Probing the Local Structure of Perovskites using Raman Scattering Spectroscopy

THESIS

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Abstract

Diffraction techniques, such as X-ray diffraction (XRD), are traditionally used to examine the structures of extended solids. However, while diffraction is an invaluable analytical tool in solid state chemistry, it is limited by the fact that it can only probe the overall, average structure. Raman scattering spectroscopy, however, has the ability to probe the local structure of a material, which may be different than the average structure. The Raman spectra of double perovskites show interesting features caused by cation disorder and octahedral tilting within the material. This thesis will examine the effects on the Raman spectrum when disorder and/or octahedral tilting are present in a material.

When cation disorder is not present in the material, as in the tungsten-based double perovskites in this study, the effects of octahedral tilting are observed in the Raman spectrum. It was found that the greater the octahedral tilting distortion, the larger number of Raman active lattice modes that were observed. A relationship between the B^{2+}-O bond distance and the frequency of the oxygen stretch vibration (υ₁) was noted, as well as a relationship between the B^{2+} ionic size and the frequency of the υ₁ mode will also be discussed.

Disorder begins to play a role in the tantalum double perovskites and interesting effects are observed in the Raman spectrum. By varying annealing temperature, Sr₂AlTaO₆ and Ba₂ScTaO₆ were both synthesized with varying degrees of B site order. As the order parameter increased, the υ₁ mode in Sr₂AlTaO₆ became narrower. The same
effect was noticed for Ba$_2$ScTaO$_6$, in addition to several, unexpected peaks in the
spectrum. These additional features became less prominent or disappeared altogether as
the B site order parameter was increased. Ca$_2$AlTaO$_6$ was investigated due to the
presence of both disorder and octahedral tilting. Raman scattering shows promise as a
tool to probe the local structure of extended solids. However, questions arise as to the
source of extraneous peaks in a disordered Raman spectrum.
Dedication

This thesis is dedicated to my husband Scott for his unfaltering love and support.
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There are many people in my life that made the completion of this thesis possible. First and foremost, I would like to thank my advisor, Dr. Patrick Woodward. His patience and understanding throughout my graduate career enabled me to truly succeed. He had a willingness to discuss any issues or concerns about my research and give me the feedback I needed. I have a deeper appreciation for chemistry because of Pat.

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pursue my goals. He had faith in me when I did not have faith in myself and has encouraged me throughout my years at Ohio State.
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Fields of Study

Major Field: Chemistry
# Table of Contents

Abstract ........................................................................................................................................... ii

Dedication .......................................................................................................................................... iv

Acknowledgments ............................................................................................................................... v

Vita ........................................................................................................................................................ vii

Fields of Study .................................................................................................................................. vii

Table of Contents ............................................................................................................................... viii

List of Tables ..................................................................................................................................... x

List of Figures .................................................................................................................................... xii

Chapter 1 Introduction .......................................................................................................................... 1

1.1 History of Perovskites ..................................................................................................................... 1

1.2 The Perovskite Structure .............................................................................................................. 2

1.3 The Tolerance Factor .................................................................................................................... 3

1.4 Octahedral Tilting .......................................................................................................................... 4

1.5 Overview of B-site Cation Ordering ............................................................................................ 7

Chapter 2 .............................................................................................................................................. 10

2.1 Overview ....................................................................................................................................... 10
2.2 Experimental Methods ........................................................................................................ 11
  2.2.1 Synthesis ....................................................................................................................... 11
  2.2.2 Raman Scattering Spectroscopy .................................................................................... 12
  2.2.3 X-ray Diffraction ........................................................................................................ 16
2.3 Results .................................................................................................................................. 17
  2.3.1 X-ray Diffraction Measurements ..................................................................................... 17
  2.3.2 Raman Scattering Measurements ................................................................................... 24
2.4 Conclusions ........................................................................................................................ 38
Chapter 3 ................................................................................................................................... 40
  3.1 Overview .............................................................................................................................. 40
  3.2 Synthesis .............................................................................................................................. 41
  3.3 X-ray Diffraction Results .................................................................................................... 42
  3.4 Effects of Disorder in the Raman Spectrum ........................................................................ 48
  3.5 Conclusion .......................................................................................................................... 62
References .................................................................................................................................... 63
Appendix A: GSAS Order Parameter Calibration Curves ............................................................. 68
Appendix B: Raman Spectra of Y₂O₃ .......................................................................................... 70
List of Tables

Table 2.1: List of perovskites synthesized, with their respective space groups, annealing temperatures, and tolerance factors................................................................. 11
Table 2.2: Factor group analysis of relevant space groups. In the above examples that will be discussed in this thesis, the B cations are centered on centrosymmetric sites, therefore their respective translations will not be observed in a Raman spectrum. ......................... 15
Table 2.3: Refined atomic positions for Sr₂CdWO₆ with an R₂₀ = 30.132 and χ² = 1.148 obtained with powder X-ray diffraction. ................................................................. 19
Table 2.4: Perovskite lattice parameter and β angle refinements as compared to literature values. .................................................................................................................. 21
Table 2.5: Perovskite lattice parameter and β angle refinements as compared to literature values. .................................................................................................................. 21
Table 2.6: Relevant bond lengths, bond angles, and distortion indices from reported neutron data, unless indicated otherwise. .................................................................. 23
Table 2.7: Relevant bond lengths, bond angles, and distortion indices from reported neutron data........................................................................................................ 23
Table 2.8: Raman shifts (in cm⁻¹) for the observed modes in P2₁/n tungsten based perovskites studied........................................................................................................ 31
Table 3.1: Synthesis parameters for perovskites in this study............................................. 42
Table 3.2: Perovskite lattice parameter and β angle refinements as compared to literature values. ................................................................. 44

Table 3.3: Atomic positions for Ca$_2$AlTaO$_6$ and Ca$_2$YTaO$_6$ obtained from powder X-ray diffraction ................................................................. 45

Table 3.4: Relevant bond lengths and octahedral tilt angles for Ca$_2$YTaO$_6$ and Ca$_2$AlTaO$_6$. ......................................................................................... 48

Table 3.5: Raman mode assignments for Ca$_2$AlTaO$_6$. ...................................................................................................................... 54

Table 3.6: Raman mode assignments for Ca$_2$YTaO$_6$. ...................................................................................................................... 62
List of Figures

