Studies of BaO – La₂O₃ – MgO – MnOₙ Compositional Space

Thesis

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Thesis

By

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ABSTRACT

A mixture with stoichiometry $\text{Ba}_{0.8}\text{La}_{0.2}\text{Mn}_{0.8}\text{Mg}_{0.2}\text{O}_3$ has been shown to be a promising candidate for decomposing NO gas at $T = 850^\circ\text{C}$, however, earlier studies did not investigate the structure or homogeneity of this composition. To address this gap in our knowledge two pseudo-ternary phase diagrams have been investigated. The compositional phase study of $\text{Ba}_{1-x}\text{La}_x\text{MnO}_3$ and $\text{BaMn}_{1-x}\text{Mg}_x\text{O}_3$ at various dopant levels, $(x = 0.1-0.7)$ was investigated and yielded unique phases that ultimately were used to identify the mixture of the proposed gas sensor. What was discovered was that at the $x = 0.2$ dopant level for both series’ contained the phases found within the gas sensor sample. These phases were $\text{Ba}_9\text{Mn}_3\text{O}_{16}$ ($\text{Cmca}$) and $\text{Ba}_{0.3}\text{La}_{0.5}\text{MnO}_3$ ($\text{Pm\bar{3}m}$). Unfortunately, due to the low scattering factor of magnesium it is unclear the phases in which it is being incorporated. An unforeseen and unexpected discovery was made while generating the $\text{BaMn}_{1-x}\text{Mg}_x\text{O}_3 - \text{BaMgO}_3$ series. At $x = 0.425$ a red compound exists with what appears to be a rare and interesting structure type. Resembling something with 2H hexagonal or multilayered rhombohedral symmetry, this structure appears to possess an incommensurate modulation of its structure.
Dedicated to

My family and friends
ACKNOWLEDGMENTS

First and foremost, I would like to acknowledge my family for their continued love and support for me in all that I do. From an early age I can remember helping my dad work on the family vehicle in our garage. He taught me everything I now know about cars. He taught me what to do to solve problems when the answer is not immediately apparent. Growing up he was always excited and willing to tackle any project I brought to the table. Most notably all of the old junk cars I decided to roll into our driveway. I cannot say enough about my dad; he is whom I want to be when I grow up. My mom is by far a teacher of life for me. She is the staple point of a kind and loving heart that I rely on every day. There has never been a time where I couldn’t rely on her for an encouraging word or a much-needed Bible verse to sustain my motivation. I am truly thankful for my parents and for everything they have helped me accomplish. I am also very thankful for my siblings. They are my best friends and I am thankful for their awesome encouragement; Lacey, Chelsea, Megan, Kayley and Chase.

It has been a brief two years since I began my work at The Ohio State University. I remember stepping foot on campus and experiencing the new sights, smells and all of the people for the first time. Fueled by my aspirations
and determination I was excited to begin this new journey and I could not wait. Some of my most fond memories are of the times spent with my incoming classmates. I am truly thankful for the comradery we shared during our time when we began our new classes within the graduate school. The long hours spent studying together and helping each other leaves an everlasting mark on my heart for the friendships that are equally everlasting. As time moved on the late night study sessions began to phase out of our daily routine when we all found our new research homes. Mine, of course, was with a phenomenal group headed by Dr. Patrick Woodward. I entered this group with my two best friends, Matt Linaburg and Eric McClure, feeling invincible with them at my side. This group was has been more than just a place for me to learn and research new and exciting things, it has been like a second family and home. My group members have been an immense help to me over the years in many ways, both personally and professionally. They have nurtured my understanding and passion for science both in and out of the lab. The memories of hanging out for drinks after a long day in the lab where we could vent our frustrations while simultaneously receiving helpful feedback and encouragement for the next day are memories not ever to be forgotten. I am incredibly thankful for all of my group members, both past and present who have influenced and encouraged me during my experience at Ohio State. I would also like to acknowledge my advisor, Dr. Patrick Woodward. Dr.
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Thank you, Pat.
VITA

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FIELD OF STUDY

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<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>°C</td>
<td>degrees Celsius</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>KM</td>
<td>Kubelka-Munk</td>
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CHAPTER 1: INTRODUCTION

1.1 General Motivation

The initial purpose of this research project was to investigate gas-sensing compounds, particularly perovskite oxide gas sensors. Perovskites are a widely known and versatile class of compounds. They have the ABX$_3$ formula where A and B are cations and X is an anion that can be oxygen, a halide or even certain small organic molecules. Because perovskites can be so easily manipulated in terms of cation substitutions and oxygen vacancies they are perfect for a vast range of applications.

Gas sensors hold a very important role in multiple facets of day-to-day life. Notable uses include carbon monoxide gas sensors for industry and domestic settings, and automobile gas sensors for measuring oxygen concentrations in order for the onboard computer to make appropriate adjustments to the air/fuel ratio. It has been reported by the Environmental Protection Agency (EPA) in 2012 that approximately 40% of N$_2$O, a primary component of the NO$_x$ family of gases, come from human activities$^1$.

Science has an uncanny ability to surprise and amaze when it comes to research. A particular highlight of this thesis is the discovery of a remarkable red compound that has many potential applications. One such application would be a vibrant red coating able to withstand extreme temperatures,
upwards of 1200°C. In this thesis, the study and understanding of a reported high-temperature gas sensor is investigated. This was performed by individually researching the compositional space of BaO – La₂O₃ – MgO and MnOₙ in the form of Ba₁₋ₓLaₓMnO₃ and BaMn₁₋ₓMgxO₃.

1.2 The Perovskite Structure

The perovskite class is one of the most versatile structure types known. With the ability to incorporate many elements from all corners of the periodic table, perovskites are ideal starting points for many solid-state applications. They have incredible electronic and magnetic properties depending on composition. They can be resilient in terms of temperature, which allows them to withstand extreme temperatures. For simplicity only three perovskite structure types will be addressed for the understanding of this research thesis.

1.2.1 Cubic Perovskites

Figure 1.1: The SrTiO₃ structure type often referred to as the ideal cubic perovskite structure has \( Pm\bar{3}m \) symmetry with an extended network of corner-sharing octahedra.
Figure 1.1 illustrates a network of corner-sharing BX₆ octahedra in what is called a cubic close packed (ccp) arrangement. The A-site (purple) is generally larger than the B-site cation and has 12-fold symmetry. The B-site cation is located inside of the light blue octahedra. As mentioned previously the “X” anion can be oxygen, or a halogen. Ideal perovskites adopt the space group \textit{Pm\bar{3}m}. \textit{SrTiO}_3 is a common example of this “ideal” perovskite.

1.2.2 Hexagonal and Rhombohedral Perovskites

![BaMnO₃ structure type](image)

Figure 1.2: \textit{BaMnO}_3 structure type – the hexagonal perovskite structure.

extended network of edge-sharing octahedra.

