresponds to the final target temperature. All attempts to streamline the synthesis by pre-reacting the starting materials at 750 °C followed by heating directly to 1050 °C lead to premature decomposition rather than the formation of highly ordered structures, as described in Chapter 2.

Powder X-ray diffraction (PXRD) data were collected in Bragg-Brentano geometry using a Bruker D8 Advance X-ray powder diffractometer (40 kV, 50 mA, sealed Cu X-ray tube). This instrument is equipped with an incident beam Ge 111 monochromator, selecting only CuKα1 radiation (λ = 1.5406 Å), and a Braun linear position sensitive detector. The data were collected over the angular range 10° < 2θ < 100° with a step size of 0.014265° and a counting time of 1 second per step. Structural refinements were completed using the Rietveld method as incorporated in the software package TOPAS Academic [27], [28]. Simulated PXRD and selected area electron diffraction (SAED) patterns of faulted systems were completed using the software package DIFFaX [25]. Faulting refinements were completed using the software package FAULTS [26].

SAED patterns and high resolution transmission electron microscopy (HRTEM) images were performed using a Phillips CM20 TEM and Joel 4000EX TEM, respectively.
Specimens were ground using an agate mortar and pestle under isopropanol and applied drop wise to lacey carbon copper TEM grids prepared in-house at the Electron Microcopy for Materials Science (EMAT) Labs, University of Antwerp.

3.3 Results

Faulting is known to occur in ordered rock salt structures such as Li$_2$MnO$_3$ [1], Li$_2$IrO$_3$ [2], Li$_2$PtO$_3$ [3], and Na$_2$PdO$_3$ [4]. Evidence for faulting in these structures is presented in the HRTEM image presented for Li$_2$IrO$_3$ prepared at 750 ºC in Figure 3.4. The arrows are used to indicate the locations of faulting. While visible in HRTEM, faulting is not easily quantified using this method, in any appreciable manner. In order to be more quantitative, diffraction methods are employed with particular emphasis being placed on PXRD and to a lesser degree SAED. Here faulting is quantified using a number of techniques including Rietveld refinements, PXRD simulations, and FAULTS refinements.

3.3.1 Rietveld Refinements

The PXRD patterns for Li$_2$IrO$_3$ and Li$_2$PtO$_3$ prepared at 750 ºC, 900 ºC, and 1050 ºC are shown in Figures 3.5, 3.6, and 3.7, respectively. The insets show enlarged views of the 19-33° 2θ regions. As previously discussed in Chapter 2, these systems possess $C2/m$ symmetry and are isostructural with Li$_2$MnO$_3$. The resulting lattice and structural parameters obtained from Rietveld refinements of Li$_2$IrO$_3$ and Li$_2$PtO$_3$ prepared at varying temperatures are reported in Table 3.1. The qualities of these refinements are
Figure 3.4: HRTEM image of Li$_2$IrO$_3$ prepared at 750 °C (LIO-750), viewed down the [001] axis. The arrows are used to identify faulting.

supported by their $R_p$, $R_{wp}$, and $\chi^2$ (goodness of fit) values. As the system becomes more ordered, using higher synthetic temperatures, improvements in the fits are observed. This is observed as $R_p$ drops from 15.658 to 14.897 for LIO-750 and LIO-1050, respectively and from 17.163 to 14.168 for LPO-750 and LPO-1050, respectively.

Poor fitting is observed in the region of 19-33° 2θ, as seen within other systems including Li$_2$MnO$_3$ [1], Na$_2$PdO$_3$ [4], and Li$_2$RuO$_3$ [29]-[31]. The relatively poor fitting is a result of the Warren fall and peak broadening, which occurs due to the presence of
Figure 3.5: Powder X-ray diffraction pattern and Rietveld refinement for Li$_2$IrO$_3$ (a) and Li$_2$PtO$_3$ (b) prepared at 750 °C: observed (•), calculated (red), and difference (green) profiles. Tick markers indicate the Bragg reflection positions.
Figure 3.6: Powder X-ray diffraction pattern and Rietveld refinement for Li$_2$IrO$_3$ (a) and Li$_2$PtO$_3$ (b) prepared at 900 °C: observed (●), calculated (red), and difference (green) profiles. Tick markers indicate the Bragg reflection positions.
Figure 3.7: Powder X-ray diffraction pattern and Rietveld refinement for Li$_2$IrO$_3$ (a) and Li$_2$PtO$_3$ (b) prepared at 1050 °C: observed (•), calculated (red), and difference (green) profiles. Tick markers indicate the Bragg reflection positions.
Table 3.1: Structural parameters obtained via Rietveld refinement for Li$_2$MO$_3$ ($M =$ Ir, Pt) prepared at 750 °C, 900 °C, and 1050 °C, respectively.

<table>
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<th>LPO-750</th>
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<td>C2/m (12)</td>
<td>C2/m (12)</td>
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<tr>
<td><strong>c (Å)</strong></td>
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<td>5.09546(8)</td>
<td>5.1113(1)</td>
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<td>109.839(2)</td>
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<td>222.16(1)</td>
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**Atomic Parameters**

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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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</table>

M1 occ. | 0.773(3) | 0.847(2) | 0.902(2) | 0.771(2) | 0.815(2) | 0.917(1) |
Li1 occ. | 0.227(3) | 0.153(2) | 0.098(2) | 0.229(2) | 0.185(2) | 0.083(1) |

<table>
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<th>Li2 (M2)</th>
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<th>0</th>
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<td>z</td>
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<td>0</td>
<td>0</td>
<td>0</td>
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</tbody>
</table>

Li2 occ. | 0.546(5) | 0.694(3) | 0.804(3) | 0.542(4) | 0.630(3) | 0.834(3) |
M2 occ. | 0.454(5) | 0.306(3) | 0.196(3) | 0.458(4) | 0.370(3) | 0.166(3) |

| Li3 | x | 0 | 0 | 0 | 0 | 0 |
|     | y | 0.805(8) | 0.814(5) | 0.810(6) | 0.789(7) | 0.799(5) | 0.823(6) |
|     | z | 0 | 0 | 0 | 0 | 0 | 0 |

| Li4 | x | 0 | 0 | 0 | 0 | 0 |
|     | y | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
|     | z | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |

| O1 | x | 0.253(6) | 0.247(4) | 0.251(4) | 0.258(6) | 0.251(5) | 0.247(5) |
|    | y | 0.308(2) | 0.316(1) | 0.316(1) | 0.305(2) | 0.309(1) | 0.319(1) |
|    | z | 0.751(3) | 0.755(2) | 0.759(2) | 0.760(3) | 0.765(2) | 0.762(2) |

| O2 | x | 0.264(8) | 0.250(5) | 0.256(5) | 0.282(7) | 0.270(6) | 0.261(5) |
|    | y | 0 | 0 | 0 | 0 | 0 | 0 |
|    | z | 0.795(5) | 0.782(3) | 0.788(3) | 0.777(4) | 0.767(3) | 0.770(3) |

| Cation B$_{so}$ | 0.34(5) | 0.09(2) | 0.37(4) | 0.50(5) | 0.23(3) | 0.18(4) |

B$_{so}$ fixed at 0.3 Å$^3$ for oxygen positions

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stacking faults and is not taken into account via traditional Rietveld refinements. Efforts to account for the limited fitting have been made by refining the fractional occupancies of the ions in the LiM₂, mixed metal, layers; thereby allowing a percentage of the platinum group metal sites within the mixed metal layer to be occupied by lithium and vice versa. Doing so is a bit artificial as it implies that some of the platinum group metal sites have been replaced by lithium, which would destroy the high degree of order found within a given layer. Evidence has been presented based on lithium nuclear magnetic resonance (NMR) that shows this is not the case in these types of structures; rather, individual layers retain their honeycomb structure within the limits of experimental resolution, ~0.2% for lithium occupancy on the transition metal site [1]. Also, it should be noted, despite efforts to account for faulting by refining site occupancies, these refinements all underestimate the intensity of the peak at ~19.9° 2θ, while over estimating the peak intensities from 20-33° 2θ. It is also worth noting that only the peaks consistent with coherent ordering of mixed metal layers are affected. All other peaks such as those at ~18.4° stay sharp and are relatively unaffected by the observed disorder.

Upon investigating the PXRD patterns it is clear increased heating temperature and additional heating time results in more ordered structures. This is seen numerically with Li₂IrO₃ which has Ir_{occ} values of 0.773(3), 0.847(2), and 0.902(2) for LIO-750, LIO-900, and LIO-1050, respectively. In the case of Li₂PtO₃, values of Pt_{occ} are 0.771(2), 0.815(2), and 0.917(1) for LPO-750, LPO-900, and LPO-1050, respectively. M_{occ} is defined as the fraction of the given site occupied by M with a balance of lithium, Li_{occ}, such that a total occupancy of 1.00 is maintained. Future references to M_{occ} specifically refer to the
occupancy of the $M_1$ sites presented in Table 3.1. A trend of increasing $M_{\text{occ}}$ is observed upon increasing heating temperature and time. However it is clear that this fitting is insufficient to fully model what is occurring in these diffraction patterns as a clear Warren fall, or tailing is observed in the difference curves present in the insets presented in Figures 3.5, 3.6, and 3.7.

A series of simulated PXRD patterns generated using a range of Ir$_{\text{occ}}$ from 66.7% (completely disordered) to 100% (fully ordered), presented in Figure 3.8, shows what is occurring while performing such refinements. As the system becomes more disordered the system begins to resemble a PXRD pattern consistent with that of the LiCoO$_2$ structure. The loss of the "superstructure" peaks, which are the result of ordering within the mixed metal layers, is caused by the mixed metal sites in the mixed metal layer becoming equivalent with ratios of 66.7% iridium or platinum and 33.3% lithium. Most importantly these refinements, or simulations, do not take into account the Warren fall, as seen by the "superstructure" peaks weakening in intensity without any broadening being observed. In order to account for the Warren fall and peak broadening, efforts were made to simulate and refine PXRD patterns using methods that take into account faults that occur between perfectly ordered layers which otherwise possess specified stacking sequences, using programs such as DIFFaX and Faults.
Figure 3.8: Simulated PXRD patterns for Li$_2$IrO$_3$ with iridium occupancies on the iridium site ranging from 66.7% (fully disordered LiM$_2$ layers) to 100% (fully ordered LiM$_2$ layers), the remaining balance is occupied by lithium.
Figure 3.9: DIFFaX simulated PXRD patterns for Li$_2$IrO$_3$ with faulting ranging from 33.3% Ideal (fully faulted) to 100% Ideal (fully ordered).
3.3.2 Faulting Confirmation and Analysis

DIFFaX Simulations

The limitations of Rietveld refinements are clear, as they are unable to address the occurrence of the Warren fall and peak broadening observed in the experimental diffraction patterns presented above. In order to more adequately model the presence of stacking faults the program DIFFaX was employed [25], the resulting simulations are given in Figure 3.9. The three potential stacking faults used in these simulations were shown in Figure 3.2. The simulations have been performed such that a fully ordered system possesses an $\alpha_{12}$ transition of 100%, while a fully faulted system possesses an $\alpha_{12}$ transition of 33%. Therefore, since $\alpha_{12}$, $\alpha_{13}$, and $\alpha_{14}$ equal 33% and sum to 100%, there is an equal probability of each successive layer going in any one of the three possible directions.