Figure 1.1: Structure of a single ideal perovskite with space group Pm\(\bar{3}\)m. The A cation is represented by the green sphere, and the B cation is in the center of the octahedra (blue) with X-anions (red) comprising the apexes of the octahedra. ............................................ 3

Figure 1.2: (top) In phase tilting of the octahedral network. (bottom) Out of phase octahedral tilting. ............................................................... 6

Figure 1.3: The fully ordered double perovskite Ba\(_2\)MgWO\(_6\). The B-site cations magnesium and tungsten are represented with the black and yellow octahedra. The green spheres represent the A-site barium cations, and the red spheres are oxygen. ............... 8

Figure 1.4: Two dimensional depiction of B-site disordering. The blue and yellow circles represent two B cations, B and B’ respectively. On the left, a completely ordered sample, with each B site neighbored by four B’ ions. On the right, a partially disordered sample, where some B cations are surrounded by one to four other B cations, rather than four B’ cations. ................................................................. 9

Figure 2.1: Energy level diagram for different scattering events in Raman spectroscopy. \(E_0\) is the ground electronic state, \(E_1\) is an excited electronic state, and \(E’\) and \(E’’\) are virtual states. Vibrational states are depicted with a v............................................. 13

Figure 2.2: (a) Schematic of an x-ray diffraction instrument. (b) Depiction of Bragg scattering of a sample during x-ray diffraction.......................................................... 17

Figure 2.3: X-ray diffraction of P2\(_1\)/n tungsten-based perovskites studied. ...................... 18
Figure 2.4: X-ray diffraction of Ba$_2$MgWO$_6$ (tolerance factor of 1.038) and Ba$_2$CaWO$_6$ (tolerance factor of 0.972)........................................................................................................ 19

Figure 2.5: Rietveld refinement of Sr$_2$CdWO$_6$. The green bars represent the SrWO$_4$ scheelite impurity.................................................................................................................. 20

Figure 2.6: Raman spectra of two double perovskites, Ba$_2$MgWO$_6$ and Ba$_2$CaWO$_6$...... 25

Figure 2.7: Depiction of the Raman active octahedral vibrations for an Fm$\overline{3}$m perovskite.

Figure altered from reference 16........................................................................................................ 27

Figure 2.8: Raman spectra of several tungsten-based perovskites with space group P2$_1$/n with their respective tolerance factors. ................................................................. 30

Figure 2.9: Close-up view of Regions I and II Raman spectra for P2$_1$/n tungsten-based perovskites. ........................................................................................................................................ 32

Figure 2.10: Graph depicting the relationship of the size of the B$^{2+}$ cation to the frequency of the $\nu_1$ Raman mode. Radii information obtained from reference 20............. 36

Figure 2.11: Graph demonstrating relationship of the frequency of the $\nu_1$ band to the B$^{3+}$-O average bond length. Sr$_2$CdWO$_6$ does not have reported neutron data, thus bond lengths cannot be accurately determined......................................................... 37

Figure 2.12: Raman spectra of the scheelite impurity phases...................................................... 38

Figure 3.1: X-ray diffraction spectra of the tantalum-based perovskites in this study with space groups of Fm$\overline{3}$m and P2$_1$/n. ........................................................................................................ 43

Figure 3.2: Rietveld refinement data for Ca$_2$YTaO$_6$. The green bars represent the Y$_2$O$_3$ impurity......................................................................................................................... 46

Figure 3.3: Rietveld refinement data for Ca$_2$AlTaO$_6$................................................................. 47
Figure 3.4: Labeled Raman spectra of varying degrees of ordering of Sr$_2$AlTaO$_6$. Spectra have been offset for clarity purposes. The inset is an example of the broad, low intensity peak at approximately 660 cm$^{-1}$, which is denoted with an asterisk in the figure above.

Figure 3.5: Graph depicting the full-width half-max (FWHM) of the $\nu_1$ peak as compared to the order parameter for Sr$_2$AlTaO$_6$.

Figure 3.6: Comparison of the location of the $\nu_1$ mode and the order parameter for Sr$_2$AlTaO$_6$.

Figure 3.7: Raman spectrum of Ca$_2$AlTaO$_6$.

Figure 3.8: Raman spectra of Ba$_2$ScTaO$_6$ with different ordering parameters. Spectra have been offset for clarity.

Figure 3.9: Graph depicting the full-width half-max (FWHM) of the $\nu_1$ peak as compared to the order parameter for Ba$_2$ScTaO$_6$. The peak was defined using a curve fitting application.

Figure 3.10: Comparison of the location of the $\nu_1$ mode and the order parameter for Ba$_2$ScTaO$_6$.

Figure 3.11: Labeled Raman spectrum of the fully ordered perovskites Ba$_2$YTaO$_6$.

Figure 3.12: Raman spectrum of Ca$_2$YTaO$_6$. 
Chapter 1

Introduction

1.1 History of Perovskites

In 1839, CaTiO$_3$ was first discovered by Gustav Rose, a German chemist and mineralogist, in a remote region of the Russian empire. It was named “perovskite” after Lev Alexeievitch Petrovsky (1972 – 1856), a Russian dignitary and military professional, who was the Secretary of the Interior in 1841 and became the Director of the Imperial Cabinet in 1852.$^1$ After some time, other compounds were found to have a similar structure to CaTiO$_3$, and now the term “perovskite” encompasses a large class of structural compounds. MgSiO$_3$, which comprises 50 – 90% of the core-mantel boundary of our planet, is thought to be the most abundant mineral on Earth.$^1$ Perovskites are one of the most important structure classes, with numerous applications. Perovskites have shown promise as dielectric, ferroelectric, magnetoresistive, and superconductive materials, and are used in many technological devices.
1.2 The Perovskite Structure

SrTiO$_3$ is commonly employed as the representative ideal perovskite, which has cubic symmetry and a space group of Pm3m. It has a stoichiometry of ABX$_3$, where the A cation is 12 coordinate, the B cation is 6 coordinate, and the X anion is coordinated by two B cations and four A cations. The A cation is typically large with a low charge, such as an alkali or alkaline earth metal, while the B cation is more electronegative, with a smaller radius. The X anion consists of oxygen, fluorine, or nitrogen, but other anions can be substituted into the lattice as well. As shown in Figure 1.1, the B-site cation rests in the center of a BX$_6$ octahedra, and the A cation occupies the cubo-octahedral cavity that is formed by the surrounding BX$_6$ octahedra. These corner sharing BX$_6$ octahedra create a three dimensional network, that is similar to ReO$_3$.$^2$
Figure 1.1: Structure of a single ideal perovskite with space group Pm\textsuperscript{3}m. The A cation is represented by the green sphere, and the B cation is in the center of the octahedra (blue) with X-anions (red) comprising the apexes of the octahedra.