The hexagonal 2H polymorph follows the hexagonal close packed (hcp) arrangement. However, other hexagonal structures stack in many different ways. The example in figure 1.2 is that of a 2H polytype. Figure 1.3 shows some different variations of hexagonal and rhombohedral stacking systems.
These hexagonal and rhombohedral polymorphs can have various means of layering, consisting of alternating layers of face-sharing and corner-sharing octahedra: hchc (4H), hhh (2H), hhchhc (9R), etc. Where “h” stands for edge sharing and “c” stands for corner-sharing.

For the purpose of this thesis it is helpful to mention the equilibrium structure of BaMnO$_3$. Reported by Negas and Roth, BaMnO$_3$ undergoes structure transformation from a 2H hexagonal $P\bar{6}$_3/mmc type to a 15-layer form rhombohedral $R\bar{3}m$ type. This transformation occurs at $1150^\circ$C with the 2H form existing at below $1150^\circ$C and the 15R rhombohedral type at above. In chapter 2 it is shown that the same 15R form is the competing phase across much of the BaMnO$_3$ - LaMnO$_3$ phase diagram. This is consistent with the literature since the samples prepared in this research were heated to $1200^\circ$C.
1.3 Overview of Relevant Literature

The pertinent literature that best relates to this research is extensive, however for the convenience and simplicity only the most relevant will be mentioned.

In a 2007 paper Iwakuni, et al. showed that a mixed metal oxide with composition Ba$_{0.8}$La$_{0.2}$Mn$_{0.8}$Mg$_{0.2}$O$_3$ acted as a NO gas sensor at 850°C. This article was the starting point for the research described in this thesis. In this paper the authors mention a compound of interest with the stoichiometry Ba$_{0.8}$La$_{0.2}$Mn$_{0.8}$Mg$_{0.2}$O$_3$, which is claimed to be a perovskite oxide related to BaMnO$_3$, but with La$^{3+}$ and Mg$^{2+}$ substituted for the Ba$^{2+}$ and Mn$^{4+}$. It is shown in the paper that this particular compound was an adequate NO gas sensor at high temperatures (850°C). However, this paper failed to supply any evidence of the purity and structural nature of this compound. For that reason it was decided more characterization was necessary.

Further literature research turned up a few other articles relating to perovskite-like gas sensors. One of which in 2008 by P.T. Moseley, et al. focused on a lanthanum-iron based tungstate gas sensor, LaFe$_{0.95}$W$_{0.05}$O$_3$. In this research they concluded that the primary mechanism is due to the mobility along the surface. They find that this particular perovskite-oxide works well for oxygen monitoring at high temperatures but fell short when trying to sensor reducing gases at high temperatures.
Another extensive literature review in 2007 by Jeffrey Fergus of Auburn University, detailed many different perovskite-oxide gas sensors; SrTiO$_3$, BaTiO$_3$, CaTiO$_3$, LaFeO$_3$ and subsequent doped analogs of those. He studied the effects of n-type and p-type gas sensors as well as the effects of each on both reducing and oxidizing gases. He concluded that the perovskite structure is an ideal candidate due to its ability to accommodate a variety of dopants. He went on to say that this inherent flexibility allows for precise tuning for gas selectivity within mixtures.

An interesting literature paper by J. Cerdà, et.al. in 2002 showed barium stannate as a decent high temperature O$_2$, NO$_2$ and CO$_2$ gas sensor. They mentioned an optimal working temperature of $T = 700^\circ$C for O$_2$ gas sensing and $T = 600^\circ$C for CO$_2$ and NO$_2$.

1.4 Ba$_{0.8}$La$_{0.2}$Mn$_{0.8}$Mg$_{0.2}$O$_3$: A Reported Gas Sensor

Reported in literature as having adequate high temperature NO$_x$ gas decomposition characteristics, Ba$_{0.8}$La$_{0.2}$Mn$_{0.8}$Mg$_{0.2}$O$_3$ was a promising focal point for a characterization study. The hope was to properly identify and characterize the structure in terms of its crystalline and electronic properties, which had not been previously performed. This information could then be used to make new compounds with even higher working temperatures.
Lacking any characterization data in the literature a working understanding of the phase or phases present in the sample was top priority. Figure 1.4 presents an XRD powder pattern the aforementioned sample, annealed at 1200°C and cooled to room temperature. At first glance the pattern seems complicated. This prompted the research project to diverge into two simpler studies where substitution of only one cation at a time was performed. The full details of these two studies and the their usefulness in identifying the two phases present in the gas sensor compound is explained in the following chapters of this thesis.
1.4.1 High-Temperature Applications

Some common high temperature applications include the use in automotive and other manufacturing industries. Many industrial practices form dangerous gases as by-products, NO\textsubscript{x} being among the variety. Sensing and limiting these gases is key to cleaner air, better efficiency and lowering runtime cost. Likewise, incorporating gas sensors in automobiles has been common practice for the many years. In fact, many automobiles include two oxygen sensors, one at the intake manifold and the other located in the exhaust pipe at or after the catalytic converter. This allows the computer to adjust the air/fuel ratio for maximum efficiency and performance. Ideally, there should be no unused fuel or oxygen after combustion occurs.
CHAPTER 2: INVESTIGATION OF Ba\textsubscript{1-x}La\textsubscript{x}MnO\textsubscript{3} PHASE DIAGRAM

2.1 Introduction

This chapter focuses on Ba\textsubscript{1-x}La\textsubscript{x}MnO\textsubscript{3} at barium-rich (x = 0.1-0.7) concentrations. It is important to understand this barium-rich region in order to understand the potential phases present in the gas sensor sample. Since the molar stoichiometry in the gas sensor sample has a 4:1 barium-lanthanum ratio, it is appropriate to study the barium-rich portion of the phase diagram. By understanding what occurs at these ratios will give insight as to what may be happening to the gas sensor as the phase or phases propagate. In this case it was found that the (1-x)BaMnO\textsubscript{3} – (x)LaMnO\textsubscript{3} phase diagram contains a two phase mixture from x ≈ 0.1 to x ≈ 0.55. A more detailed discussion is presented in subsequent sections.

2.2 Experimental

2.2.1 Synthesis

The series, Ba\textsubscript{1-x}La\textsubscript{x}MnO\textsubscript{3} (x=0.1-0.7), was synthesized using the standard solid-state method. The starting materials used were BaCO\textsubscript{3} (Alfa Aesar, 99.997%), La\textsubscript{2}O\textsubscript{3} (GFS, 99.99%), MnO\textsubscript{2} (Alfa Aesar, 99.99%). La\textsubscript{2}O\textsubscript{3} was heated to 900°C for 10 hours to remove any absorbed water. Reactants were
ground together for 15 minutes and placed in an alumina crucible. The mixture was then fired at 900°C for 10 hours. All samples were ground for another 15 minutes then fired at 1200°C for 20 hours and characterized.

2.2.2 Characterization

Phase fraction analyses of the samples were checked using a Rigaku Miniflex II diffractometer (30kV, 15mA). A scan range of 10-75° 2θ and a step size of 0.02° 2θ were used.