The DIFFaX simulations given in Figure 3.9 are found to model both the Warren fall and peak broadening, specifically from 19.5°-33° 2θ, as a result of considering perfectly ordered layers that are faulted rather than considering variations in site occupancies. The DIFFaX simulations produce severe distortion in some peaks while other peaks show no change, which was not truly seen in the Rietveld refinements. In Figure 3.9, this is most apparent where the peak at ~18.4° shows no distortion even when the structure is fully disordered ($\alpha_{12} = 33.3\%$). Under the same conditions the peaks from 20.5°-35° 2θ are broadened to the point that they are no longer observed. Also worth noting is that contrary to what is observed when varying site occupancies, that is all the "super-
structure" peaks have zero intensity, the DIFFaX simulations retain one "super-structure" peak at 19.9° with a significant Warren fall. The peak at 19.9° is a direct result of retaining the highly ordered layer which behaves as a 2-dimentional crystal within the frame work of a larger 3-dimensional crystal. Refining the site occupancies destroys this order, which accounts for the loss of the peak occurring at 19.9°. Similar affects are observed for two sets of higher order reflections beginning at ~40° and 55°, respectively. Thus it appears DIFFaX is correctly modeling these systems.

DIFFaX does not refine experimental PXRD patterns. However it does allow one to compare experimental results to patterns simulated at varying stacking fault percentages in a semi-quantitative manner. Such comparisons are given for Li$_2$IrO$_3$ and Li$_2$PtO$_3$ prepared with the varying heat treatments in Figure 3.10. LIO-750, LIO-900, and LIO-1050 show good peak intensity and shape agreement with $\alpha_{12}$ percentages of 66%, 90%, and 94%, respectively. Similarly, LPO-750, LPO-900, and LPO-1050 show good peak intensity and shape agreement with $\alpha_{12}$ percentages of 70%, 92%, and 96%, respectively. However there exist certain limitations in this modeling method. One such limitation is the inability to fully account for the sharpness of experimentally observed peaks between 20° and 34° 2θ, which is highly apparent in the samples prepared at 900 °C and 1050 °C. The cause of this is believed to be the presence of both disordered and ordered crystallites within a given sample. Thus it would appear the stacking faults are not homogenously distributed in these samples. Such a system would result in the superposition of a highly ordered and a highly faulted PXRD patterns. In order to further analyze this potential scenario, selected area electron diffraction was performed.
Figure 3.10: DIFFaX simulated (blue) and experimental (red) PXRD patterns comparisons for Li$_2$IrO$_3$ (a) and Li$_2$PtO$_3$ (b).
Selected Area Electron Diffraction

SAED has been performed to study the isostructural Na$_2$PdO$_3$ as well as Li$_2$MnO$_3$ [4], [32]. In these studies, the diffraction spots with $h$-$k$ $\neq$ $3n$ streak in the $c^*$-direction due to faulting, while diffraction spots with $h$-$k$ $=$ $3n$ are unaffected. The degree of streaking is dependent on the percentage of faulting present within sample. Similar to PXRD, DIFFaX was used to simulate SAED patterns along [1 1 0], with $\alpha_{12}$ percentages of 100%, 82%, 58%, and 33% are given below in Figure 3.11. As expected the diffraction pattern with 100% $\alpha_{12}$ transition probability, see Figure 3.11a, behaves as a normal single crystal as it does not have stacking faults. However, upon going to an $\alpha_{12}$ of 82% streaking starts to become apparent, as seen in Figure 3.11b. As expected from previous studies it is the $h$-$k$ $\neq$ $3n$ diffraction spots that are streaked, such that (1 0 0) is streaked while (3 3 1) remains as a simple un-streaked spot. Upon lowering $\alpha_{12}$, thereby increasing the faulting, streaking becomes stronger as seen with $\alpha_{12}$ of 58% in Figure 3.11c. The streaking continues to increase until a fully faulted system is reached with an $\alpha_{12}$ of 33%, see Figure 3.11d. At this point no spots can be seen for the $h$-$k$ $\neq$ $3n$ positions, rather only continuous diffuse streaking is observed. However, despite the complete disorder with respect to the Li$M_2$ layering the $h$-$k$ $=$ $3n$ reflections, such as (3 3 1), are unaffected.

Experimentally obtained SAED patterns show good agreement with predictions based on the DIFFaX simulations. A high degree of streaking in observed in the SAED patterns of LIO-750 and LPO-750, Figure 3.12. The significant streaking clearly indicates these
Figure 3.11: Simulated SAED patterns for Li$_2$IrO$_3$ with $\alpha_{12}$ percentages of 100% (a), 82% (b), 58% (c) and 33% (d) produced using DIFFaX along [1 1 0] based on C2/m symmetry. Note that for hkl with $h-k = 3n$ no streaking is observed.
systems are highly faulted. Since individual spots are observed it indicates that they are not completely random in stacking, as some degree of ordering is present, as predicted by the simulations in Figure 3.11. These results are consistent with the results obtained via Rietveld refinements and the PXRD DIFFaX simulations. It is also worth noting that experimentally there appears to be affects due to dynamical scattering (multiple scattering), which DIFFaX cannot take into account as it only accounts for kinematical scattering (single scattering). It is believed that the limited, yet significant, streaking observed for $h-k = 3n$ reflections are the result of the proposed dynamical effects. Additional spots are occasionally observed as well, which appear to be the result of secondary crystals contributing to the patterns given in Figure 3.12. Efforts to reduce these dynamical effects were made using beam procession with negligible results.

**Figure 3.12:** SAED patterns for Li$_2$IrO$_3$ (a) and Li$_2$PtO$_3$ (b) prepared at 750 °C along [1 1 0]. Streaking is observed in [0 0 1] direction for $h-k \neq 3n$ reflections.
SAED patterns for a given sample of Li$_2$IrO$_3$ prepared at 900 °C both highly faulted crystals (a) and less faulted crystals (b) are observed.

**Figure 3.13:** SAED patterns for a given sample of Li$_2$IrO$_3$ prepared at 900 °C both highly faulted crystals (a) and less faulted crystals (b) are observed.

SAED allows us to probe whether the disorder in moderately faulted samples as determined by PXRD is the result of uniformly faulted crystals or a number of crystals with varying degrees of faulting. SAED patterns were obtained for LIO-900 and are given in Figure 3.13. For a given sample, varying degrees of faulting are observed for different crystals, thereby indicating the particles are not uniform in their degree of faulting. Figure 3.13a presents a diffraction pattern for one crystal from the LIO-900 sample that clearly shows significant streaking, while Figure 3.13b shows another pattern from the same LIO-900 sample, which clearly shows less streaking and a greater degree of order. Thus, these results seem to indicate that the degree of ordering within one sample is not uniform, but varies from crystal to crystal. So it appears samples are inhomogeneous with both highly ordered and highly faulted crystals in a given system.
While DIFFaX has allowed us to simulate both PXRD and SAED patterns for various
degrees of faulting it is not quite sufficient as it only allows qualitative assignments of
estimated faulting values based on visual observations in the case of PXRD, while the
simulated SAED patterns are even less quantitative. While very valuable, these
simulations still have significant limitations in that one is unable to refine structural
parameters using this method. It is for this reason FAULTS was developed [26].
FAULTS is a refinement program capable of refining structural parameters as well
faulting percentages and was used to provide a more quantitative approach to studying
the degree of faulting found in Li₂IrO₃ and Li₂PtO₃ systems.

FAULTS REFINEMENTS

Structural refinements for Li₂IrO₃ and Li₂PtO₃ heated to 750 °C, 900 °C, and 1050 °C
using FAULTS are given in Figures 3.14, 3.15, and 3.16 with the resulting structural
parameters found in Table 3.2. A sample input file has been provided in Appendix A.2,
which includes the refined lattice parameters, particle size - broadening, atomic positions,
iridium thermal parameter and the layer transition probabilities. When broadening no
longer is affected by the particle size it may take any value greater than 5000 Å, as such it
is simply reported as being greater than 5000 Å. The layer transition probabilities are
consistent with those previous defined, such that an α₁₂ of 100% refers to a fully ordered
Figure 3.14: Powder X-ray diffraction pattern and Faults refinement for Li$_2$IrO$_3$ (a) and Li$_2$PtO$_3$ (b) prepared at 750 °C: observed (•), calculated (red), and difference (green) profiles. Tick markers indicate the Bragg reflection positions.
Figure 3.15: Powder X-ray diffraction pattern and Rietveld refinement for Li$_2$IrO$_3$ (a) and Li$_2$PtO$_3$ (b) prepared at 900 °C: observed (•), calculated (red), and difference (green) profiles. Tick markers indicate the Bragg reflection positions.
Figure 3.16: Powder X-ray diffraction pattern and Rietveld refinement for Li$_2$IrO$_3$ (a) and Li$_2$PtO$_3$ (b) prepared at 1050 °C: observed (●), calculated (red), and difference (green) profiles. Tick markers indicate the Bragg reflection positions.
Table 3.2: Structural parameters obtained via FAULTS refinement for Li$_2$IrO$_3$ and Li$_2$PtO$_3$ prepared at 750 °C, 900 °C, and 1050 °C, respectively. FAULTS is incapable of calculating estimated standard deviations, as such they are not provided.