Perovskites have a great deal of chemical flexibility. Almost every naturally occurring element on the periodic table is able to be incorporated into the perovskite structure, with the exception of beryllium, boron, phosphorous, and the noble gases. It is the versatility of perovskites that make this particular structure an interesting topic of research.

1.3 The Tolerance Factor

Along with other factors, the relative sizes of the A and B cations are instrumental in understanding the perovskite structure. The tolerance factor is a measure of fit of the A
cation within the cubooctahedral cavity in relation to the surrounding B-site octahedra (Figure 1.1). In an ideal perovskite, the unit cell edge, $a$, is equal to twice the B – X bond length and twice the A – X bond length is equal to the face diagonal. This relationship leads to the following equation for the tolerance factor:

$$\tau = \frac{R_A + R_x}{\sqrt{2}(R_B + R_x)}$$

where $R_A$, $R_B$, and $R_x$ are ionic radii representing the A cation, B cation, and anion respectively. In the case of complex perovskites where there are multiple A or B cations, the average radius is used for $R_A$ or $R_B$. The perovskite structure is stable within the $0.78 < \tau < 1.05$ tolerance factor range.

The size match between the A and B cations is perfect when $\tau$ is equal to one. When $\tau$ is larger than one, the size of the A cation is too large for the size of the cubooctahedral cavity of the perovskite, and when $\tau$ is less than one, the A cation is too small for the cavity. The ideal cubic perovskite structure, SrTiO$_3$ for example, occurs when $\tau$ is equal to one, but these ideal structures are rare. When $\tau$ is not equal to one, structural distortions must occur to allow the cations to account for the size differences.

### 1.4 Octahedral Tilting

The most common type of distortion that occurs in perovskites is octahedral tilting. If the tolerance factor is less than one, meaning the size of the A cation is too small for the cavity of the BX$_6$ network, the octahedra will cooperatively rotate as rigid units to accommodate the size difference. Tilting allows for shorter A – X bonds, while keeping the B – X bond length unchanged. Octahedral tilting will change the
coordination environment of the A cation to less than twelve, as well as lower the
symmetry of the perovskite to below cubic. It is important that the corner sharing of the
octahedral network is maintained.

There are two types of tilting that can occur, in phase and out of phase tilting. When looking down an axis, if each layer of octahedra is tilting the same direction as the layer above and below it, in phase tilting has occurred. If one layer of octahedra are tilted in a particular fashion, and the next is tilted differently, this is referred to as out of phase tilting. Both types of tilting are shown in Figure 1.2 a and b. In 1972, Glazer described the complete series of possible octahedral tilts. In Glazer’s tilt system, $a$, $b$, and $c$ are the axis notations, while superscripts of $+$, $-$, or 0 denote the type of tilt. A $+$ means that there is an in phase tilt normal to that particular axis, while a $-$ denotes an out of phase tilt. A 0 means there is no tilt normal to that axis. If the letter of the axis is the same, the magnitude of the tilt along those axes is equal. For example, space group $P2_1/n$ has a tilt system of $a^- a^- c^+$, with out of phase tilting occurring about the $a$ and $b$ axes, and in phase tilting occurring about the $c$ axis. Space group $Pm3m$ has no tilting, so the Glazer notation is $a^0 a^0 a^0$. There is a total of 32 Glazer tilt systems, with each tilt relating to a specific space group.
Figure 1.2: (top) In phase tilting of the octahedral network. (bottom) Out of phase octahedral tilting.
1.5 Overview of B-site Cation Ordering

A double perovskite has the formula AA’BB’X₆, where the structure can now accommodate two unique A cations and two different B cations. The unit cell is now expanded, and the cell dimensions for a double perovskite are roughly twice that of a single perovskite. It is also possible to substitute multiple anions on the anion site, for example oxygen and fluorine, but this thesis will only be concerned with B-site cation mixing. Thus, for the purposes of this thesis, the structure will be referred to as simply A₂BB’X₆. An example of the double perovskite Ba₂MgWO₆ is shown in Figure 1.3 below.
**Figure 1.3:** The fully ordered double perovskite \( \text{Ba}_2\text{MgWO}_6 \). The B-site cations magnesium and tungsten are represented with the black and yellow octahedra. The green spheres represent the A-site barium cations, and the red spheres are oxygen.

Since there are now multiple B-sites that are occupied by two distinct cations, ordering can occur. Although A-site ordering can happen, it is not commonly encountered and will not be addressed in this thesis. Ordering effects have a couple of main driving factors, particularly size and charge of the cations occupying a particular site. If there is a large charge or size difference between the two B-site cations, the probability of obtaining a 100% B-site ordered sample is greater than if the two cations are similar in charge or size. If, for example, a given perovskite contains a \( \text{M}^{2+} \) cation and a \( \text{M}^{6+} \) cation, it becomes more difficult for the two B cations to “switch places,” meaning, for the \( \text{M}^{6+} \)
cation to occupy an M$^{2+}$ site, or vice-versa. Order can also be driven by thermal effects, when a disordered or partially disordered perovskite is heated to a certain point at which it becomes ordered. A two dimensional depiction of cation disorder is shown in Figure 1.4. In a double perovskite, rock salt type ordering is common, in which there are alternating layers of B and B’ cations normal to the 111 $hkl$ direction. Figure 1.3 shows a fully ordered perovskite that has this rock salt type ordering.