2.3 Phase Fractions

Figure 2.1 shows an overlay of the different samples prepared at varying x-values. The series suggests that under these conditions the samples are within a two-phase region of the phase diagram.
Figure 2.1: Powder-Pattern Overlay of Ba$_{1-x}$La$_x$MnO$_3$ series

(x = 0.10 to 0.70)

This is easily recognizable simply by noticing the disappearance of two peaks at approximately 25° and 27° 2θ. These two peaks belong to the 15R Ba$_{1-x}$La$_x$MnO$_3$ structure as well as the major peak at around 31.5° 2θ. As x increases the relative amount of this 15R structure decreases until x ≈ 0.5 when it becomes negligible in concentration. The two phases have been determined by means of Rietveld refinements. Phase A for samples x = 0.1 to x ≈ 0.5 has been identified as Ba$_{0.5}$La$_{0.5}$MnO$_3$ having cubic symmetry, $Pm\bar{3}m$. Phase B has been identified as Ba$_{1-a}$La$_a$MnO$_{3-n}$ stoichiometrically labeled with the variable ‘a’ due to an insufficient data, existing with same 15R rhombohedral symmetry, $R\bar{3}m$ mentioned in chapter 1. From the phase diagram reported by Slobodin, et al,
A pure phase of composition $\text{Ba}_{0.45}\text{La}_{0.55}\text{MnO}_3$ and space group $\text{R}\overline{3}\text{c}$ is reported at the point of the three intersecting phase boundary lines. Experimental data supports the existence of this phase and it is therefore determined that at $x > 0.55$ one crosses over completely to a solid solution of the rhombohedral phase; this phase will be referred to as Phase $C$. Figure 2.3 illustrates the crystal structures for these three identified phases.

Figure 2.2: $\text{BaO} - \text{MnO}_x - \text{LaMnO}_3$ ternary isothermal section at $1500^\circ\text{C}$.\textsuperscript{13}
Figure 2.3: Rendered Crystal Structures for Phases A (Ba_{0.5}La_{0.5}MnO_3, \textit{Pm\={3}m}), B (Ba_{1-x}La_xMnO_3, x \approx 0.1, \textit{R\={3}m}) and C (Ba_{1-x}La_xMnO_3, x > 0.53, \textit{R\={3}c}).

In the plot of the phase fraction versus the dopant level x, figure 2.4, the experimental data indicates the approximate phase boundary is at x = 0.53. Therefore, at x < 0.53 a two phase region exists consisting of a 15R rhombohedral Ba_{1-x}La_xMnO_3 and a cubic Ba_{0.5}La_{0.5}MnO_3 structure. In the region of 0.5 < x < 0.55 it is suggested that the cubic perovskite is in a solid solution. This is a 3C perovskite similar to phase A but has \textit{R\={3}c} symmetry. It is closely related to the cubic structure but is distorted by out-of-phase rotations of the octahedra about the [111] axis and has rhombohedral symmetry. Since La^{3+} is smaller than Ba^{2+} upon incorporating more La^{3+} into the A-site of the
perovskite a decrease in the tolerance factor occurs causing octahedral tilting. Beyond \( x = 0.5 \) it is observed that the data points seem to plateau. From this point on the identified phase has \( R\overline{3}c \) symmetry and is in a region of solid solution. This phase is identified to be \( Ba_{1-x}La_xMnO_3 \).

![Phase Fraction vs. Dopant level](image)

Figure 2.4: Phase Fractions vs. Dopant value, \( x \). The phase transition from phase A (\( Pm\overline{3}m \), blue diamonds) to phase C (\( R\overline{3}c \), blue triangles) is observed at approximately \( x = 0.53 \).
Figure 2.5: Lanthanum series, single temperature, phase diagram. The dashed lines indicate approximate phase boundaries.

Figure 2.5 shows an approximate representation of a phase diagram in which the different regions are organized. Tables 2.1 and 2.2 organize the results of the Rietveld refinements.
<table>
<thead>
<tr>
<th>Phase A</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
</tr>
</thead>
<tbody>
<tr>
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<td>3.90847(39)</td>
<td>3.91718(25)</td>
<td>3.91782(19)</td>
<td>3.91443(21)</td>
<td>3.90965(10)</td>
</tr>
<tr>
<td>$V$, Å³</td>
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<td>60.106</td>
<td>60.135</td>
<td>59.979</td>
<td>59.76</td>
</tr>
<tr>
<td>$%_{\text{Frac}}$</td>
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<td>45.04</td>
<td>64.91</td>
<td>75.92</td>
<td>91.11</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Phase B</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$, Å</td>
</tr>
<tr>
<td>$c$, Å</td>
</tr>
<tr>
<td>$V$, Å³</td>
</tr>
<tr>
<td>$%_{\text{Frac}}$</td>
</tr>
</tbody>
</table>

Table 2.1: Unit Cell Parameters for $x < 0.5$ samples for Phase A and Phase B in Ba$_{1-x}$La$_x$MnO$_3$. 
Table 2.2: Unit cell parameters for $x > 0.5$ samples for phase $B$ and phase $C$ in $\text{Ba}_{1-x}\text{La}_x\text{MnO}_3$.

Above $x = 0.5$ it is presumed that phase $B$ should not exist. However, due to issues in achieving equilibrium a small amount remains in the sample. For clarity, the refinement values have been included. It is strongly believed that upon reaching equilibrium, as previously suggested, phase $B$ would cease to coexist with phase $A$ at or around $x = 0.5$.

Illustrative refinements are shown in Figures 2.6 through 2.13 for the lanthanum series. It is worth emphasizing that upon examination of the $x = 0.2$
sample Phase $A$ exists in its cubic form. This particular sample is worth mentioning due to its similarity with the overarching gas sensor sample, \( \text{Ba}_{0.8}\text{La}_{0.2}\text{Mn}_{0.8}\text{Mg}_{0.2}\text{O}_3 \), but absent of magnesium and will be discussed further in chapter 4.

![Rietveld refinement for the Ba\(_{0.9}\)La\(_{0.1}\)MnO\(_3\) sample. The top tick marks belong to the cubic, \( Pm\bar{3}m \) structure and the bottom tick marks belong to the rhombohedral, \( R\bar{3}m \) structure.](image)