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<th>LIO-1050</th>
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<td>$D_g \times 10^3$ (Å)</td>
<td>2.45</td>
<td>&gt;5.00</td>
<td>&gt;5.00</td>
<td>4.45</td>
<td>&gt;5.00</td>
<td>&gt;5.00</td>
</tr>
<tr>
<td>$D_l \times 10^3$ (Å)</td>
<td>4.22</td>
<td>3.43</td>
<td>&gt;5.00</td>
<td>&gt;5.00</td>
<td>4.71</td>
<td>&gt;5.00</td>
</tr>
<tr>
<td>x Ir1</td>
<td>0.850</td>
<td>8.450</td>
<td>0.836</td>
<td>0.835</td>
<td>0.835</td>
<td>0.845</td>
</tr>
<tr>
<td>x Ir2</td>
<td>0.182</td>
<td>1.780</td>
<td>0.168</td>
<td>0.170</td>
<td>0.168</td>
<td>0.180</td>
</tr>
<tr>
<td>Ir $B_{iso}$</td>
<td>0.402</td>
<td>0.714</td>
<td>0.509</td>
<td>0.952</td>
<td>0.839</td>
<td>0.440</td>
</tr>
<tr>
<td>$\alpha_{12}$ (%)</td>
<td>66.2</td>
<td>87.3</td>
<td>94.7</td>
<td>74.8</td>
<td>85.8</td>
<td>96.8</td>
</tr>
<tr>
<td>$\alpha_{13}$ (%)</td>
<td>16.9</td>
<td>6.4</td>
<td>2.6</td>
<td>12.6</td>
<td>7.1</td>
<td>1.6</td>
</tr>
<tr>
<td>$\alpha_{14}$ (%)</td>
<td>16.9</td>
<td>6.4</td>
<td>2.6</td>
<td>12.6</td>
<td>7.1</td>
<td>1.6</td>
</tr>
<tr>
<td>$R_p$</td>
<td>17.980</td>
<td>15.240</td>
<td>15.655</td>
<td>18.832</td>
<td>17.536</td>
<td>18.237</td>
</tr>
</tbody>
</table>

$D_g$ and $D_l$ are isotropic size broadening terms, Gaussian and Laurentian, respectively.

Structure and an $\alpha_{12}$ of 33% refers to a fully faulted structure. These values and the quality of the fits are determined by monitoring the reported $R_p$ index values given in Table 3.2. FAULTS is incapable of calculating estimated standard deviations thus they are not provided. Only subtle changes are observed in the refined parameters between various heating conditions with the exception of layer transition probabilities, $\alpha_{12}$. The $\alpha_{12}$ values are 66.2%, 87.3%, and 94.7% for LIO-750, LIO-900, and LIO-1050, respectively, while they are 74.8%, 85.8%, and 96.8% for LPO-750, LPO-900, and LPO-1050, respectively. The quality of these fits is seen visually in Figures 3.14, 3.15, and 3.16 and statistically with the $R_p$ index values provided. Of particular interest are the fits from 19°-33° 2θ, which are expanded in the insets provided. Compared to the fits
obtained by Rietveld methods, the refinements obtained from FAULTS provide an improved fit of the Warren fall particularly when looking in the regions found between peaks. However, the broadening of the peaks is greater than what is observed experimentally and is most evident for LIO-900 and the LPO-750. The cause of this is believed to be the presence of crystallites with varying degrees of faulting, which has been supported via SAED results presented above. Thus it is believed that LPO-750 has a small fraction of crystallites that are highly ordered, which results in the presence of peaks appearing on top of the tail from the Warren fall of the highly faulted crystallites.

3.4 Discussion

From the results presented here it is clear that the degree of faulting can be controlled by varying the heating temperatures and time. Previous work has shown similar results for \( \text{Li}_2\text{MnO}_3 \) [1], but this is the first time it has been reported for \( \text{Li}_2\text{IrO}_3 \) and \( \text{Li}_2\text{PtO}_3 \). The importance of this has been addressed previously in that the properties of these systems depend on the degree of faulting [5]. As such the ability to control and quantify the degree of faulting is vital.

As shown there are a number of ways one may attempt to quantify the degree of faulting, such as monitoring site mixing using traditional Rietveld refinements, DIFFaX simulations, as well as FAULTS refinements. The advantage of monitoring site mixing is that it is done using the conventional Rietveld methods, which is readily available and straightforward for many solid state chemists and materials scientists. It is also relatively fast, at most a couple minutes per refinement step, and well accepted in the scientific
community. One potential drawback of using Rietveld refinements is the propensity for incorrectly estimating peak intensities because of poor fit to the peak shape due to the Warren fall and peak broadening. FAULTS more adequately estimates peak shape and broadening as it already takes the Warren fall and broadening into account thereby preventing those features from influencing the peaks unaffected by faulting.

Another major drawback of Rietveld refinements is the fact that it is an incorrect assumption that there is random site mixing in the LiM$_2$ layers. As was reported for the isostructural Li$_2$MnO$_3$ [1], using NMR techniques, there is evidence that the LiM$_2$ layers stay perfectly ordered. Thus, what is being refined is not what is truly taking place, which is the faulting of perfectly ordered layers. However, as long as there is the understanding that this method simply reflects the relative disorder in stacking ordered layers it proves to be a relatively straightforward way to quantify the degree of faulting observed.

The two other methods used to quantify faulting were the DIFFaX simulations and the FAULTS refinements. Both methods require significant effort and understanding in order to create an appropriate input file, such as the ones provided in Appendix A. These input files are constructed such that the c-axis is perpendicular to the structure's layers, as in the case of Li$_2$IrO$_3$ and Li$_2$PtO$_3$ differs from that of its conventional unit cell where the c-axis is at ~109° to the LiM$_2$ layers. Once the input files have been generated, simulating a series of PXRD patterns with DIFFaX is relatively straightforward and quick, but is only qualitative in nature. Then one may compare simulated and
experimental patterns to obtain an estimate of the stacking fault percentage, but this method is based on simple observation and is qualitative at best.

The advantage of FAULTS is that it is truly a quantitative method for determining the percentage of faulting by monitoring the refined layer transition probabilities. FAULTS allows for the refinement of parameters traditionally seen in Rietveld refinements such as pseudo-voigt parameters, lattice parameters, atomic positions, and thermal parameters, but also allows one to refine a percentage of faulting rather than site occupancies. Thus we were able to refine the transition probabilities, degree of faulting, rather than simply assigning probabilities based on visual comparison as is done using DIFFaX. One major drawback with FAULTS is that it is computationally expensive, taking up to an hour to perform a single refinement step. This is contrary to Rietveld refinements that are computationally cheap taking no longer than a couple minutes for a single refinement step.

A comparison of FAULTS layer transition probabilities and Rietveld refinement $M$ occupancies is possible using the ordering parameters (OP), Rietveld and Faults defined below:

$$OP(\text{Rietveld}) = (M_{\text{occ}} - 0.667)/0.333$$  \hspace{1cm} (3.4)

$$OP(\text{FAULTS}) = (\alpha_{12} - 0.333)/0.667$$  \hspace{1cm} (3.5)

These order parameters are defined such that a fully ordered, unfaulted, system has a value of 100%, while a fully disordered system is 0.0%. Such a comparison is given in
Figure 3.17 in addition to a calibration curve obtain by performing Rietveld refinements on the PXRD patterns generated at specific stacking fault percentages using DIFFaX. These comparisons shows that only a small number of stacking faults is required to cause a significant drop off in $M_{\text{occ}}$. It is quite clear that relationship is not linear particularly at the extremes. The advantage of estimating the $\alpha_{12}$ values in this way is the speed of traditional Rietveld refinements while still retaining the understanding that $M$ occupancies are being used simply as a tool to quantify $\alpha_{12}$. The accuracy of measuring faulting becomes increasingly difficult at higher faulting, caution must be taken when attempting to be quantitative in highly faulted systems, and this may account for the lack of linearity in Figure 3.17. The key point is that an understanding of what is truly being modeled and refined when performing these refinements is needed.

### 3.5 Conclusions

The degree of faulting present in Li$_2$IrO$_3$ and Li$_2$PtO$_3$ plays a significant role in various physical properties. Methods of controlling and characterizing the faulting were presented. Based on these studies it was determined that lower temperatures, 750 °C, and shorter heating times result in systems which are highly faulted. When increasing to higher temperatures, 1050 °C and using longer heating times the result was more ordered systems. However upon further heating reduction of the platinum group metal was observed, as opposed to seeing further ordering.
Figure 3.17: A plot of OP(Rietveld) derived from $a_{12}$ (%) layer transition probability versus OP(Faults) derived from $M$ occupancy ($M = \text{Ir, Pt}$) obtained from refinements is presented. Calibration curve obtained via Rietveld refinement of DIFFaX simulations.
The faulting was analyzed via PXRD and SAED refinements and simulations. Both Rietveld and FAULTS refinements as well as DIFFaX simulations proved capable of reflecting the degree of faulting found in a given sample. Certainly DIFFaX shows beyond doubt that disorder in the layer stacking impacts the XRD and SAED in a more different way than random site disorder under Rietveld refinement. Additionally DIFFaX does a reasonably good job at qualitatively estimating the degree of faulting, while FAULTS may prove more quantitative it is much more time consuming. Each technique has various advantages and disadvantages including traditional Rietveld refinements using site occupancies. Ultimately, what is most important is that one understands how each method takes faulting into account. As long as it is clear that each layer is perfect with no appreciable disorder and that the distortion observed in the respective diffraction patterns is the result of faulting, then Rietveld refinements prove to be sufficient to obtain values from metal site occupancies that can used to semi-quantitatively compare the degree of faulting between various systems for a given compound.

3.6 References


[5] M. O'Malley $\text{Li}^+/\text{H}^+$ Ion Exchanged $\text{Li}_2\text{MO}_3$ ($M = \text{Ir, Pt}$) and Carbonated Melt Oxidized IrOx pH Sensors. Unpublished Master's Thesis, The Ohio State University, Columbus, Ohio (2008).