**Figure 1.4:** Two dimensional depiction of B-site disordering. The blue and yellow circles represent two B cations, B and B’ respectively. On the left, a completely ordered sample, with each B site neighbored by four B’ ions. On the right, a partially disordered sample, where some B cations are surrounded by one to four other B cations, rather than four B’ cations.
Chapter 2

Raman Studies of Octahedral Tilting of $A_2M^{2+}WO_6$ ($A = \text{Ba, Sr, Ca}; M^{2+} = \text{Mg, Zn, Ca, Cd}$) Perovskites

2.1 Overview

Tungsten based perovskites with the general formula $A_2M^{2+}WO_6$ are known to be completely ordered due to the large charge difference of the $M^{2+}$ and $W^{6+}$ cations. As disorder is not a factor in these perovskites, octahedral tilting can be effectively studied. The perovskites selected for this study have tolerance factor ranging from 1.038 (Ba$_2$MgWO$_6$) to 0.867 (Ca$_2$CaWO$_6$) and have tilt angles down to 140°, compared to the expected 180° for a perovskite without octahedral tilting. Extensive structural studies have been performed on all perovskites in this chapter, and neutron data is available for all, except for Sr$_2$CdWO$_6$. To the best of our knowledge, with the exception of Sr$_2$CaWO$_6$ and Sr$_2$ZnWO$_6$, detailed Raman studies have not been performed on these perovskites.
2.2 Experimental Methods

2.2.1 Synthesis

All syntheses were performed using conventional solid state synthesis methods. \( \text{Sr}_2\text{CaWO}_6, \ \text{Ba}_2\text{MgWO}_6, \ \text{and} \ \text{Ca}_2\text{MgWO}_6 \) were obtained from Paris Barnes, which were also synthesized following conventional solid state methods, as according to references 6 and 7. High purity (>99% starting materials \( \text{BaCO}_3, \ \text{SrCO}_3, \ \text{CdO}, \ \text{MgO}, \ \text{ZnO}, \ \text{CaCO}_3, \ \text{and} \ \text{WO}_3 \) were used. Stoichiometric amounts of the starting materials were ground in an agate mortar and pestle and heated in a ceramic crucible for 12 – 24 hours. Multiple heating cycles were necessary for some materials. Phase purity was verified with powder X-ray diffraction (XRD). Table 2.1 lists the details of all tungsten – based perovskites synthesized for this study. Small amounts of a secondary scheelite phase (\( \text{M}^{2+}\text{WO}_4 \)) were present in all synthesized perovskites. For Raman purposes, scheelite phases were synthesized following the same conventional solid state synthesis method at 1100 °C.

<table>
<thead>
<tr>
<th>Composition ( \text{M}_2\text{WO}_6 )</th>
<th>Space Group</th>
<th>( \text{Final Annealing Temperature (°C)} )</th>
<th>Tolerance Factor (( \tau ))</th>
<th>Other Phases Present</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ba}_2\text{MgWO}_6 )</td>
<td>( \text{Fm} \bar{3} \text{m} )</td>
<td>1300</td>
<td>1.038</td>
<td>( \text{3% BaWO}_4 )</td>
</tr>
<tr>
<td>( \text{Sr}_2\text{ZnWO}_6 )</td>
<td>( \text{P}2_1/\text{n} )</td>
<td>1000</td>
<td>0.976</td>
<td>&lt; 1% ( \text{SrWO}_4 )</td>
</tr>
<tr>
<td>( \text{Ba}_2\text{CaWO}_6 )</td>
<td>( \text{I}4/\text{m} )</td>
<td>1300</td>
<td>0.972</td>
<td>&lt; 1% ( \text{BaWO}_4 )</td>
</tr>
<tr>
<td>( \text{Sr}_2\text{CdWO}_6 )</td>
<td>( \text{P}2_1/\text{n} )</td>
<td>950</td>
<td>0.930</td>
<td>2% ( \text{SrWO}_4 )</td>
</tr>
<tr>
<td>( \text{Ca}_2\text{MgWO}_6 )</td>
<td>( \text{P}2_1/\text{n} )</td>
<td>1300</td>
<td>0.926</td>
<td>&lt; 1% ( \text{CaWO}_4 )</td>
</tr>
<tr>
<td>( \text{Sr}_2\text{CaWO}_6 )</td>
<td>( \text{P}2_1/\text{n} )</td>
<td>1300</td>
<td>0.917</td>
<td>&lt; 1% ( \text{SrWO}_4 )</td>
</tr>
<tr>
<td>( \text{Ca}_2\text{CaWO}_6 )</td>
<td>( \text{P}2_1/\text{n} )</td>
<td>1200</td>
<td>0.867</td>
<td>&lt; 1% ( \text{CaWO}_4 )</td>
</tr>
</tbody>
</table>

Table 2.1: List of perovskites synthesized, with their respective space groups, annealing temperatures, and tolerance factors.
2.2.2 Raman Scattering Spectroscopy

Raman spectroscopy is a light scattering technique that is used to study the vibrational characteristics of a material. Raman relies on the inelastic scattering of monochromatic light in the ultraviolet-visible region ($10^2 - 10^4$ cm$^{-1}$) of the electromagnetic spectrum. When a sample is irradiated with a strong laser beam, of frequency $\nu_0$, two types of scattering can occur, Rayleigh and Raman. Elastic Rayleigh scattering is intense and has the same frequency as the original laser beam ($\nu_0$), while Raman scattering is weak (approximately $10^{-5}$ weaker than the incident beam) and has frequencies of $\nu_0 \pm \nu_m$, where $\nu_m$ is the vibrational frequency of a molecule. Raman scattering consists of both Stokes and anti-Stokes lines, $\nu_0 - \nu_m$ and $\nu_0 + \nu_m$ respectively. Figure 2.1 depicts the types of scattering that can occur in Raman spectroscopy.$^8$
Figure 2.1: Energy level diagram for different scattering events in Raman spectroscopy. $E_0$ is the ground electronic state, $E_1$ is an excited electronic state, and $E'$ and $E''$ are virtual states. Vibrational states are depicted with a $v$.