Figure 2.6: Rietveld refinement for the Ba\(_{0.9}\)La\(_{0.1}\)MnO\(_3\) sample. The top tick marks belong to the cubic, \( Pm\bar{3}m \) structure and the bottom tick marks belong to the rhombohedral, \( R\bar{3}m \) structure.
Figure 2.7: Rietveld refinement for the Ba$_{0.8}$La$_{0.2}$MnO$_3$ sample. The top tick marks belong to the cubic, $Pm\bar{3}m$ structure and the bottom tick marks belong to the rhombohedral, $R\bar{3}m$ structure.
Figure 2.8: Rietveld refinement for the Ba$_{0.7}$La$_{0.3}$MnO$_3$ sample. The top tick marks belong to the cubic, \textit{Pm}$\overline{3}$m \textit{structure and the bottom tick marks belong to the rhombohedral, R}$\overline{3}$m \textit{structure.}
Figure 2.3.9: Rietveld refinement for the Ba$_{0.6}$La$_{0.4}$MnO$_3$ sample. The top tick marks belong to the cubic, $Pm\bar{3}m$ structure and the bottom tick marks belong to the rhombohedral, $R\bar{3}m$ structure.
Figure 2.10: Rietveld refinement for the $\text{Ba}_{0.5}\text{La}_{0.5}\text{MnO}_3$ sample. The top tick marks belong to the cubic, $\text{Pm}$-$3\text{m}$ structure and the bottom tick marks belong to the rhombohedral, $\text{R}$-$3\text{m}$ structure.
Figure 2.11: Rietveld refinement for the $\text{Ba}_{0.45}\text{La}_{0.55}\text{MnO}_3$ sample, with observed splitting in the inset. The top tick marks belong to the rhombohedral, $R\bar{3}c$ structure and the bottom tick marks belong to the rhombohedral, $R\bar{3}m$ structure.
Figure 2.12: Rietveld refinement for the Ba$_{0.4}$La$_{0.6}$MnO$_3$ sample. The top tick marks belong to the rhombohedral, $R\bar{3}c$ structure and the bottom tick marks belong to the rhombohedral, $R\bar{3}m$ structure.
Figure 2.13: Rietveld refinement for the Ba$_{0.3}$La$_{0.7}$MnO$_3$ sample. The top tick marks belong to the rhombohedral, $R\bar{3}c$ structure and the bottom tick marks belong to the rhombohedral, $R\bar{3}m$ structure.

From $x = 0.5$ to $x = 0.55$ a noticeable phase transition occurs. As mentioned previously as well as shown in the literature a phase with rhombohedral $R\bar{3}c$ symmetry arises past $x = 0.5$. This is shown within the magnified regions of figures 2.10 and 2.11. For the $x = 0.5$ sample there appears to be no observable splitting in the peak around 68 degrees 20. However, notice the evident peak splitting found in the same magnified region of the $x = 0.55$ sample for the reflection around 68 degrees 20. When this sample is refined using the cubic model an $R_w$ value, which indicates how well the calculated fit matches the observed pattern, is found to be 9.649 and is
larger than that of the rhombohedral model, which is 8.928. This difference in the fit for the x = 0.55 sample as well as the observed splitting suggest that the phase transitions into the rhombohedral structure type at or around this dopant level.

2.4 Conclusions

The lanthanum series yielded understanding to the phase diagram at annealing temperatures of 1200°C. Findings indicate a region within the phase diagram that is occupied by two distinct phases, \( \text{Ba}_{0.45} \text{La}_{0.55} \text{MnO}_3 \) (Phase A) with cubic symmetry, \( Pm\bar{3}m \), and \( \text{Ba}_{1.4} \text{La}_{1.4} \text{MnO}_3 \) (Phase B) with rhombohedral symmetry, \( R\bar{3}m \) where \( a \approx 0.1 \). These two phases remained throughout the doping analysis from \( x = 0.1 \) to 0.55 upon which Phase A transitioned into a new phase with rhombohedral symmetry \( R\bar{3}c \) and persisted through \( x = 0.7 \).

It is concluded that since the parent compound, \( \text{BaMnO}_3 \) is hexagonal, \( P6_3/mmc \) in symmetry then when a small concentration of \( \text{La}^{3+} \) is introduced to the structure it transitions to the observed rhombohedral phase. However, phase B is only stable at low concentrations of \( \text{La}^{3+} \), thus as more \( \text{La}^{3+} \) is introduced a new phase forms having cubic, \( Pm\bar{3}m \) symmetry. Furthermore, between \( x = 0.5 \) and \( x = 0.55 \) the phase with cubic symmetry transitions into a new phase with rhombohedral symmetry, referred to as phase C and considered to have \( \text{Ba}_{0.45} \text{La}_{0.55} \text{MnO}_3 \) stoichiometry. This phase persists and is in a solid solution region of the phase diagram. The lanthanum series was helpful in
identifying the secondary phase within the gas sensor compound, $\text{Ba}_{0.8}\text{La}_{0.2}\text{Mn}_{0.8}\text{Mg}_{0.2}\text{O}_3$, which will be explained more thoroughly in chapter 4.

Further analysis could be done to determine the exact stoichiometry for Phase B by closely examining the dopant region between $x = 0$ and $x = 0.1$. Furthermore, the samples in this study are believed to have not reached equilibrium and thus the errors in the observed values are rather high. Therefore, each sample should be annealed for a longer duration until equilibrium is reached.
3.1 Introduction

Surprisingly the BaMn$_{1-x}$Mg$_x$O$_3$ system has not been extensively studied or reported in the literature, which could be due to many factors. One such factor is the difficulty in identifying the occupancy of Mg$^{2+}$ using laboratory x-ray diffraction, due to its low scattering factor. However, studying this system is important in regards to the understanding and identification of the gas sensor phase fractions. In particular, this system includes the 4:1 manganese-magnesium molar ratio, similar to that of the gas sensor sample.

Another notable advantage in studying this system is the possibility of discovering something new or that has not been adequately reported in the literature. In particular, this series yielded a novel red pigment-like compound that has proven to be quite a challenge and is still not fully characterized. This compound emerges at approximately 30% Mg$^{2+}$ and purest at approximately 42.5% Mg$^{2+}$. A more detailed discussion is presented in section 3.4.
3.2 Experimental

3.2.1 Synthesis

The series, BaMn$_{1-x}$Mg$_x$O$_3$ ($x=0.1-0.5$), was synthesized using the standard solid-state method. The starting materials used were BaCO$_3$ (Alfa Aesar, 99.997%), MnO$_2$ (Alfa Aesar, 99.99%), MgO, (B&A, 99.99%). Reactants were ground together for 15 minutes and placed in an alumina crucible. The mixture was then fired at 900°C for 10 hours. All samples were ground for another 15 minutes then fired at 1200°C for 20 hours and characterized.

3.2.2 Characterization

The phase purity of the sample was checked using a Bruker D8 advance diffractometer (40kV, 50mA) equipped with a Lynx Eye position sensitive detector and a Ge 111 incident beam monochromator. A scan range of 10-90° 2θ and a step size of 0.015° 2θ were used. X-ray diffraction measurements were also obtained with a Rigaku Miniflex II (30kV, 15mA) for phase fraction identification and purity verification. Synchrotron x-ray diffraction ($\lambda = 0.413961$ Å) was collected via the mail in service at the 11-BM beamline at the Advanced Photon Source, at Argonne National Laboratory. Structural refinements on the x-ray and synchrotron data were performed using Topas Academic.
3.3 Phase Fractions

The manganese-rich portion of the BaMn$_{1-x}$Mg$_x$O$_3$ ($x=0.1-0.425$) phase diagram was studied. Studying this system, absent of lanthanum, gave insight into the affects of incorporating magnesium into BaMnO$_3$. The following figures, 3.1 through 3.5 illustrate the data and their corresponding Rietveld refinements.