[28] A. Coelho *Topas Academic* 2004


CHAPTER 4

A COMPUTATIONAL STUDY OF BONDING IN Li$_2$MO$_3$

ORDERED ROCK SALT STRUCTURES

4.1 Introduction

Ordered rock salt structures have a number of interesting properties leading to their use in lithium ion battery materials [1], $p_H$ sensors [2] and even superconductors [3]. Due to these applications ordered rock salt have been the focus of much research in recent years. However in order to truly optimize the properties of these systems an understanding of the structure and bonding found in these systems is necessary. The focus of the work presented here is on the ordered rock salt, Li$_2$MO$_3$, systems which are known to possess three structure types: Li$_2$MnO$_3$ [4], [5], $\beta$-Li$_2$SnO$_3$ [6], [7], and Li$_2$ZrO$_3$ [7], [8]. Additionally, an effort to shed light on metal-metal bonding in the Li$_2$MnO$_3$ structure types is presented.
4.1.1 Ordered Rock Salt Structure Types: $\text{Li}_2\text{MnO}_3$, $\beta\text{Li}_2\text{SnO}_3$, or $\text{Li}_2\text{ZrO}_3$

To be an ordered rock salt structure the system must possess a cubic close packing of oxygen ions. Additionally, all the octahedral interstitial sites must be fully occupied with cations that have average oxidation state of +2. These constraints are met with the $\text{Li}_2\text{M}\text{O}_3$ composition with $\text{M}$ having an oxidation state +4. The three occurring structure types that obey these rules are the previously mentioned $\text{Li}_2\text{MnO}_3$, $\beta\text{Li}_2\text{SnO}_3$ and $\text{Li}_2\text{ZrO}_3$ structures shown in Figures 4.1-4.3. The compositions and symmetries of these systems are compared in Table 4.1. The $\text{Li}_2\text{MnO}_3$ structure, shown in Figure 4.1, is a layered structure that possesses cation layers that alternate between pure lithium and hexagonal mixed metal, LiMn$_2$, layers (Figure 4.1a). The stacking vector for the mixed metal layers is [0 0 1] using $C2/m$ symmetry. The result is a linear channel of LiO$_6$ octahedra formed through the LiMn$_2$ layers resulting in the formation of other lithium planes that are perpendicular to the $ab$-plane (Figures 4.1b and 4.1c).

The $\beta\text{Li}_2\text{SnO}_3$ structure, shown in Figure 4.2, is similar to that of the $\text{Li}_2\text{MnO}_3$ structure except that the stacking vector is [0 $\pm1/6$ 1/2] using $C2/c$ symmetry. The result is an undulating, zigzagging, channel of LiO$_6$ octahedra formed through the LiSn$_2$ layers running parallel to the $c$-axis. As a result the $\beta\text{Li}_2\text{SnO}_3$ and the $\text{Li}_2\text{MnO}_3$ structure types are very similar and only differ in the location of successive mixed metal layers.
Figure 4.1: Li$_2$MnO$_3$ structure showing the layered arrangement alternating between pure lithium and mixed metal, LiMn$_2$, layers (a), the linear lithium channels through the LiMn$_2$ layers (b) and stacking of the LiMn$_2$ layers themselves, with oxygen and pure lithium layers omitted for clarity (c).
Figure 4.2: \( \beta \)-Li\(_2\)SnO\(_3\) structure showing the layered arrangement alternating between pure lithium and mixed metal, LiSn\(_2\), layers (a), the undulating, zig-zagging, lithium channels through the LiSn\(_2\) layers (b) and stacking of the LiSn\(_2\) layers themselves, with oxygen and pure lithium layers omitted for clarity (c).
Figure 4.3: Li$_2$ZrO$_3$ structure showing the layered arrangement solely composed of mixed metal, Li$_2$Zr, layers (a), the edge sharing ZrO$_6$ octahedra passing through the Li$_2$Zr layers (b) and stacking of the Li$_2$Zr layers themselves, with oxygen layers omitted for clarity (c).
Table 4.1:  Symmetry and compositional variations in Li$_2$MnO$_3$, $\beta$-Li$_2$SnO$_3$, and Li$_2$ZrO$_3$.

<table>
<thead>
<tr>
<th>Space Group</th>
<th>Li$_2$MnO$_3$</th>
<th>$\beta$-Li$_2$SnO$_3$</th>
<th>Li$_2$ZrO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z</td>
<td>4</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>$M$</td>
<td>1</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td># of Wyckoff Sites</td>
<td>Li 3</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>O 2</td>
<td>3</td>
<td>2</td>
</tr>
</tbody>
</table>

The Li$_2$ZrO$_3$ structure, on the other hand, differs significantly from the Li$_2$MnO$_3$ and $\beta$-Li$_2$SnO$_3$, as seen in Figure 4.3. Li$_2$ZrO$_3$ retains the cubic close packing oxygen ions network, while no longer possessing pure lithium layers. Instead, Li$_2$ZrO$_3$ is composed of cation layers that only have a Li$_2$Zr ratio. The resulting layers have ZrO$_6$ octahedra that are not connected within a given layer as is observed in the previous structures. Rather, the ZrO$_6$ octahedra are isolated within a given layer, but are edge sharing with ZrO$_6$ octahedra in the layers above and below. These ZrO$_6$ octahedra connections are presented in Figure 4.3b. It should also be noted that a hexagonal network is still observed in this system (Figure 4.3b), but in this case the hexagonal network is formed by the lithium ions in each layer rather than by the 4+ cations in every other layer as is the case for the Li$_2$MnO$_3$ and $\beta$-Li$_2$SnO$_3$.

The metals that take on these various structure types are presented below in Table 4.2, where Li$_2$MnO$_3$ [4, 5], Li$_2$NiO$_3$ [9], Li$_2$RuO$_3$ [10], [11], Li$_2$PdO$_3$ [14], and Li$_2$PtO$_3$ [15] have the Li$_2$MnO$_3$ structure type; Li$_2$TiO$_3$ [16], Li$_2$SnO$_3$ [6], [7], and Li$_2$PbO$_3$ [17] have
Table 4.2: Metals possessing Li$_2$MnO$_3$, $\beta$-Li$_2$SnO$_3$, and Li$_2$ZrO$_3$ structure types. *The Li$_2$MoO$_3$ system is so highly faulted it is reported with the LiCoO$_2$ structure type.

<table>
<thead>
<tr>
<th>Structure Type</th>
<th>$M^{4+}$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$MnO$_3$</td>
<td>Mn</td>
<td>[4], [5]</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>[9]</td>
</tr>
<tr>
<td></td>
<td>Mo$^*$</td>
<td>[10], [11]</td>
</tr>
<tr>
<td></td>
<td>Ru</td>
<td>[12], [13]</td>
</tr>
<tr>
<td></td>
<td>Pd</td>
<td>[14]</td>
</tr>
<tr>
<td></td>
<td>Pt</td>
<td>[15]</td>
</tr>
<tr>
<td>$\beta$-Li$_2$SnO$_3$</td>
<td>Ti</td>
<td>[16]</td>
</tr>
<tr>
<td></td>
<td>Sn</td>
<td>[6], [7]</td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td>[17]</td>
</tr>
<tr>
<td>Li$_2$ZrO$_3$</td>
<td>Zr</td>
<td>[7], [8]</td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td>[17]</td>
</tr>
</tbody>
</table>

The $\beta$-Li$_2$SnO$_3$ structure type; and Li$_2$ZrO$_3$ [7], [8] and Li$_2$PbO$_3$ [17] have been reported to possess the Li$_2$ZrO$_3$ structure type. It should be noted that the Li$_2$MoO$_3$ structure appears to have LiMo$_2$ mixed metal layers and isostructural with Li$_2$MnO$_3$, but as a result of a strong Warren fall effect the structure is reported as being isostructural with LiCoO$_2$ [10], [11].

Upon studying the $M^{4+}$ crystal radii, given by Shannon [18], the Pauling electronegativities [19], and the d-electron counts a couple of trends are observed when plotted, as shown in Figures 4.4 and Figure 4.5. It is quite apparent that metals possessing d-electron counts of any value other than $d^0$ or $d^{10}$ have the Li$_2$MnO$_3$ structure type, while those that do have $d^0$ or $d^{10}$ electron counts have either the Li$_2$ZrO$_3$
Figure 4.4: Plots of $M^{4+}$ Ionic radii versus d-electron count for the metals observed to occur in the Li$_2$MO$_3$ ordered rock salt structure.

Figure 4.5: Plot of $M^{4+}$ Ionic radii versus electronegativity (Pauling) for the metals observed to occur in the Li$_2$MnO$_3$, $\beta$-Li$_2$SnO$_3$, and Li$_2$ZrO$_3$ structure types.
or the $\beta$-Li$_2$SnO$_3$ structure type, as seen in Figure 4.4. Additional insight is also obtained by looking at the plot of ionic radii versus electronegativity (Pauling) shown in Figure 4.5. Metals with smaller ionic radii and larger electronegativities tend to prefer the Li$_2$MnO$_3$ structure types while those with larger radii and smaller electronegativities prefer the Li$_2$ZrO$_3$ structure type. Intermediate radii and electronegativities prefer the $\beta$-Li$_2$SnO$_3$ structure type. It is worth noting that lead lays between the Li$_2$ZrO$_3$ and $\beta$-Li$_2$SnO$_3$ region, which may be the reason it is observed in both structure types. Similarly, as molybdenum lies near the Li$_2$MnO$_3$ region and the $\beta$-Li$_2$SnO$_3$ region, this may be the cause of the Li$_2$MoO$_3$ possessing such a high degree of faulting.

In order to understand the structure stabilizing forces at work it is useful to separate the ionic interactions from the covalent interactions. Lattice energy and electronic structure calculations are ideal tools for doing such studies. In order to consider the ionic interactions, via lattice energies, the General Utility Lattice Program (GULP) [20] was employed as it considers the electrostatic interactions and the short range repulsive interactions, while neglecting any covalent contribution. In order to study all the bonding contributions, including covalent interactions, density functional theory (DFT) was employed via the Cambridge Serial Total Energy Package (CASTEP) [21]. Doing these calculations in parallel allows us to separate ionic and covalent interactions to shed light on the various bonding environments observed in these ordered rock salt structures.
4.1.2 Metal-Metal Bonding (Ru-Ru)

In addition to the occurrence of three structure types for Li$_2$MO$_3$ another structural variation has been observed. The other variation is a structural distortion of the Li$_2$MnO$_3$ structure type such that metal-metal bonding, or dimerization, is observed. To date the only compound that has been observed to undergo this distortion is Li$_2$RuO$_3$ [15], [22], [23]. At high temperatures Li$_2$RuO$_3$ is reported to possess the traditional Li$_2$MnO$_3$ structure type with C2/m symmetry (Figure 4.6a). However upon cooling below 540 K metal-metal bonding is observed lowering the symmetry to P2$_1$/m (Figure 4.6b). In the high temperature phase bond lengths of 2.966 Å (C$_1$) and 2.894 Å (C$_2$) are observed, while the low temperature phase has bond lengths of 3.045 Å (P$_1$), 3.049 Å (P$_2$) and 2.568 Å (P$_3$) [22].