In Raman scattering, an electron is promoted to a “virtual state,” $E'$ and $E''$ in Figure 2.1 above, which lies below the excited electronic state, $E_1$ in the figure. Stokes lines start from a lower vibrational level compared to anti-Stokes lines. By the Maxwell-Boltzmann distribution, the lower vibrational level $v = 1$ will have a higher population than $v = 2$, making Stokes lines are much more intense than anti-Stokes lines. Thus the Stokes part of the Raman spectra is commonly reported. Infrared (IR) and Raman spectroscopy are techniques complementary to one another. Raman requires a change in polarizability while IR requires a change in the dipole moment of a molecule. Infrared spectroscopy is simply the change in vibrational levels within an electronic level, as shown in Figure 2.1. The mutual exclusion principle, which holds for molecules with an inversion center, states that a given mode may either be Raman or IR active, but not both.
The number of vibrational degrees of freedom for a molecule is $3N - 6$, or $3N - 5$ for a linear molecule, where $N$ is the number of atoms.\(^8\)

Group theory analysis will determine the number of vibrational allowed modes in a particular crystal system. Factor group analysis for relevant space groups is shown in Table 2.2. An ideal single perovskite with space group $Pm\bar{3}m$ does not have any Raman-active modes, so should not produce a Raman spectrum. However, a double perovskite now has the space group of $Fm\bar{3}m$ and has four Raman-active modes expected. Analysis of Raman data will be discussed further in the experimental section of this chapter.
Table 2.2: Factor group analysis of relevant space groups. In the above examples that will be discussed in this thesis, the B cations are centered on centrosymmetric sites, therefore their respective translations will not be observed in a Raman spectrum.
Raman measurements were performed on a Renishaw Smith Raman IR microprobe, with most measurements performed using a 514 nm Argon ion laser. It was discovered that nearly all perovskites studied in this thesis exhibit strong fluorescence with the 633 nm laser, but changing to the 514 nm laser solved this problem. Unless otherwise stated, all Raman spectra shown in this study will have been obtained with a 514 nm Argon ion laser.

2.2.3 X-ray Diffraction

Powder X-ray diffraction (XRD) is an excellent technique for identification of materials and to explore the structure and order of a compound. All materials studied in this thesis are known compounds, so XRD was used primarily to look at the identity, lattice parameters, purity, and ordering of the B-site cations of the compounds. XRD was performed on a Bruker D8 Advance diffractometer (40 kV, 50 mA, copper source \( \lambda = 1.5406 \text{ Å} \)). A \( \theta-2\theta \) scan was performed and analyzed with a Rietveld refinement. In an x-ray diffraction experiment, the sample is irradiated with an x-ray beam, commonly created by bombarding a copper source with electrons from a tungsten filament. The x-rays are constructively diffracted from the sample according to the Bragg equation:

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

where \( \lambda \) is the wavelength of the x-ray source, \( n \) is an integer, \( d \) is the spacing between lattice planes, and \( \theta \) is the angle of diffraction. Figure 2.2 shows a schematic of an XRD instrument (a) and Bragg scattering of a sample in XRD (b).
Figure 2.2: (a) Schematic of an x-ray diffraction instrument. (b) Depiction of Bragg scattering of a sample during x-ray diffraction.

2.3 Results

2.3.1 X-ray Diffraction Measurements

X-ray diffraction was performed on all perovskites discussed in this study, including those materials obtained from another source. X-ray spectra for all perovskites are shown in Figures 2.3 and 2.4. Refinements of structure and lattice parameters closely
matched neutron data from the literature. Refinements were performed using the Rietveld method and Topas Academic software.\textsuperscript{9} \(\text{Sr}_2\text{CdWO}_6\) does not have neutron data reported, thus experiment powder X-ray diffraction data was analyzed for this study. The refined atomic positions for \(\text{Sr}_2\text{CdWO}_6\) can be found in Table 2.3 and the Rietveld refinement spectrum in Figure 2.5. Most refined lattice parameters matched the literature with a 0.01 Å accuracy, with the exception of \(\text{Sr}_2\text{CaWO}_6\) which matched the literature to a 0.1 Å accuracy. Beta (\(\beta\)) angles for \(\text{P}2_1/\text{n}\) perovskites were accurate to 0.1 degrees.\textsuperscript{6,10,11,12,13} Refined data as compared to literature are shown in Tables 2.4 and 2.5.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.3.png}
\caption{X-ray diffraction of \(\text{P}2_1/\text{n}\) tungsten-based perovskites studied.}
\end{figure}
**Figure 2.4:** X-ray diffraction of Ba$_2$MgWO$_6$ (tolerance factor of 1.038) and Ba$_2$CaWO$_6$ (tolerance factor of 0.972).

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff Position</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
<th>B$_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr</td>
<td>4e</td>
<td>0.0074(4)</td>
<td>0.5371(9)</td>
<td>0.2520(5)</td>
<td>1</td>
<td>0.577(7)</td>
</tr>
<tr>
<td>Cd</td>
<td>2c</td>
<td>0.5</td>
<td>0.5</td>
<td>0</td>
<td>1</td>
<td>0.402(9)</td>
</tr>
<tr>
<td>W</td>
<td>2d</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.402(9)</td>
</tr>
<tr>
<td>O1</td>
<td>4e</td>
<td>0.0700(9)</td>
<td>0.0142(5)</td>
<td>-0.2312(5)</td>
<td>1</td>
<td>1.003(0)</td>
</tr>
<tr>
<td>O2</td>
<td>4e</td>
<td>0.2604(9)</td>
<td>-0.1883(2)</td>
<td>0.0300(2)</td>
<td>1</td>
<td>1.003(0)</td>
</tr>
<tr>
<td>O3</td>
<td>4e</td>
<td>0.1812(5)</td>
<td>0.2665(4)</td>
<td>0.0444(0)</td>
<td>1</td>
<td>1.003(0)</td>
</tr>
</tbody>
</table>

**Table 2.3:** Refined atomic positions for Sr$_2$CdWO$_6$ with an R$_{wp} = 30.132$ and $\chi^2 = 1.148$ obtained with powder X-ray diffraction.
Figure 2.5: Rietveld refinement of $\text{Sr}_2\text{CdWO}_6$. The green bars represent the $\text{SrWO}_4$ scheelite impurity.
During the synthesis of these particular tungsten based perovskites, a secondary scheelite ($M^{2+}WO_4$) phase formed. Most secondary phases were less than 1%, with a couple of exceptions, as shown in Table 2.1. The prominent scheelite impurity peak in these perovskites is shown with an asterisk on the XRD patterns shown in Figures 2.3 and
2.4 and as green bars in Figure 2.5. From these results, it was concluded that all target perovskites were synthesized with reasonable purity.