Figure 3.1: Rietveld refinement for the BaMn$_{0.9}$Mg$_{0.1}$O$_3$ sample. The top tick marks belong to the 2H hexagonal, $P6_3/mmc$ structure and the bottom tick marks belong to the orthorhombic, $Cmca$ 6:5:16 structure type.
Figure 3.2: Rietveld refinement for the BaMn$_{0.8}$Mg$_{0.2}$O$_3$ sample. The top tick marks belong to the orthorhombic, \textit{Cmca} 6:5:16 structure type and the bottom tick marks belong to the orthorhombic, \textit{Cmca} 4:3:10 structure type.
Figure 3.3: Rietveld refinement for the \( \text{BaMn}_{0.7}\text{Mg}_{0.3}\text{O}_3 \) sample. The top tick marks belong to the rhombohedral, \( R\bar{3}m \) structure type and the bottom tick marks belong to the orthorhombic, \( Cmca \) 4:3:10 structure type.
Figure 3.4: Rietveld refinement for the BaMn$_{0.6}$Mg$_{0.4}$O$_3$ sample. The top tick marks belong to the 2H hexagonal, $P6_3/mmc$ structure type and the bottom tick marks belong to the orthorhombic, $Cmca$ 4:3:10 structure type.
Just like in the lanthanum series, it is beneficial to look closely at the 20% doping level (x = 0.2) in this magnesium series. This 20% level is most similar, stoichiometrically, to the prepared gas sensor. Both phases observed in this sample have the same symmetry, \( \text{Cmca} \), but differ in unit cell parameters. \( \text{Ba}_4\text{Mn}_3\text{Mg}_y\text{O}_{10} \) (\( \text{Cmca}, a = 5.685\text{Å}, b = 13.120\text{Å}, c = 12.732\text{Å} \)) and \( \text{Ba}_6\text{Mn}_5\text{Mg}_z\text{O}_{16} \) (\( \text{Cmca}, a = 5.703\text{Å}, b = 13.179\text{Å}, c = 19.916\text{Å} \)). The magnesium molar amounts are denoted by the letters \( y \) and \( z \) due to the difficulty in adequately identifying the exact ratio via Rietveld refinements and laboratory X-Ray diffraction. The models used to refine these samples follow the 4:3:10 and 6:5:16 (Ba:Mn:O) stoichiometry.\(^8\)
The two phases mentioned above were not observed in the lanthanum series. Likewise, in this magnesium series there was no phase with cubic symmetry. Therefore, it can be inferred that the presence of Mg$^{2+}$ destabilizes the hexagonal symmetry of BaMnO$_3$ resorting in the formation of phases with orthorhombic symmetry at lower dopant levels. Closer examination of the $x = 0.2$ samples, which closely resembles the gas sensor sample, but without the addition of La$^{3+}$, the majority phase has the 6:5:16 stoichiometry. The 6:5:16 phase was found to match the pattern of the primary phase in the gas sensor sample, Ba$_{0.8}$La$_{0.2}$Mn$_{0.8}$Mg$_{0.2}$O$_3$. Further analysis is required to determine the amount of Mg$^{2+}$ incorporated into this 6:5:16 structure type.
Figure 3.7: Magnesium series, single temperature, phase diagram. The dashed lines indicate approximate phase boundaries and the solid line indicates a definite phase boundary. In this case the purity of the unknown red compound at \( x = 0.425 \).

A phase diagram for the prepared samples is shown in figure 3.7. It is believed that in the low dopant \( x \)-values (0.1-0.3) this system is behaving as if MgO is an inert reactant. This notion is supported by the observation that the formed phases shown in figure 3.7 fall within the expected regions had MgO been left out of the synthesis. To further clarify, if MgO were left out of the synthesis, but the same molar amounts were used for each of the other
reactants then one would expect a pure form of $\text{Ba}_6\text{Mn}_5\text{O}_{16}$ at $x = 0.17$, $\text{Ba}_4\text{Mn}_3\text{O}_{10}$ at $x = 0.25$ and $\text{Ba}_3\text{Mn}_2\text{O}_8$ at $x = 0.33$. Therefore, there is strong reasoning to suggest that MgO does not play a large synthetic role in the formation of these phases. However, at $x > 0.33$ it is strongly suggested that magnesium plays a very important role in the synthetic nature of the unknown red phase that emerges. Studies show that without MgO present in the sample this new red phase does not form, see section 3.4. This phase diagram is incomplete in terms of temperature analysis; it is still useful in understanding what is happening with the addition of magnesium. At higher amounts of $\text{Mg}^{2+}$ the formation of a novel compound believed to have either hexagonal or rhombohedral symmetry was discovered around 40% $\text{Mg}^{2+}$. This phase is a deep red color and believed to be incommensurate in structure type. The discussion for this novel red compound is continued in section 3.4.

3.4 Characterization of Novel Red Phase

A novel compound with stoichiometry $\text{BaMn}_{0.575}\text{Mg}_{0.425}\text{O}_3$ has been prepared and has an intriguing red color. Red was an unexpected color for $\text{Ba}^{2+} - \text{Mn}^{n+} - \text{Mg}^{2+}$ containing compounds. Manganese is one of the most versatile elements on the periodic table. It has the ability to occupy oxidation states ranging from $\text{Mn}^{2+}$ to $\text{Mn}^{7+}$. Each oxidation state tends to be analogous with a color. For instances the permanganate anion, $\text{MnO}_4^-$ is an intense purple. However, in its $\text{Mn}^{2+}$ form, $\text{MnCl}_2$ exhibits a pale pink color. In its $+3$
oxidation state manganese is prone to Jahn-Teller distortions, and tends to exhibit a purple-red color as in the case of MnF$_3$.

A reasonable Pawley fit to the lab x-ray diffraction data can be obtained using space group symmetry $P6_3/mmc$ and cell parameters, $a = 5.81$ and $c = 4.10$ Å. This unit cell suggests the structure is related to the simple 2H perovskite structure; however, we are unable to carry out satisfactory Rietveld refinements using a 2H hexagonal model and therefore the structure must be more complicated than a simple 2H perovskite.

Figures 3.8 below nicely illustrate the color of red that this novel compound exhibits. Reflectance data, which has been transformed using the Kubelka-Munk (KM) transformation, is shown in figure 3.9. Currently, without knowing the crystal structure it is unknown as to why the compound is red. However, from the reflectance data it is believed there is a low energy d-d transition occurring at around 1.9 eV. In the BaMn$_{0.575}$Mg$_{0.425}$O$_3$ stoichiometry the manganese oxidation state is Mn$^{5.47+}$; however, if this is true then during the synthesis the manganese must have oxidized from its Mn$^{4+}$ oxidation state. However, if there were oxygen vacancies present then the manganese oxidation states would be lower. For instance if the stoichiometry were actually BaMn$_{0.575}$Mg$_{0.425}$O$_{2.575}$ then manganese would be in its +4 oxidation state. Since oxygen is so light and thus has a very low scattering factor it is difficult to determine the occupancy of oxygen using standard laboratory XRD data.
Without an accurate structural model it becomes impossible. It has been reported that an orthorhombic version of the brownmillerite structure containing Mn$^{5+}$ in a tetrahedral coordination exist in colors of turquoise and green. However, red compounds containing barium, manganese and magnesium have not been reported in the literature. For that reason this particular discovery is very interesting. The potential low-toxicity and particular color of this compound makes it a very intriguing discovery.