Figure 4.6: LiRu$_2$ layer of Li$_2$RuO$_3$ C2/m symmetry (a) and P2$_1$/m symmetry (b).
Further evidence for this structural transition is found in the electronic and magnetic properties. Upon cooling below 540 K a steep increase in electrical resistance is observed in addition to a steep drop in magnetic susceptibility [22]. Efforts by Miura et-al have been made to explain the cause of this behavior. It has been suggested that the cause of this dimerization is a "dimer Jahn-Teller" effect [23], resulting in a loss of octahedral $t_{2g}$ degeneracy. The end result is the formation of $\sigma$, $\pi$, and $\delta$-interactions between the now degenerate orbitals, which are depicted in Figure 4.7. However, these interactions should be weak to nonexistent for $\pi$ and $\delta$. It is the spin pairing associated with this dimerization that causes the dramatic reduction in magnetic susceptibility upon cooling below 540 K. These observations may play an important role in the discrepancy between metallic and semi-conducting properties of Li$_2$RuO$_3$, but will not be addressed here.

Figure 4.7: Energy level diagram for Ru$^{4+}$-Ru$^{4+}$ dimers, where the electrons and their spins are presented by arrows.
What is left to be answered is if this is unique to Li$_2$RuO$_3$ or should one expect to observe dimerization in other Li$_2$MnO$_3$ structures, real and hypothetical, such as Li$_2$ReO$_3$, Li$_2$OsO$_3$, Li$_2$IrO$_3$, and Li$_2$PtO$_3$. As such we are able to study the effect of the d-electron count in the various metals and determine the role that this plays in these structures. Efforts to study these systems were performed using DFT via CASTEP calculations. These calculations allowed us to probe the geometrically optimized structure and lowest energies assuming both $C2/m$ and $P2_1/m$ structures for the above mentioned metals.

4.2 Experimental

Lattice energy calculations, based on ionic interactions, were performed using the General Utility Lattice Program (GULP). To determine the lattice energy for a given structure GULP considers the electrostatic interactions holding an ionic crystal together. GULP also considers the short-range repulsive interactions thereby preventing the bonds from becoming unreasonably short. The inter-atomic interactions considered are of a two-body type, which are separated into long-range Coulombic and the short range forces. A Buckingham potential, shown below, is used to model the short-range interactions

$$A_{ij} \exp \left( -\frac{r_{ij}}{\rho_{ij}} \right) - C_{ij}/r_{ij}^6$$

where $r_{ij}$ is the distance between ions $i$ and $j$, while $A_{ij}$, $\rho_{ij}$, and $C_{ij}$ are empirical parameters used to describe the interaction between respective ions. Table 4.3 provides a full list of empirical parameters employed in this study as determined by Woodley, et al. [26] and Bush, et al [27].
In order to more thoroughly evaluate these systems covalent character needs to be considered. As such total electronic energy calculations were performed to evaluate stability and geometrically optimize the structure types with the given metals discussed above. The total electronic energy calculations were performed using DFT using CASTEP via a Materials Studio user interface provide by Accelrys [21], which uses plane wave basis sets for valence electrons. The influence of core electrons is included using pseudopotential theory [28], while a generalized gradient-corrected approximation (GGA) is used to treat the electron-correlation potential of the electron gas.

### 4.3 Results and Discussion

#### 4.3.1 Li₂MnO₃, β- Li₂SnO₃, and Li₂ZrO₃, Structure Types

##### 4.3.1.1 GULP Analysis

As discussed previously GULP calculations take into account ionic interactions, both attractive and repulsive. The results for core-only potential calculations are presented in

<table>
<thead>
<tr>
<th></th>
<th>A (eV)</th>
<th>σ (Å)</th>
<th>C (eV/Å⁶)</th>
<th>qcore (e⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li¹⁺ – O²⁻</td>
<td>479.837</td>
<td>0.3000</td>
<td>5.34</td>
<td>1</td>
</tr>
<tr>
<td>Mn⁴⁺ – O²⁻</td>
<td>3329.388</td>
<td>0.2642</td>
<td>9.22</td>
<td>4</td>
</tr>
<tr>
<td>Sn⁴⁺ – O²⁻</td>
<td>6327.497</td>
<td>0.2610</td>
<td>31.11</td>
<td>4</td>
</tr>
<tr>
<td>Zr⁴⁺ – O²⁻</td>
<td>7290.347</td>
<td>0.2610</td>
<td>10.32</td>
<td>4</td>
</tr>
<tr>
<td>O²⁻ – O²⁻</td>
<td>25.410</td>
<td>0.6937</td>
<td>32.32</td>
<td>-2</td>
</tr>
</tbody>
</table>

*Table 4.3: Potential parameters utilized for the lattice energy calculations (GULP)*
### Table 4.4

<table>
<thead>
<tr>
<th>Structure Type</th>
<th>Mn</th>
<th>Sn</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$MnO$_3$</td>
<td>-78.687</td>
<td>-73.712</td>
<td>-72.493</td>
</tr>
<tr>
<td>$\beta$-Li$_2$SnO$_3$</td>
<td>-78.656</td>
<td>-73.729</td>
<td>-72.803</td>
</tr>
<tr>
<td>Li$_2$ZrO$_3$</td>
<td>-79.645</td>
<td>-74.745</td>
<td>-73.626</td>
</tr>
</tbody>
</table>

Lattice energies per formula unit for Li$_2$MnO$_3$, $\beta$-Li$_2$SnO$_3$, and Li$_2$ZrO$_3$ structure types with Mn, Sn, and Zr metals via GULP calculations.

### Figure 4.8

Lattice energy per formula unit incorporating Mn, Sn, and Zr into Li$_2$MnO$_3$, Li$_2$SnO$_3$, and Li$_2$ZrO$_3$ structure types.
Table 4.4 as well as plotted in Figure 4.8. The results show that when covalency is not considered the Li$_2$ZrO$_3$ structure type is preferred for all three metals used in this study: Mn, Sn, and Zr. The results are as expected since the ionic interactions should favor a system that reduces the interactions of highly charged ions such as the metals of the 4+ oxidation state, $M^{4+}$. In the Li$_2$ZrO$_3$ structure each $M^{4+}$ octahedron has only 2 second nearest neighbors of a 4+ oxidation state that are located in layers above and below the Li$_2$Zr layer of Li$_2$ZrO$_3$, whereas each $M^{4+}$ octahedron shares edges with 3 $M^{4+}$ octahedra in the Li$_2$MnO$_3$ and $\beta$-Li$_2$SnO$_3$ structures. Thus ionic considerations appear to be sufficient to correctly predict the structure of the Li$_2$ZrO$_3$.

However it is quite clear to see that ionic considerations appear to be insufficient to predict the structures of Li$_2$MnO$_3$ and Li$_2$SnO$_3$. The Li$_2$MnO$_3$ and $\beta$-Li$_2$SnO$_3$ structures have 3 second nearest neighbors of a 4+ oxidation state; they are not favored by ionic interactions. Given the structural similarity between the Li$_2$MnO$_3$ and $\beta$-Li$_2$SnO$_3$ structure types it is not surprising the energies are nearly equivalent. Thus it is quite apparent that one must consider covalent interactions in these structures to understand the true bonding environment.

4.3.1.2 Castep Analysis

Table 4.5 shows the total electronic energies calculated using CASTEP for the three structure types possessing Mn, Sn, Zr, and Pb, while Figure 4.9 plots $\Delta$-Energy versus structure type. ($\Delta$ Energy is the difference between the respective structure type and the
Table 4.5: Total electronic energies per formula unit for Li$_2$MnO$_3$, β-Li$_2$SnO$_3$, and Li$_2$ZrO$_3$ structure types for Mn, Sn, Zr, and Pb metals obtained from CASTEP calculations. Δ Energy is the difference between the respective structure type and the highest energy structure type.

<table>
<thead>
<tr>
<th>Structure Type</th>
<th>Mn</th>
<th>Sn</th>
<th>Zr</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$MnO$_3$</td>
<td>-2355.382</td>
<td>-1799.905</td>
<td>-2992.254</td>
<td>-3362.805</td>
</tr>
<tr>
<td></td>
<td>(0.000)</td>
<td>(-0.048)</td>
<td>(0.000)</td>
<td>(0.000)</td>
</tr>
<tr>
<td>β-Li$_2$SnO$_3$</td>
<td>-2355.408</td>
<td>-1799.914</td>
<td>-2992.267</td>
<td>-3362.825</td>
</tr>
<tr>
<td></td>
<td>(-0.025)</td>
<td>(-0.058)</td>
<td>(-0.013)</td>
<td>(-0.020)</td>
</tr>
<tr>
<td>Li$_2$ZrO$_3$</td>
<td>-2355.390</td>
<td>-1799.857</td>
<td>-2992.429</td>
<td>-3362.829</td>
</tr>
<tr>
<td></td>
<td>(-0.008)</td>
<td>(0.000)</td>
<td>(-0.176)</td>
<td>(-0.024)</td>
</tr>
</tbody>
</table>

Figure 4.9: Total energy calculations incorporating Mn, Sn, Zr and Pb into the Li$_2$MnO$_3$, Li$_2$SnO$_3$, and Li$_2$ZrO$_3$ structure types. Δ Energy is the difference between the respective structure type and the highest energy structure type per formula unit.
The most apparent result of these calculations is the clear preference for zirconium to occur in the zirconium structure type. Additionally, as was seen previously based on the lattice energy calculations obtained from GULP, the $\beta$-Li$_2$SnO$_3$ structure for zirconium is more stable than the Li$_2$MnO$_3$ structure likely due to the same ionic reasons discussed previously.

However there exist clear differences between the GULP and CASTEP calculations for the manganese and tin systems. Firstly, the CASTEP calculations shown in Figure 4.9 do not show a clear preference for the Li$_2$ZrO$_3$ structure type in all cases as was observed based on the lattice energy calculations. The differences must be due to the covalent character of the manganese and tin systems. Secondly, the CASTEP calculations accurately predicts the most stable form for tin to be the $\beta$-Li$_2$SnO$_3$ structure, while the Li$_2$MnO$_3$ structure is fairly close in energy. Due to the structural similarities between the Li$_2$MnO$_3$ and $\beta$-Li$_2$SnO$_3$ the proximity of the energies is expected. Finally, we come to the manganese systems where the results are much less clear or consistent with expectations. Overall the energies are all fairly close in values, but nonetheless the most stable structure type for manganese is calculated to be the $\beta$-Li$_2$SnO$_3$ structure. The Li$_2$ZrO$_3$ structure and the Li$_2$MnO$_3$ are close, but Li$_2$ZrO$_3$ is still lower in energy. It is postulated that limited difference in energy between these structure types is the reason for the faulting being observed in the Li$_2$MnO$_3$ structures (see Chapter 3), while it is not observed in the $\beta$-Li$_2$SnO$_3$ and Li$_2$ZrO$_3$ structure types. It is also possible that metal-
metal bonding may be playing a role in these structures as indicated by the results presented below.