The octahedral tilt angle plays a crucial role in the Raman scattering effect in some perovskites, and is closely related to the tolerance factor. Another important factor to consider is any deviation in the octahedra itself. This can be measured with the distortion index ($\Delta_d$), which is calculated as follows:

$$\Delta_d = \frac{1}{6} \sum_{n=1,6} \left( \frac{d_n - \langle d \rangle}{\langle d \rangle} \right)^2$$

where $d_n$ is an individual M-O bond length and $\langle d \rangle$ is the average M-O bond length. It is believed that octahedra with significant deviations have values of $\Delta_d$ greater than $10^{-3}$. Due to the small X-ray scattering factor of oxygen, the oxygen positions cannot be determined as accurately with XRD as they can be determined with neutron powder diffraction. For this reason, XRD is not the best method for determining bond lengths and bond angles. However, neutron powder diffraction can accurately evaluate oxygen positions, and these bond lengths and bond angles involving oxygen. As neutron data is available for all samples, with the exception of Sr$_2$CdWO$_6$, literature data was used to evaluate tilt angles, bond lengths, and, ultimately, the distortion index. This is reported in Tables 2.6 and 2.7.
### Relevant bond distances (Å) and bond angles (deg)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond Distance 1</th>
<th>Bond Distance 2</th>
<th>Bond Distance 3</th>
<th>Bond Distance 4</th>
</tr>
</thead>
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<tr>
<td>Ba$_2$MgWO$_6$</td>
<td>180.0</td>
<td>167.6</td>
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<td>157.07(8)</td>
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<tr>
<td>Sr$_2$ZnWO$_6$</td>
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<td></td>
</tr>
<tr>
<td>Ba$_2$CaWO$_6$</td>
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<td>158.52(1)</td>
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<tr>
<td>Sr$_2$CdWO$_6$</td>
<td></td>
<td></td>
<td></td>
<td>152.12(1)</td>
</tr>
</tbody>
</table>

### Distortion indices (Δd; x 10$^{-5}$)

<table>
<thead>
<tr>
<th>Compound</th>
<th>M$^{2+}$</th>
<th>M$^{6+}$</th>
<th>W$^{6+}$</th>
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</thead>
<tbody>
<tr>
<td>Ba$_2$MgWO$_6$</td>
<td>-0.16</td>
<td>2.26</td>
<td>**</td>
</tr>
<tr>
<td>Sr$_2$ZnWO$_6$</td>
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<td>**</td>
</tr>
<tr>
<td>Ba$_2$CaWO$_6$</td>
<td>0.11</td>
<td>3.47</td>
<td>**</td>
</tr>
<tr>
<td>Sr$_2$CdWO$_6$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* No neutron data available. Experimental XRD data is shown.

** Distortion index cannot be accurately calculated due to lack of neutron data.

### Table 2.6: Relevant bond lengths, bond angles, and distortion indices from reported neutron data, unless indicated otherwise.

<table>
<thead>
<tr>
<th>Relevant bond distances (Å) and bond angles (deg)</th>
<th>Ca$_2$MgWO$_6$</th>
<th>Sr$_2$CaWO$_6$</th>
<th>Ca$_2$CaWO$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M$^{2+}$ - O1 - M$^{6+}$</td>
<td>152.3</td>
<td>153.9</td>
<td>147.2</td>
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<tr>
<td>M$^{2+}$ - O2 - M$^{6+}$</td>
<td>151.1</td>
<td>149.1</td>
<td>140.9</td>
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<tr>
<td>M$^{2+}$ - O3 - M$^{6+}$</td>
<td>152.1</td>
<td>147.1</td>
<td>141.4</td>
</tr>
<tr>
<td>M$^{2+}$ - O1</td>
<td>2 x 2.0691</td>
<td>2 x 2.3134</td>
<td>2 x 2.2715</td>
</tr>
<tr>
<td>M$^{2+}$ - O2</td>
<td>2 x 2.0774</td>
<td>2 x 2.3439</td>
<td>2 x 2.3317</td>
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<tr>
<td>M$^{2+}$ - O2</td>
<td>2 x 2.0607</td>
<td>2 x 2.3590</td>
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<td>M$^{6+}$ - O1</td>
<td>2 x 1.9244</td>
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<td>M$^{6+}$ - O2</td>
<td>2 x 1.9271</td>
<td>2 x 1.9144</td>
<td>2 x 1.9292</td>
</tr>
<tr>
<td>M$^{6+}$ - O3</td>
<td>2 x 1.9139</td>
<td>2 x 1.9199</td>
<td>2 x 1.9316</td>
</tr>
</tbody>
</table>

### Distortion indices (Δd; x 10$^{-5}$)

<table>
<thead>
<tr>
<th>Compound</th>
<th>M$^{2+}$</th>
<th>M$^{6+}$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$_2$MgWO$_6$</td>
<td>1.06</td>
<td>6.58</td>
<td>11.6</td>
</tr>
<tr>
<td>Sr$_2$ZnWO$_6$</td>
<td></td>
<td></td>
<td>**</td>
</tr>
<tr>
<td>Ca$_2$CaWO$_6$</td>
<td>1.91</td>
<td>2.49</td>
<td>1.36</td>
</tr>
</tbody>
</table>

**Table 2.7: Relevant bond lengths, bond angles, and distortion indices from reported neutron data.**
As expected, cubic Ba$_2$MgWO$_6$ has a M-O-M’ angle of 180°, but when the space group is lowered to P2$_1$/n or I4/m, the M-O-M’ angles begin to deviate from 180°. As a general rule, the lower the tolerance factor, the greater the tilt angle distortion. From the low distortion index values above, it can be concluded that for Sr$_2$ZnWO$_6$, Ba$_2$CaWO$_6$, Ca$_2$MgWO$_6$, and Sr$_2$CaWO$_6$, there are no significant irregularities in the M$^{2+}$ or M$^{6+}$ octahedra. The bond angles within the octahedra for these materials are close to 90°. However, Ca$_2$CaWO$_6$ has a distortion index of 1.16 x 10$^{-4}$ for the calcium B-site octahedron, thus having a higher level of distortion than the other perovskites studied. This distortion is also present in the internal bond angles of the calcium octahedron: O1-Ca-O3 = 94.83° and O2-Ca-O3 = 95.08°. According to Day et. al., this can be attributed to the large octahedral tilting distortion and relatively ionic Ca-O bonds. The large distortions in Ca$_2$CaWO$_6$ make this particular perovskite interesting to study with Raman scattering.