Figure 3.8: Image of synthesized red compound, $\text{BaMn}_{0.575}\text{Mg}_{0.425}\text{O}_3$
Figure 3.9: Kubelka-Munk transformed reflectance data of BaMn_{0.575}Mg_{0.425}O_3

The aforementioned chemical formula was determined after many stoichiometrically diverse syntheses. It is shown in this section that the important factor in the making of this phase is the manganese to barium molar ratio, \((\text{Ba}^{2+}/\text{Mn}^{n+} = 1.739)\). However, the magnesium concentration is also a purity-determining factor.

A disclaimer should be noted before proceeding further into this discussion. The characterization of this red compound at the time of this written thesis is incomplete. The conjectures and findings from this point on for this compound, which is referred to as the red compound, are the culmination of a year and a half worth of research. It is hopeful that by documenting what has been done, perhaps a future scientist can figure out this puzzle.
During the attempted characterization process of this unknown red compound it was found that two distinct space groups are semi useful in explaining most of the peaks. The first is a hexagonal model with $2H \ P6_3/mmc$ symmetry and the second is a rhombohedral model with $R\bar{3}m$ symmetry. The cell parameters have been determined to be approximately $a = b = 5.82$ Å and $c = 4.10$ Å for the $2H \ P6_3/mmc$ model and $a = b = 5.82$ Å and $c = 20.82$ Å for the $R\bar{3}m$ model. Notice that $a$ and $b$ parameters of both plausible structures are the same. The $c$ parameter is approximately 5 times larger than that of the $2H$ hexagonal structure type. See figure 3.10 for the rendered crystal structures.
Figure 3.10: Rendered Crystal Structures for 2H $P6_3/mmc$ (A) and $R3m$ (B) models.

One major difference in the two crystal structures in figure 3.10 is the coordination number for the manganese site cation. In the 2H hexagonal model it is 6-coordinate octahedral whereas in the rhombohedral model it is 4-coordinate tetrahedral. This could have an impact on the understanding of why the compound is red. It has been reported in the literature that manganese(V) containing compounds in 4-coordinate tetrahedral geometry display green colors. However, in that particular article their compounds also contained
indium. This gives credence to the idea that there are oxygen vacancies in this sample instead of the oxidation state being Mn$^{5.47+}$ as mentioned previously in this section. If the oxidation state was indeed Mn$^{5.47+}$ then it could be inferred that this compound should be green instead of red, based on this article and if the manganese has tetrahedral coordination. Regardless, it is worth mentioning and considering upon moving forward with this research. The model used for refining the rhombohedral structure type is Ba$_3$Mn$_2$O$_8$. This is a known compound and structure type, however, it does not entirely explain the powder pattern and is not any more useful in terms of Rietveld refinements than the 2H model. A comparison of simulated powder patterns with experimental data is shown below in figure 3.11. Panels B and C are simulated patterns for the 2H and the rhombohedral structures, respectively. There are interesting similarities between these two patterns as well as differences. The difference in $c$–edge length explains the difference in the number of peaks in both patterns. However, what is most interesting is the similarity in the most intense peaks. As can be seen in the figure, most of the more intense peaks are observed in both patterns. Furthermore, the experimental data shows similarities to both patterns. This further supports the notion that the correct structure of this red compound is something similar to these two models, but obviously different. The incommensurate nature of this red phase is apparent when compared to these simulated patterns.
Figure 3.11: Simulated powder pattern comparison between the experimental data (A), the $2H P6_3/mmc$ structure (B), and the $R\overline{3}m$ structure (C).
In attempt to characterize the mysterious red compound a multitude of differing samples were synthesized. A set of samples were, which will be referred to as varied barium, where the Mn$^{2+/3+}$/Mg$^{2+}$ ratio was held constant but the amount of Ba$^{2+}$ was manipulated slightly. These samples were Ba$_{1.1}$Mn$_{0.6}$Mg$_{0.4}$O$_3$ and Ba$_{0.9}$Mn$_{0.6}$Mg$_{0.4}$O$_3$. Comparing these two new samples to the previously prepared sample from Figure 3.4 a similar set of minor peaks is noticeable between the Ba$_{0.9}$Mn$_{0.6}$Mg$_{0.4}$O$_3$ and BaMn$_{0.6}$Mg$_{0.4}$O$_3$ samples. For instances there are two reflections, one at approximately 29° and another at approximately 31° that are not observed in Ba$_{1.1}$Mn$_{0.6}$Mg$_{0.4}$O$_3$. The results indicate that in fact the amount of barium does matter. From this it can be assumed that the ratio of barium to manganese for the pure form of this red compound is somewhere between: 1.0/0.6 = 1.666 and 1.1/0.6 = 1.833. This further confirms the previously mentioned barium to manganese ratio of 1.0/0.575, which is 1.739 that has been found to be the most chemically pure form synthesized. Figure 3.12 illustrates this data.
Figure 3.12: Overlay of Rietveld refinements for varied barium study including samples: $\text{Ba}_{0.9}\text{Mn}_{0.6}\text{Mg}_{0.4}\text{O}_3$, $\text{BaMn}_{0.6}\text{Mg}_{0.4}\text{O}_3$ and $\text{Ba}_{1.1}\text{Mn}_{0.6}\text{Mg}_{0.4}\text{O}_3$.

A different set of samples was prepared in attempt to incorporate magnesium into the manganese-bonding site of the $\text{Ba}_6\text{Mn}_5\text{O}_{16}$ (6:5:16) structure type in the following manner $\text{Ba}_6\text{Mn}_{5-z}\text{Mg}_z\text{O}_{16-n}$, From the XRD data obtained it clear that there is a two-phase mixture noted by the vertical tick-marks for each phase. The 2H hexagonal model was used as a means of identifying the reflections belonging to the red compound. However, it is still unclear as to the exact symmetry of the red compound crystal structure. For simplicity, the 2H hexagonal structure type will be used for most of the proceeding data as a means of identifying the peaks belonging to the red
compound. Figures 3.13 and 3.14 show samples prepared using the 6:5:16 structure type.

Figure 3.13: Preparation of the $\text{Ba}_6\text{Mn}_4\text{MgO}_{16}$ sample. The top tick marks belong to the 2H hexagonal, $P\overline{6}_3/mmc$ structure type and the bottom tick marks belong to the orthorhombic, $Cmca$ 4:3:10 structure type.
Figure 3.14: Preparation of the $\text{Ba}_6\text{Mn}_{3.5}\text{Mg}_{1.5}\text{O}_{16}$ sample. The top tick marks belong to the 2H hexagonal, $P6_3/mmc$ structure type and the bottom tick marks belong to the orthorhombic, $Cmca$ 4:3:10 structure type.