In order to validate our understanding of these systems we chose to probe the stability of Li$_2$PbO$_3$ in the three different structure types, particularly since there is discrepancy in the literature as seen in Figures 4.4 and 4.5. The Li$_2$ZrO$_3$ structure is most stable when Li$^+$ and the M$^{4+}$ cations are similar in size, as significant size differences will tend to prefer the layered structures of Li$_2$MnO$_3$ and β-Li$_2$SnO$_3$. Additionally, the Li$_2$ZrO$_3$ structure is preferred based on ionic interactions, while Li$_2$MnO$_3$ and β-Li$_2$SnO$_3$ is preferred based on covalent interactions. Thus with the lead system there will be competing forces. The size match of Pb$^{4+}$ with Li$^+$ is very good at 0.915 Å and 0.900 Å, respectively [18]. However, electronegativity of Pb$^{4+}$ is much greater than that of Zr$^{4+}$, with 2.29 versus 0.09 (Sanderson electronegativity) [29]. So, Pb$^{4+}$ will prefer more covalent interactions.

Using these ideas we are able to analyze the geometry optimized structures possessing lead. The energies for Li$_2$MnO$_3$, β-Li$_2$SnO$_3$, and Li$_2$ZrO$_3$ structures types possessing lead are -3362.805 (0.000), -3362.825 (-0.020), and -3362.829 (-0.024) eV/formula unit, respectively. These results are in excellent agreement with reports in the literature as they indicate that lead is reasonably stable in both the β-Li$_2$SnO$_3$, and Li$_2$ZrO$_3$ structure types, while unstable in the Li$_2$MnO$_3$ structure. Thus it appears the increased covalent character in lead has caused the structure to no longer prefer the Li$_2$ZrO$_3$, which should
have been observed based on ionic and size consideration alone. However it should be noted that overall these energy differences are small in comparison to those of Li$_2$ZrO$_3$.

### 4.3.2 Metal-Metal Bonding

The total electronic energies of geometry optimized Li$_2$RuO$_3$, Li$_2$ReO$_3$, Li$_2$OsO$_3$, Li$_2$IrO$_3$, and Li$_2$PtO$_3$ using $P2_1/m$ and $C2/m$ space groups using CASTEP are presented in Table 4.6. Using $C2/m$ symmetry prohibits the formation of metal-metal dimers due to symmetry constraints; this is not the case when using $P2_1/m$ symmetry as the formation of metal-metal dimers is now symmetrically permitted. The comparison of the energies for each system using different symmetries is most easily done by looking at the energy differences upon subtracting the energy of $C2/m$ ($E_{C2/m}$) from the energy of $P2_1/m$ ($E_{P21/m}$). A plot of energy difference between $P2_1/m$ and $C2/m$ ($E_{P21/m} - E_{C2/m}$) versus respective group number is provide in Figure 4.10. The more negative this difference the larger the driving force dimerization. Additionally the resulting metal-metal distances for both $P2_1/m$ and $C2/m$ symmetry are presented in Table 4.7 and Figure 4.11.

A couple of things are clear based on these energy differences and bond distances. The geometry optimized Li$_2$ReO$_3$ strongly prefers the $C2/m$ symmetry by 3.1 eV. Based on the metal-metal distances of the Li$_2$ReO$_3$ models, it appears that this system wants to possess three nearly equal Re-Re distances of ~2.8 Å with $C2/m$ symmetry, rather than two short bonds of ~2.6 Å and one long bond of ~3.3 Å with $P2_1/m$ symmetry. This combination is different from the Li$_2$RuO$_3$ behavior where there are 2 long bonds and
### Table 4.6

<table>
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<tr>
<th>Material</th>
<th>Total Electronic Energies (eV/F.U.)</th>
<th>E(<em>{P2/m} - E</em>{C2/m}) (eV/F.U.)</th>
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<tr>
<td>Li(_2)RuO(_3)</td>
<td>-4307.64123 -4307.56528</td>
<td>-0.0760</td>
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<td>Li(_2)ReO(_3)</td>
<td>-4166.82765 -4169.95578</td>
<td>3.1281</td>
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<tr>
<td>Li(_2)OsO(_3)</td>
<td>-4234.43710 -4234.40825</td>
<td>-0.0288</td>
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<tr>
<td>Li(_2)IrO(_3)</td>
<td>-2260.70107 -2260.53014</td>
<td>-0.1709</td>
</tr>
<tr>
<td>Li(_2)PtO(_3)</td>
<td>-2420.14570 -2420.13685</td>
<td>-0.0088</td>
</tr>
</tbody>
</table>

Total electronic energies per formula unit obtained via CASTEP calculations using \(P2_1/m\) and \(C2/m\) symmetries and the energy differences \((E_{P2_1/m} - E_{C2/m})\).

### Figure 4.10

Plot of energy difference per formula unit between \(P2_1/m\) and \(C2/m\) \((E_{P2_1/m} - E_{C2/m})\) versus respective group number.

\*Re = 3.1281 eV
Table 4.7: Metal-metal distances obtained via CASTEP calculations using $P2_1/m$ and $C2/m$ symmetries along with average metal-metal distances and average metal-oxygen distances. The most stable symmetries are shaded.

<table>
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<th>Re</th>
<th>Os</th>
<th>Ir</th>
<th>Pt</th>
</tr>
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<td>$C2/m$</td>
<td>C1</td>
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<td>2.788</td>
<td>3.186</td>
<td>3.103</td>
<td>3.068</td>
</tr>
<tr>
<td></td>
<td>C2 x2</td>
<td>2.748</td>
<td>2.768</td>
<td>2.710</td>
<td>2.970</td>
<td>3.076</td>
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<tr>
<td></td>
<td>Average</td>
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<td>2.775</td>
<td>2.868</td>
<td>3.014</td>
<td>3.073</td>
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<tr>
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<td>$M^{4+}$-O</td>
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<td>2.0431</td>
<td>2.0440</td>
<td>2.0663</td>
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<td>$P2_1/m$</td>
<td>P1</td>
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<tr>
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<td>2.579</td>
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<td>3.147</td>
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</tr>
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<td>P3</td>
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<td>2.508</td>
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<td>3.072</td>
</tr>
<tr>
<td></td>
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</tr>
<tr>
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<td>$M^{4+}$-O</td>
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<td>2.0394</td>
<td>2.0712</td>
<td>2.0777</td>
</tr>
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</table>

Figure 4.11: Plot of $M^{4+}$-$M^{4+}$ distances versus respective group number.
1 short bond, as shown previously. At the other extreme is Li$_2$PtO$_3$ which appears to show no preference for either structure type with an energy difference of -0.0354 eV. Additionally, Li$_2$PtO$_3$ structure calculations are in decent agreement with those reported experimentally, 3.068 Å and 3.076 Å calculated versus 2.990(1) Å and 2.995(3) Å [15].

These calculations show the occurrence of Ru-Ru dimerization with metal-metal distances of 2.514 Å, 3.092 Å, and 3.121 Å, while experimentally they were determined to be 2.568 Å (P$_3$), 3.045 Å (P$_1$), 3.049 Å (P$_2$) [22]. The experimental diffraction pattern for Li$_2$RuO$_3$, Chapter 2, is compared to the simulated diffraction patterns generated from the geometry optimized structures using $C2/m$ and $P2_1/m$ symmetries are presented in Figure 4.12a. It is clear from this figure that Li$_2$RuO$_3$ is most appropriately described using $P2_1/m$ symmetry due to the observation of the additional peak near 18.9°. However, it is also clear that the lattice parameters calculated by CASTEP are shifted from their expected experimental passions, the cause of this is not clear and to truly address these issues full refinements should be completed.

Additionally, dimerization is predicted to occur for Li$_2$IrO$_3$, with 2.640 Å, 3.147 Å, and 3.151 Å metal-metal distances, and for Li$_2$OsO$_3$, with 2.508 Å, 3.051 Å, and 3.174 Å metal-metal distances. To date metal-metal dimerization has not been reported for Li$_2$IrO$_3$. The experimental diffraction pattern for Li$_2$IrO$_3$, Chapter 2, is compared to the simulated diffraction patterns generated from the geometry optimized structures using $C2/m$ and $P2_1/m$ symmetries presented in Figure 4.12b. Peaks associated with
Figure 4.12: Experimental and simulated powder X-ray diffraction patterns for Li$_2$RuO$_3$ (a) and Li$_2$IrO$_3$ (b). Simulated patterns generated from C2/m and P2$_1$/m structures obtained with CASTEP geometry optimizations. Arrows indicate peaks associated with P2$_1$/m superstructure.
dimerization as a result of dropping to $P2_1/m$ symmetry near 18.6° are not observed experimentally. The reason dimerization is not observed is not entirely clear. Future efforts should attempt to address this issue using both magnetometry and real space diffraction methods such as pair distribution function (PDF) analysis. Also, as $\text{Li}_2\text{OsO}_3$ has yet to be synthesized the occurrence of dimerization cannot be determined.

The cause of dimerization, as described previously, is the result of the "dimer Jahn-Teller" effect which results in a loss of octahedral $t_{2g}$ degeneracy, shown in Figure 4.7. This model is supported by the results plotted in Figure 4.13. When one has a $d^6$ system such as $\text{Pt}^{4+}$ there is no stabilization achieved by losing this degeneracy and in agreement with our calculations and experimental observations, this compound shows no evidence for forming dimers. Upon going to the $d^5$ system of $\text{Ir}^{4+}$, one $t_{2g}$ orbital per metal is now available for bonding and results in bond order of 1 between the two metal centers. The result is one short bond and two nearly equivalent bonds. It is believed that it is for this reason that dimerization is observed based on geometry optimized DFT calculations and should be observed experimentally, but to date has not been observed. Proceeding to $d^4$ with $\text{Ru}^{4+}$ and $\text{Os}^{4+}$, two $t_{2g}$ orbitals become available for bonding per metal center. As only the sigma bond should have significant overlap with metal-metal bond distances of ~2.5 Å and ~2.6 Å only one strong interaction is expected to occur, with little to no $\pi$ interaction expected to be present. A result of the little to no $\pi$ interaction the occurrence of one short bond is expected, which is shown for both $\text{Li}_2\text{RuO}_3$ and $\text{Li}_2\text{OsO}_3$ in
Figure 4.13: Plot of average $M^{f+}$ - $M^{f+}$ distances versus average $M^{f+}$ - O distances for the most stable geometry optimized Li$_2$MO$_3$ structures.
Finally, we come to the \( d^3 \) metal of \( \text{Re}^{4+} \), which has all three \( t_{2g} \) orbitals available for bonding per metal center. As a result all three metal-metal distances are shortened. The DFT calculations support this model even though \( C2/m \) symmetry is retained. The retention of \( C2/m \) symmetry is due to the structure retaining two equivalent bond lengths and a third bond length only slightly different. Thus a reduction in symmetry is not needed to obtain these results.