### 2.3.2 Raman Scattering Measurements

As discussed earlier, the highest possible symmetry for a double perovskite with the general formula A$_2$BB’O$_6$ is Fm$\overline{3}$m. As shown in Table 2.2, group theoretical analysis shows that there are four Raman bands expected with the irreducible representation of

$$\Gamma = A_{1g} + E_g + 2F_{2g}$$

where the “g” subscript (gerade) indicates a Raman active mode. When the symmetry is lowered to I4/m through an octahedral tilting distortion, the irreducible representation now becomes
\[ \Gamma = 3A_g + 3B_g + 3E_g \]

with nine Raman active bands. Figure 2.6 shows the Raman spectra of two double perovskites, \( \text{Ba}_2\text{MgWO}_6 \) with space group \( \text{Fm3m} \) and \( \text{Ba}_2\text{CaWO}_6 \) with space group \( \text{I4/m} \).

**Figure 2.6:** Raman spectra of two double perovskites, \( \text{Ba}_2\text{MgWO}_6 \) and \( \text{Ba}_2\text{CaWO}_6 \). The simplicity of an \( \text{Fm3m} \) Raman spectra allows for the assignment of every mode, but as these are polycrystalline powders, it can be rather difficult to assign each mode in an unpolarized Raman spectrum. Liegeois-Duyckaerts and Tarte stated that due to the fact the \( \text{M}^{6+}\text{O}_6 \) octahedra is strongly bonded compared to the \( \text{M}^{2+}\text{O}_6 \) octahedra, only the internal modes of the \( \text{M}^{6+}\text{O}_6 \) octahedron are of vibrational importance. It is
believed that this vibrational dependence on the M$^{6+}$O$_6$ octahedron is due to the fact that a hexavalent cation will bond to an oxygen atom much more strongly than a divalent cation. The stronger M$^{6+}$ – O bond also results in shorter bond lengths and a greater interaction of the M$^{6+}$ cation and oxygen anion. However, the M$^{2+}$O$_6$ octahedron and the A cation can weakly affect the frequency of certain Raman vibrations, depending on certain factors of the cation in question, as will be discussed later in this chapter.$^{15}$

When considering a basic Fm$ar{3}$m Raman spectrum with four bands expected, analysis becomes simple for an ordered perovskite, and can be rewritten in a more useful form:

$$\Gamma = T(F_{2g}) + \nu_1(A_{1g}) + \nu_2(E_g) + \nu_5(F_{2g})$$

The $\nu_1$ mode is one of the most distinctive vibrations in a perovskite. It shows as a strong, relatively broad, somewhat asymmetric peak in the region of 750 – 900 cm$^{-1}$. It is the symmetric oxygen stretch vibration of the octahedra, during which all cations are at rest and the oxygen atoms are moving along the B – O – B’ axis.$^{15}$ Just as there is an oxygen symmetric stretch, there is also an oxygen asymmetric stretching vibration, known as the $\nu_2$ mode. Again, during a $\nu_2$ vibration, all cations are at rest while the oxygen atoms travel along the B – O – B’ axis.$^{15}$ The internal $F_{2g}$, $\nu_5$ mode, which generally occurs in the 305 – 420 cm$^{-1}$ region, is due to an oxygen bending motion in the octahedra and can be influenced by the chemical nature of the B cations. Figure 2.7 displays the internal Raman vibrations that are related to the octahedra. The second, external $F_{2g}$ (T) mode in the 100 – 300 cm$^{-1}$ region arises from translations of the A cation, and is often referred to as a translational lattice mode.$^{15}$ Another type of lattice
mode, librational ($L$), is caused by rotations of the A cation. The libration mode is silent in an Fm$\overline{3}$m spectrum. Lattice modes are found at low frequencies due to their low energy, and are considering external modes. In Ba$_2$MgWO$_6$, the peaks at approximately 126, 441, and 812 cm$^{-1}$ are assigned to $T$, $\nu_5$, and $\nu_1$ respectively. A weak, or in some cases non-existent, $\nu_2$ mode (543 cm$^{-1}$) is typical for these highly ordered perovskites.

![Diagram of vibrations](image)

**Figure 2.7**: Depiction of the Raman active octahedral vibrations for an Fm$\overline{3}$m perovskite. Figure altered from reference 16.

When lowering the symmetry to I4/m, as in the case of Ba$_2$CaWO$_6$, nine Raman bands are now expected. Another way to write the irreducible representation, considering only Raman active vibrations, for an I4/m material is as follows:

$$\Gamma = 2T(B_g + E_g) + 2L(A_g + E_g) + \nu_1(A_g) + 2\nu_2(A_g + B_g) + 2\nu_5(B_g + E_g)$$

In the equation above, $T$, $L$, $\nu_1$, $\nu_2$, and $\nu_5$ are the translational lattice, librational lattice, symmetric oxygen stretch, asymmetric oxygen stretch, and oxygen bending modes.
respectively. Compared to a cubic Raman spectrum, it is expected that certain modes (\(\nu_2\) and \(\nu_5\)) will split into multiple peaks. However, as shown in Figure 2.6, only three bands are visible. This is common in lower symmetry polycrystalline samples, and is due to several factors: bands showing below the spectrum cut-off at 100 cm\(^{-1}\), bands that are too weak to be visible, or strong bands overlapping a weak band. In the case of perovskites with octahedral tilting, the degree of the distortion can also play a role in the number of peaks observed in a Raman spectrum, and Table 2.6 shows that the tilting angle is 176\(^\circ\) versus the 180\(^\circ\) that corresponds to a perovskite without octahedral tilting. The Raman spectrum for Ba\(_2\)CaWO\(_6\) is so similar to that of a cubic material that Liegeois-Duyckaerts and Tarte believed that it was an Fm\(\bar{3}\)m perovskite, but later refinements showed it to have a space group of I4/m.\(^6\)\(^,\)\(^15\) The bands appearing at approximately 834, 410, and 103 cm\(^{-1}\) can be assigned to \(\nu_I\), \(\nu_5\), and \(T\) modes respectively for Ba\(_2\)CaWO\(_6\). The small octahedral tilting distortion and pseudocubic nature of Ba\(_2\)CaWO\(_6\) may help explain the low number of peaks observed for this compound.