The primary difference in the synthesis of these two samples is the ratio of manganese to magnesium. As it appears in the data, upon addition of the magnesium from a 4/1 to a 3.5/1.5 ratio the red compound, denoted with the 2H tick-marks, seems to dominate the phase fraction. Furthermore, the current best-prepared sample, $\text{BaMn}_{0.575}\text{Mg}_{0.425}\text{O}_3$, has a Mn/Mg molar ratio of 0.575/0.425, which confirms the trend observed in these two prepared samples. The purpose of preparing these samples as well as some of the later samples in this section was to attempt to determine the exact stoichiometry of the red
compound. Until an understanding of its true chemical make-up is discovered a proper crystal structure characterization will be substantially more difficult. These samples were red in color but not with the same intensity as other prepared samples.

The following figure 3.15 shows the data obtained from a synthesis with the sole purpose of probing the stoichiometry. Other than determining that the stoichiometry was incorrect this sample was not helpful in the pursuit of the identity of the red compound. This sample was red in color but not with the same intensity as other prepared samples.

Figure 3.15: Preparation of the Ba$_3$Mn$_{12}$Mg$_{18}$O$_{20}$ sample. The top tick marks belong to the 2H hexagonal, $P6_3/mmc$ structure type and the bottom tick marks belong to MgO.
The final synthesis study that was attempted involved annealing the 40% magnesium substituted sample, BaMn$_{0.6}$Mg$_{0.4}$O$_3$, to higher temperatures; 1300°C and 1400°C. Figure 3.16 shows the overlaid XRD patterns from 1200°C to 1400°C. Table 3.1 shows a trend of the unit cell parameters that would have been missed had this study not happened. The data suggests that as the synthesis temperature increases so does the $c$ unit cell parameter. From 1200°C to 1300°C to 1400°C the $c$ parameter increase by approximately 0.05Å, although it is not a substantial change it is still enough to be curious. It is believed that the crystal structure of this red compound is incommensurate and this new finding supports that hypothesis. Another unique observation that is noted in the laboratory notebook is the apparent color change. Upon heating to 1300°C and 1400°C the color became darker red. However, while the samples were sitting out on the lab bench exposed to air over the course of a month the dark red color changed back to its original shade of red, which was brighter. It is unclear as to why this tends to happen and this result has not been repeated. It is simply another unique and fascinating characteristic of this mysterious red compound.
Figure 3.16: Overlay of XRD powder patterns for raised temperature analysis of BaMn$_{0.6}$Mg$_{0.4}$O$_3$ - 1200$^\circ$C, 1300$^\circ$C and 1400$^\circ$C
<table>
<thead>
<tr>
<th></th>
<th>1200°C</th>
<th>1300°C</th>
<th>1400°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a, \text{Å})</td>
<td>5.81937(57)</td>
<td>5.83102(39)</td>
<td>5.82886(33)</td>
</tr>
<tr>
<td>(c, \text{Å})</td>
<td>4.15371(52)</td>
<td>4.20220(38)</td>
<td>4.24544(32)</td>
</tr>
</tbody>
</table>

Table 3.1: Results from initial rietveld refinements for raised temperature analysis of BaMn_{0.6}Mg_{0.4}O_{3} - 1200°C, 1300°C and 1400°C refined with the \(2H\) \(P6_3/mmc\) Model

The following figure 3.17 shows the XRD data collected on the sample of stoichiometry BaMn_{0.6}O_{3}. This sample was synthesized for the purpose of determining the importance magnesium in the discovered red compound. Previously in this chapter it was mentioned how the barium to manganese ratio is important, thus in this sample the barium to manganese is held constant and the magnesium is completely left out. The black pattern is the sample without magnesium and the red pattern is the same sample but with magnesium. As it is clearly evident, the two patterns do not match up. In fact, upon performing simple phase searching in the ICSD database the majority phase of the black pattern is that of Ba_{4}Mn_{3}O_{10}. The pattern in general is quite chaotic and therefore the secondary phases have been difficult to decipher. However, it is clear that the red compound is not formed without magnesium present in the sample since the most intense peak at around 31 degrees 2\(\theta\) of the red pattern is
not shown at all in the black pattern. Furthermore, it should be noted that this synthesized sample, BaMn_{0.6}O_{3}, is in fact a dark green/black color with no physical resemblance to the red compound.

![XRD pattern overlay of samples BaMn_{0.6}Mg_{0.4}O_{3} and BaMn_{0.6}O_{3}](image)

Figure 3.17: XRD pattern overlay of samples BaMn_{0.6}Mg_{0.4}O_{3} and BaMn_{0.6}O_{3}

Due to the difficulty in peak indexing, synchrotron data was collected for the sample BaMn_{0.575}Mg_{0.425}O_{3}.\textsuperscript{14} By using a synchrotron source for diffraction yields higher resolution, lower background and better signal to noise. Unfortunately, a satisfactory Rietveld refinement could not be generated with this new data. However, upon analyzing the pattern it was noticed that a set of peaks, which have notoriously given problems in previous refinements, seem to have curious peak shapes. Previous lower-resolution laboratory data was unable to capture these asymmetric peak shapes.
These peak shapes, which are highlight in figure 3.18 below, have interesting asymmetry that is seemingly difficult to model. Upon closer review it appears reflections to the left of 11 degrees 2θ have tailing issues, where the indicated peaks to the right of 11 degrees 2θ have some fronting issues. These peaks appear to be pointing away from the larger peak at 11 degrees. This kind of behavior could be due to small variations and non-systematic repeating units of the superstructure. In the initial stages of this red compound discovery it was thought that these peaks did not belong to the red phase in question. However, it is now believed that they in fact do belong to the red phase and that this red phase is incommensurate in structure type.

![Graph](image)

Figure 3.18: Synchrotron analysis of BaMn$_{0.375}$Mg$_{0.625}$O$_3$ on the 11-BM beam line at the Argonne Nation Laboratory
Finally, it is worth mentioning a research article published in 2001 by K. E. Stitzer, et al. It is outlined in this article the difficulty in solving incommensurate crystal structures. The 2H hexagonal structure is mentioned as being solvable by higher ordered mathematical methods. An incommensurate crystal structure is one that deviates the standard model and therefore becomes exponentially more difficult to solve. Solving these types of structures require higher order mathematical models that are not directly intuitive. Standard 2-dimensional or even 3-dimensional approaches do not suffice. In this particular research paper the authors address the $A_{1+x}(A_xB_{1-x})O_3$ 2H-hexagonal structure type. Various compositions studied in this article were found to be incommensurate. Solving structures within this compositional space require the use of what is called a superspace group approach to structural determination. Incommensurate crystal structures are often rare as well as difficult to solve.