### 4.4 Conclusions

The results presented here shed light on the cause of the varying ordered rock salt structures possessing a \( \text{Li}_2\text{MO}_3 \) composition. The trend indicates that the larger the ionic radii and the smaller the electronegativity the more likely the structure is to be dictated by ionic interactions, which prefer the \( \text{Li}_2\text{ZrO}_3 \) structure type. The one clear trend that really stands out is the role d-electron count plays in determining the observed structure. The \( \text{Li}_2\text{ZrO}_3 \) and \( \text{Li}_2\text{SnO}_3 \) structures occur for \( d^0 \) and \( d^{10} \) systems, and the \( \text{Li}_2\text{MnO}_3 \) structure for other d-counts. Additionally, although less convincingly, as the ionic radii is reduced and the electronegativity increased for \( M^{4+} \) the structures begin to possess a layered structure such that the layers alternate between pure lithium and \( \text{LiM}_2^{4+} \); \( \text{Li}_2\text{MnO}_3 \) and \( \beta\)-\( \text{Li}_2\text{SnO}_3 \) possess this structural feature. The structural differences between \( \text{Li}_2\text{MnO}_3 \) and \( \beta\)-\( \text{Li}_2\text{SnO}_3 \) are much more subtle and differ only in the stacking sequence of their respective mixed metal layers. The GULP calculations clearly show that \( \text{Li}_2\text{ZrO}_3 \) is most favorable if considering only ionic interactions. The CASTEP calculations show that when all bonding is taken into account only \( \text{Li}_2\text{ZrO}_3 \) has a clear preference for one
structure over the others. By all measures the Li₂MnO₃ and β-Li₂SnO₃ structures have similar energies; hence the occurrence of stacking faults should not come as a surprise.

Metal-metal dimerization assuredly occurs in Li₂RuO₃ as reported above in Chapter 2 as well as in the literature [22]. Calculations presented here also seem to indicate that such dimerization is likely for Li₂IrO₃ and Li₂OsO₃, but has yet to be observed experimentally. Even upon obtaining Li₂IrO₃ specimens with a significant degree of order the presence of dimerization has yet to be observed, as shown in Chapter 2 as well. Thus, additional research should be directed towards studying these systems in order to verify the bonding consideration suggest by this work.

4.5 References


BIBLIOGRAPHY

53. M. O'Malley *Li+/H+ Ion Exchanged Li$_2$MO$_3$ (M = Ir, Pt) and Carbonated Melt Oxidized IrOx pH Sensors*. Unpublished Master's Thesis, The Ohio State University, Columbus, Ohio (2008).
Appendix A

FAULTING CALCULATION INPUT FILES

A.1 Sample Input File - DIFFaX

INSTRUMENTAL
{Header for instrumental section}
X-RAY
{Simulate X-ray diffraction}
1.5406
{X-ray wavelength}
{gaussian 0.1 trim}
{Instrumental broadening (much faster)}
PSEUDO-VOIGT 0.16 -0.12 0.034 0.65 TRIM
{Instrumental broadening (muchsl)}
STRUCTURAL
{Header for structural section}
5.1839 5.1839 4.8037 120.0
{unit cell coordinates, a, b, c, gamma}
UNKNOWN
{hexagonal, c = cubic [111]}
9
{111 sheet, plus its mirror}
infinite
{Layers are very wide in the a-b plane}

LAYER 1
None
Ir4+  2  1/9  5/9  0  2.0  1.0{a}
Ir4+  2  4/9  2/9  0  2.0  1.0
Li1+  1  7/9  8/9  0  2.0  1.0
O  2-  3  1/9  8/9  1/4  2.0  1.0{b}
O  2-  3  4/9  5/9  1/4  2.0  1.0
O  2-  3  7/9  2/9  1/4  2.0  1.0
Li1+  1  1/9  2/9  1/2  2.0  1.0{c}
Li1+  1  4/9  8/9  1/2  2.0  1.0
Li1+  1  7/9  5/9  1/2  2.0  1.0
O  2-  3  1/9  5/9  3/4  2.0  1.0{a}
O  2-  3  4/9  2/9  3/4  2.0  1.0
O  2-  3  7/9  8/9  3/4  2.0  1.0

LAYER 2 = 1
LAYER 3 = 1
LAYER 4 = 1
LAYER 5 = 1
LAYER 6 = 1
LAYER 7 = 1
LAYER 8 = 1
LAYER 9 = 1
### STACKING

- **recursive**: Statistical ensemble
- **infinite**: Infinite number of layers

### TRANSITIONS

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<tr>
<td>0.0500</td>
<td>0/3 1/3</td>
<td>1.0</td>
<td>layer 3 to layer 5</td>
</tr>
<tr>
<td>0.9000</td>
<td>1/3 0/3</td>
<td>1.0</td>
<td>layer 3 to layer 6</td>
</tr>
<tr>
<td>0.0000</td>
<td>2/3 0/3</td>
<td>1.0</td>
<td>layer 3 to layer 7</td>
</tr>
<tr>
<td>0.0000</td>
<td>0/3 2/3</td>
<td>1.0</td>
<td>layer 3 to layer 8</td>
</tr>
<tr>
<td>0.0000</td>
<td>1/3 1/3</td>
<td>1.0</td>
<td>layer 3 to layer 9</td>
</tr>
</tbody>
</table>

#### [Transitions from layer 4]

<table>
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<th>Probability</th>
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<th>Layer Destination</th>
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<tr>
<td>0.0000</td>
<td>2/3 0/3</td>
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<td>layer 4 to layer 1</td>
</tr>
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<td>0/3 2/3</td>
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<td>layer 4 to layer 2</td>
</tr>
<tr>
<td>0.0000</td>
<td>1/3 1/3</td>
<td>1.0</td>
<td>layer 4 to layer 3</td>
</tr>
<tr>
<td>0.0000</td>
<td>0/3 0/3</td>
<td>1.0</td>
<td>layer 4 to layer 4</td>
</tr>
<tr>
<td>0.0000</td>
<td>1/3 2/3</td>
<td>1.0</td>
<td>layer 4 to layer 5</td>
</tr>
<tr>
<td>0.0000</td>
<td>2/3 1/3</td>
<td>1.0</td>
<td>layer 4 to layer 6</td>
</tr>
<tr>
<td>0.0500</td>
<td>0/3 1/3</td>
<td>1.0</td>
<td>layer 4 to layer 7</td>
</tr>
<tr>
<td>0.9000</td>
<td>1/3 0/3</td>
<td>1.0</td>
<td>layer 4 to layer 8</td>
</tr>
<tr>
<td>0.0500</td>
<td>2/3 2/3</td>
<td>1.0</td>
<td>layer 4 to layer 9</td>
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</table>

#### [Transitions from layer 5]

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<th>Layer Destination</th>
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<tbody>
<tr>
<td>0.0000</td>
<td>1/3 1/3</td>
<td>1.0</td>
<td>layer 5 to layer 1</td>
</tr>
<tr>
<td>0.0000</td>
<td>2/3 0/3</td>
<td>1.0</td>
<td>layer 5 to layer 2</td>
</tr>
<tr>
<td>Layer Transition</td>
<td>Probability</td>
<td>Weighted Transition</td>
<td>Details</td>
</tr>
<tr>
<td>------------------</td>
<td>-------------</td>
<td>---------------------</td>
<td>---------</td>
</tr>
<tr>
<td>5 \rightarrow 3</td>
<td>0.0000</td>
<td>0/3 2/3 1.0</td>
<td>layer 5 to layer 3</td>
</tr>
<tr>
<td>5 \rightarrow 4</td>
<td>0.0000</td>
<td>2/3 1/3 1.0</td>
<td>layer 5 to layer 4</td>
</tr>
<tr>
<td>5 \rightarrow 5</td>
<td>0.0000</td>
<td>0/3 0/3 1.0</td>
<td>layer 5 to layer 5</td>
</tr>
<tr>
<td>5 \rightarrow 6</td>
<td>0.0500</td>
<td>1/3 2/3 1.0</td>
<td>layer 5 to layer 6</td>
</tr>
<tr>
<td>5 \rightarrow 7</td>
<td>0.0500</td>
<td>1/3 0/3 1.0</td>
<td>layer 5 to layer 7</td>
</tr>
<tr>
<td>5 \rightarrow 8</td>
<td>0.0500</td>
<td>0/3 1/3 1.0</td>
<td>layer 5 to layer 8</td>
</tr>
<tr>
<td>5 \rightarrow 9</td>
<td>0.9000</td>
<td>1/3 2/3 1.0</td>
<td>layer 5 to layer 9</td>
</tr>
</tbody>
</table>

**{Transitions from layer 6}**

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<th>Probability</th>
<th>Weighted Transition</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 \rightarrow 1</td>
<td>0.0000</td>
<td>0/3 2/3 1.0</td>
<td>layer 6 to layer 1</td>
</tr>
<tr>
<td>6 \rightarrow 2</td>
<td>0.0000</td>
<td>1/3 1/3 1.0</td>
<td>layer 6 to layer 2</td>
</tr>
<tr>
<td>6 \rightarrow 3</td>
<td>0.0000</td>
<td>2/3 0/3 1.0</td>
<td>layer 6 to layer 3</td>
</tr>
<tr>
<td>6 \rightarrow 4</td>
<td>0.0000</td>
<td>1/3 2/3 1.0</td>
<td>layer 6 to layer 4</td>
</tr>
<tr>
<td>6 \rightarrow 5</td>
<td>0.0000</td>
<td>0/3 0/3 1.0</td>
<td>layer 6 to layer 5</td>
</tr>
<tr>
<td>6 \rightarrow 6</td>
<td>0.9000</td>
<td>1/3 0/3 1.0</td>
<td>layer 6 to layer 6</td>
</tr>
<tr>
<td>6 \rightarrow 7</td>
<td>0.0500</td>
<td>2/3 2/3 1.0</td>
<td>layer 6 to layer 7</td>
</tr>
<tr>
<td>6 \rightarrow 8</td>
<td>0.0500</td>
<td>0/3 1/3 1.0</td>
<td>layer 6 to layer 8</td>
</tr>
</tbody>
</table>