3.5 Conclusions

Studying the compositional space outlined by $\text{BaMn}_{1-x}\text{Mg}_x\text{O}_3$ ($x = 0.1 – 0.425$) was useful in identifying various phases, both known and unknown. Although the exact level of doping achieved with the magnesium is still in question. However, it is suggested from the data that up to 30% magnesium there is minimal incorporation into the formed structures. Above 30% it is apparent that magnesium plays an important role in the synthesis due to the new red phase being formed. It has been shown that there exist multiple two-
phase regions within this compositional space. Most importantly is the phase present at $x = 0.2$. A phase modeled with the $\text{Ba}_9\text{Mn}_5\text{O}_{16}$ structure type was identified as the majority phase. This phase is important, as will be discussed in chapter 4, because it is also found to be the primary phase of the gas sensor compound in question.

Lastly, an interesting discovery of a novel compound was made during the exploration of the more $\text{Mg}^{2+}$ concentrated region. It was determined that at $x = 0.425$ of $\text{BaMn}_{1-x}\text{Mg}_x\text{O}_3$ a compound with a red color exists. This particular $x$ value has been decided as the most pure form based on multiple stoichiometrically diverse syntheses outlined previously in this chapter. Although the exact crystal structure remains unsolved for this mysterious red compound, it is believed the true structure is either rhombohedral or hexagonal in nature and resembles $2\text{H}$ structural stacking. Therefore, this research remains unsolved and open.
CHAPTER 4: IDENTIFICATION OF $\text{Ba}_{0.8}\text{La}_{0.2}\text{Mn}_{0.8}\text{Mg}_{0.2}\text{O}_3$ PHASE FRACTIONS

4.1 Introduction

$\text{Ba}_{0.8}\text{La}_{0.2}\text{Mn}_{0.8}\text{Mg}_{0.2}\text{O}_3$ has been reported as a potential high temperature ($850^\circ\text{C}$) $\text{NO}_x$ and $\text{O}_2$ gas sensor. Further understanding of this compound was required due to the lack in supporting information of the crystal symmetry and purity of this sample. The research presented in this thesis draws conclusions to the identity of the mixture of two phases present in the sample.

4.2 Experimental

4.2.1 Synthesis

The sample, $\text{Ba}_{0.8}\text{La}_{0.2}\text{Mn}_{0.8}\text{Mg}_{0.2}\text{O}_3$, was synthesized using the standard solid-state method. The starting materials used were $\text{BaCO}_3$ (Alfa Aesar, 99.997%), $\text{La}_2\text{O}_3$ (GFS, 99.99%), $\text{MnO}_2$ (Alfa Aesar, 99.99%), $\text{MgO}$ (B&A, 99.9%). $\text{La}_2\text{O}_3$ was heated to $900^\circ\text{C}$ for 10 hours to remove any absorbed water. Reactants were ground together for 15 minutes and placed in an alumina crucible. The mixture was then fired at $900^\circ\text{C}$ for 10 hours. All samples were ground for another 15 minutes then fired at $1200^\circ\text{C}$ for 20 hours and characterized.
4.2.2 Characterization

Diffraction measurements of the sample were made using a Bruker D8 advance diffractometer (40kV, 50mA) equipped with a Lynx Eye position sensitive detector and a Ge 111 incident beam monochromator. A scan range of 10-90° 2θ and a step size of 0.015° 2θ were used.

4.3 Discussion

The prepared sample, \( \text{Ba}_{0.8}\text{La}_{0.2}\text{Mn}_{0.8}\text{Mg}_{0.2}\text{O}_3 \) is shown with its corresponding Rietveld refinement in Figure 4.1. The fit is shown to be adequate for identifying the two phases present in the mixture.

From the lanthanum series it found that in the presence of \( \text{La}^{3+} \) a phase arises with cubic symmetry with stoichiometry \( \text{Ba}_{0.5}\text{La}_{0.5}\text{MnO}_3 \). This phase is positively identified in the gas sensor as the secondary phase. The primary phase, identified as \( \text{Ba}_6\text{Mn}_5\text{O}_{16} \), has been confirmed through the analysis of the \( \text{BaMn}_{1-x}\text{Mg}_x\text{O}_3 \) magnesium series. The 6:5:16 structure type has orthorhombic symmetry. Table 4.1 summarizes the results from the Rietveld refinement analysis. At this time the exact level of magnesium that is being incorporated into either identified structure is not certain. Quite possibly MgO remains unreacted within this sample as hypothesized in chapter 3.
Figure 4.1: Rietveld refinement for the Ba$_{0.8}$La$_{0.2}$Mn$_{0.8}$Mg$_{0.2}$O$_3$ sample. The top tick marks are for Ba$_{0.5}$La$_{0.5}$MnO$_3$ cubic phase. The lower tick marks are for Ba$_6$Mn$_5$O$_{16}$ orthorhombic phase.
As mentioned in chapter 2 the cubic structure of phase A undergoes a phase transition at \( x = 0.55 \) into a rhombohedral structure type. Upon examining the gas sensor sample carefully it was determined that the secondary phase is indeed the cubic form and not the rhombohedral form. This determination is based on the lack of peak splitting at the reflection around 68 degrees 2\( \theta \). Also, recall that in the \( x = 0.2 \) lanthanum-series sample the lanthanum-rich phase, phase \( A \), was found to be in its cubic form. Therefore, the phase is determined to be the cubic form, \( \text{Ba}_{0.47}\text{La}_{0.53}\text{MnO}_{3.3} \), in the gas sensor sample.

Pure forms of both fractions have been synthesized. However, it is unclear as to the exact level of Mg\(^{2+} \) that is incorporated in both phases or if it
behaves inert in the synthesis. In chapter 3 it is suggested that the MgO behaves as an inert species in the synthesis until \( x > 0.3 \). This is a possibility here as well. Unfortunately, due to the low scattering factor of \( \text{Mg}^{2+} \) a complete understanding of the magnesium incorporating is unclear. An attempted synthesis of the 6:5:16 phase with the incorporation of magnesium has proven difficult and thus, supporting the notion that \( \text{Mg}^{2+} \) does not play a role in the formation of \( \text{Ba6Mn5O16} \).

4.4 Conclusions

Reported as a successful, high-temperature gas sensor, \( \text{Ba}_{0.8}\text{La}_{0.2}\text{Mn}_{0.8}\text{Mg}_{0.2}\text{O}_3 \) is in fact a mixture of two individual phases. The primary phase is the 6:5:16 (Ba:Mn:O) orthorhombic structure making up 63.7% of the sample and a secondary phase identified as \( \text{Ba}_{0.47}\text{La}_{0.53}\text{MnO}_3 \) in its cubic form. This phase makes up 36.3% of the sample.

Unfortunately, due to time constraints, a proper analysis of the gas sensing capabilities of both of these phases was not performed. It is unclear at this time as to whether or not these phases act synergistically with one another or if one phase does all of the gas sensing. Synthesizing pure forms of each phase and analyzing the gas sensing individually can answer this question. If indeed both phases play a role in the gas sensing ability, then further analyses should be performed by preparing samples of known ratios of both phases and testing their gas sensing ability.
BIBLIOGRAPHY


(14) 11-BM Beamline at Argonne National Laboratory