**{Transitions from layer 7}**

<table>
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<th>Layer Transition</th>
<th>Probability</th>
<th>Weighted Transition</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 \rightarrow 1</td>
<td>0.0500</td>
<td>2/3 2/3 1.0</td>
<td>layer 7 to layer 1</td>
</tr>
<tr>
<td>7 \rightarrow 2</td>
<td>0.0500</td>
<td>0/3 1/3 1.0</td>
<td>layer 7 to layer 2</td>
</tr>
<tr>
<td>7 \rightarrow 3</td>
<td>0.9000</td>
<td>1/3 0/3 1.0</td>
<td>layer 7 to layer 3</td>
</tr>
<tr>
<td>7 \rightarrow 4</td>
<td>0.0000</td>
<td>0/3 2/3 1.0</td>
<td>layer 7 to layer 4</td>
</tr>
<tr>
<td>7 \rightarrow 5</td>
<td>0.0000</td>
<td>2/3 1/3 1.0</td>
<td>layer 7 to layer 5</td>
</tr>
<tr>
<td>7 \rightarrow 6</td>
<td>0.0000</td>
<td>0/3 0/3 1.0</td>
<td>layer 7 to layer 6</td>
</tr>
<tr>
<td>7 \rightarrow 7</td>
<td>0.0000</td>
<td>2/3 1/3 1.0</td>
<td>layer 7 to layer 7</td>
</tr>
<tr>
<td>7 \rightarrow 8</td>
<td>0.0000</td>
<td>1/3 0/3 1.0</td>
<td>layer 7 to layer 8</td>
</tr>
</tbody>
</table>

**{Transitions from layer 8}**

<table>
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<tr>
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<th>Probability</th>
<th>Weighted Transition</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 \rightarrow 1</td>
<td>0.9000</td>
<td>1/3 0/3 1.0</td>
<td>layer 8 to layer 1</td>
</tr>
<tr>
<td>8 \rightarrow 2</td>
<td>0.0500</td>
<td>2/3 2/3 1.0</td>
<td>layer 8 to layer 2</td>
</tr>
<tr>
<td>8 \rightarrow 3</td>
<td>0.0500</td>
<td>0/3 1/3 1.0</td>
<td>layer 8 to layer 3</td>
</tr>
<tr>
<td>8 \rightarrow 4</td>
<td>0.0000</td>
<td>2/3 0/3 1.0</td>
<td>layer 8 to layer 4</td>
</tr>
<tr>
<td>8 \rightarrow 5</td>
<td>0.0000</td>
<td>0/3 2/3 1.0</td>
<td>layer 8 to layer 5</td>
</tr>
<tr>
<td>8 \rightarrow 6</td>
<td>0.0000</td>
<td>2/3 1/3 1.0</td>
<td>layer 8 to layer 6</td>
</tr>
<tr>
<td>8 \rightarrow 7</td>
<td>0.0000</td>
<td>0/3 0/3 1.0</td>
<td>layer 8 to layer 7</td>
</tr>
<tr>
<td>8 \rightarrow 8</td>
<td>0.0000</td>
<td>1/3 2/3 1.0</td>
<td>layer 8 to layer 8</td>
</tr>
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</table>

**{Transitions from layer 9}**

<table>
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<tr>
<th>Layer Transition</th>
<th>Probability</th>
<th>Weighted Transition</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>9 \rightarrow 1</td>
<td>0.0500</td>
<td>0/3 1/3 1.0</td>
<td>layer 9 to layer 1</td>
</tr>
<tr>
<td>9 \rightarrow 2</td>
<td>0.9000</td>
<td>1/3 0/3 1.0</td>
<td>layer 9 to layer 2</td>
</tr>
<tr>
<td>9 \rightarrow 3</td>
<td>0.0500</td>
<td>2/3 2/3 1.0</td>
<td>layer 9 to layer 3</td>
</tr>
<tr>
<td>9 \rightarrow 4</td>
<td>0.0000</td>
<td>1/3 1/3 1.0</td>
<td>layer 9 to layer 4</td>
</tr>
<tr>
<td>9 \rightarrow 5</td>
<td>0.0000</td>
<td>2/3 0/3 1.0</td>
<td>layer 9 to layer 5</td>
</tr>
<tr>
<td>9 \rightarrow 6</td>
<td>0.0000</td>
<td>0/3 2/3 1.0</td>
<td>layer 9 to layer 6</td>
</tr>
<tr>
<td>9 \rightarrow 7</td>
<td>0.0000</td>
<td>1/3 2/3 1.0</td>
<td>layer 9 to layer 7</td>
</tr>
<tr>
<td>9 \rightarrow 8</td>
<td>0.0000</td>
<td>2/3 1/3 1.0</td>
<td>layer 9 to layer 8</td>
</tr>
<tr>
<td>9 \rightarrow 9</td>
<td>0.0000</td>
<td>0/3 0/3 1.0</td>
<td>layer 9 to layer 9</td>
</tr>
</tbody>
</table>
A.2 Sample Input File - FAULTS

INSTRUMENTAL AND SIZE BROADENING
!type of radiation
x-ray
!wavelength
1.5406
!instr. broadening u v w x Dg Dl trim keyword
pseudo-voigt 0.1632738 -9.800575E-05 1.267895E-02 1.41793E-03 5594.97 1688.47 trim
11.0 21.0 31.0 41.0 0.0 0.0 (0.01 0.01 0.01 0.01 100.0 100.0 )

STRUCTURAL
!a b c gamma
5.14746952 5.14746952 4.81021166 60.00
51.0 51.0 61.0 0.0 (0.01 0.01 0.1 0.1 )
!Laue simmetry
-1
!number of layer types
4
infinite

LAYER 1 {origen en li1}
!Layer simmetry
centrosymmetric
!Atom name number x y z Biso Occ
li1+ 1 0.0 0.0 0.0 1.0 0.5
0.0 0.0 0.0 0.0 (0.1 0.1 0.1 0.1)
li1+ 2 0.333333333 0.333333333 0.0 1.0 0.5
0.0 0.0 0.0 0.0 (0.1 0.1 0.1 0.1)
li1+ 3 0.666666667 0.666666667 0.0 1.0 0.5
0.0 0.0 0.0 0.0 (0.1 0.1 0.1 0.1)
O 2- 4 0.0 0.0 0.0 0.0 1.0 1.0
0.0 0.0 0.0 0.0 (0.1 0.1 0.1 0.1)
O 2- 5 0.333333333 0.0 0.25 1.0 1.0
0.0 0.0 0.0 0.0 (0.1 0.1 0.1 0.1)
O 2- 6 0.666666667 0.333333333 0.25 1.0 1.0
0.0 0.0 0.0 0.0 (0.1 0.1 0.1 0.1)

LAYER 2 {origen en li1:A1}
!Layer simmetry
none
!Atom name number x y z Biso Occ
Ir4+ 7 0.8508 0.8508 0.0 0.55 1.0
0.0 0.0 0.0 71.0 (0.1 0.1 0.1 0.1)
Ir4+ 8 0.1756 0.1756 0.0 0.55 1.0
0.0 0.0 0.0 71.0 (0.1 0.1 0.1 0.1)
Li1+ 9 0.50 0.50 0.0 1.0 1.0
0.0 0.0 0.0 0.0 (0.1 0.1 0.1 0.1)
LAYER 3 = 2 \{origen en li1 : B1\}

LAYER 4 = 2 \{origen en li1 : C1\}

STACKING

RECURSIVE

Infinite

TRANSITIONS

\!

layer 1 to layer 1
0.0  0.0  0.0  0.0
0.0  0.0  0.0  0.0  ( 0.3 0.1 0.1 0.1)

layer 1 to layer 2
0.92  -1/6  1/6  0.5
0.0  0.0  0.0  0.0  ( 0.3 0.1 0.1 0.1)

layer 1 to layer 3
0.04  1/6  0.5  0.5
0.0  0.0  0.0  0.0  ( 0.3 0.1 0.1 0.1)

layer 1 to layer 4
0.04  0.5  5/6  0.5
0.0  0.0  0.0  0.0  ( 0.3 0.1 0.1 0.1)

layer 2 to layer 1
1.0  -1/6  1/6  0.5
0.0  0.0  0.0  0.0  ( 0.1 0.1 0.1 0.1)

layer 2 to layer 2
0.0  0.0  0.0  0.0
0.0  0.0  0.0  0.0  ( 0.3 0.1 0.1 0.1)

layer 2 to layer 3
0.0  0.0  0.0  0.0
0.0  0.0  0.0  0.0  ( 0.3 0.1 0.1 0.1)

layer 2 to layer 4
0.0  0.0  0.0  0.0
0.0  0.0  0.0  0.0  ( 0.3 0.1 0.1 0.1)

layer 3 to layer 1
1.0  1/6  0.5  0.5
0.0  0.0  0.0  0.0  ( 0.3 0.1 0.1 0.1)

layer 3 to layer 2
0.0  0.0  0.0  0.0
0.0  0.0  0.0  0.0  ( 0.3 0.1 0.1 0.1)

layer 3 to layer 3
0.0  0.0  0.0  0.0
0.0  0.0  0.0  0.0  ( 0.3 0.1 0.1 0.1)

layer 3 to layer 4
0.0  0.0  0.0  0.0
0.0  0.0  0.0  0.0
0.0  0.0  0.0  0.0  (0.3 0.1 0.1 0.1)

!layer 4 to layer 1
1.0  0.5  5/6  0.5
0.0  0.0  0.0  0.0  (0.3 0.1 0.1 0.1)

!layer 4 to layer 2
0.0  0.0  0.0  0.0
0.0  0.0  0.0  0.0  (0.3 0.1 0.1 0.1)

!layer 4 to layer 3
0.0  0.0  0.0  0.0
0.0  0.0  0.0  0.0  (0.3 0.1 0.1 0.1)

!layer 4 to layer 4
0.0  0.0  0.0  0.0
0.0  0.0  0.0  0.0  (0.3 0.1 0.1 0.1)

CALCULATION

! SIMULATION {type of optimization}
! 10.0 0.0 0.02 {2Tmin, 2Tmax, step}

SIMPLEX {type of optimization}

100 {MXfun: max no of function evaluations. Recommended 20 * no of parameters to refine}
1 {eps: stopping criterion}
1 {iout: Input, print control parameter}
  { < 0 No printing}
  { = 0 Printing of parameter values and the function value after initial evidence of convergence.}
  { > 0 As for C%IOUT = 0 plus progress reports after every}

10.0E-10 {acc: ACC is a user supplied estimate of ma}

EXPERIMENTAL

LIO_H133_data.dat {} 10 0.01443 100.1875
free {}
sim2.bgr {}
interpolation {}