Perovskites with the monoclinic space group P2\(_1\)/n have a greater octahedral tilting distortion than those with an I4/m space group. Considering only Raman active modes, the irreducible representation for a P2\(_1\)/n perovskite can be rewritten as:

\[
\Gamma = 6T(3A_g + 3B_g) + 6L(3A_g + 3B_g) + 2\nu_1(A_g + B_g) + 4\nu_2(2A_g + 2B_g) + 6\nu_5(3A_g + 3B_g)
\]

Now there are 24 bands anticipated in the Raman spectra for a P2\(_1\)/n material. However, for the P2\(_1\)/n perovskites studied, only six to fourteen bands were present (Figure 2.8). As the space group P2\(_1\)/n indicates a primitive cell, and the number of atomic units per unit
cell (Z) is two for these perovskites, a coupling effect between the \( A_g \) and \( B_g \) can occur in the \( \nu_1, \nu_2, \) and \( \nu_5 \) modes. Degenerate \( A_g \) and \( B_g \) modes are commonly observed experimentally, resulting in half the splitting calculated by group theory analysis in these modes. Thus, it is expected that \( \nu_1 \) will not split into multiple peaks, \( \nu_2 \) will be split into two peaks, and \( \nu_5 \) into three peaks. Again, as these are polycrystalline samples, it is more useful to describe the modes in terms of the internal octahedral vibrations and external lattice vibrations. For clarity, the Raman spectra in Figure 2.8 have been broken into three regions.

I. Region I, from 100 – 190 cm\(^{-1}\), is characterized by several low intensity translational lattice vibrational modes.

II. Region II, from 190 – 510 cm\(^{-1}\), is characterized by several low intensity libration lattice modes and the characteristic internal oxygen bending mode, appearing as a singlet or a doublet. A secondary phase scheelite peak may be present in this region, as denoted by an asterisk in Figure 2.8.

III. Region III, from 510 – 1000 cm\(^{-1}\) is characterized by a broad peak with extremely low intensity (the asymmetric oxygen stretch) and a broad, intense peak (oxygen symmetric stretch). A scheelite impurity peak may be present in this region and is noted with an asterisk in Figure 2.8.
Figure 2.8: Raman spectra of several tungsten-based perovskites with space group P2₁/n with their respective tolerance factors.

As stated previously, low intensity lattice modes are expected at low frequencies due to the low energy of the vibrations. Translation and libration lattice vibrations are caused by translational and rotational movements respectively. In a perovskite with a P2₁/n space group, six translation and six libration lattice modes are expected, by a triplet splitting of the $A_g$ and $B_g$ modes. Ayala et. al. assigned the libration lattice modes to frequencies of 190 – 310 cm⁻¹, and translation lattice modes to frequencies less than 190 cm⁻¹ for P2₁/n perovskites. However, it appears that the $v_5$ mode for these tungsten-based materials is shifted to higher energies than in Ayala’s cobalt-based perovskites, as lattice modes to not appear at frequencies higher than 310 cm⁻¹ in the cobalt
perovskites. In the case of the tungsten perovskites in this study, lattice modes appear at frequencies up to 425 cm$^{-1}$ for Ca$_2$MgWO$_6$, as shown in the mode assignments in Table 2.8. It should be noted that a polarized Raman spectra is needed to accurately differentiate libration and translation lattice modes, and as such, it is impossible to set a definitive point where lattice modes will be translation or libration. Thus in Table 2.8, there is a sort of buffer region of a few wavenumbers where a lattice mode could be of either type.

<table>
<thead>
<tr>
<th>$\nu$ Sr$_2$ZnWO$_6$</th>
<th>$\nu$ Sr$_2$CdWO$_6$</th>
<th>$\nu$ Ca$_2$MgWO$_6$</th>
<th>$\nu$ Sr$_2$CaWO$_6$</th>
<th>$\nu$ Ca$_2$CaWO$_6$</th>
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<td>$T$</td>
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<td>594</td>
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<td>$u_1$</td>
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<td>-</td>
<td>908</td>
<td>918</td>
<td>-</td>
<td>Imp.</td>
</tr>
</tbody>
</table>

**Table 2.8**: Raman shifts (in cm$^{-1}$) for the observed modes in P2$_1$/n tungsten based perovskites studied.
In Figure 2.9, a close-up view of Region I is shown, where translation lattice modes are expected. Ayala et. al. stated that translation and libration lattice modes are extremely sensitive to the octahedral distortion. Six translation lattice modes are expected, by two sets of triplet splitting.\textsuperscript{17} Sr\textsubscript{2}ZnWO\textsubscript{6} (tolerance factor of 0.976) only shows a doublet in this region, but with peaks of moderate intensity. There is a broad tailing effect occurring after the mode at 152 cm\textsuperscript{-1} and it is possible that there may be another weak translation mode there. Looking back at Table 2.6, the most distorted angle is 164°, sixteen degrees away the 180° in a perovskite with a cubic structure. It could be
argued that the small octahedral distortion angle allows for a somewhat greater intensity for the translation lattice peaks for this perovskite. Lentz’s reported Raman spectra for Sr$_2$ZnWO$_6$ showed weak bands at 78, 105, and 116 cm$^{-1}$ which are not observed in this study. However, Lentz did report modes at 140 and 153 cm$^{-1}$, corresponding to the translational lattice modes observed here. $^{18}$ Sr$_2$CdWO$_6$ (tolerance factor of 0.930) on the other hand, shows a definitive triplet splitting in the peaks at 129, 151, and 172 cm$^{-1}$, albeit with low intensity. The octahedral distortion angle has now lowered to 152$^\circ$, resulting in a greater peak splitting than observed for Sr$_2$ZnWO$_6$ for the translational lattice modes. However, reported angles for Sr$_2$CdWO$_6$ are based on XRD, rather than neutron data. Ca$_2$MgWO$_6$ (tolerance factor of 0.926), with a distortion angle of 151$^\circ$, has four translational modes observed. Five translational lattice modes are present for Sr$_2$CaWO$_6$ and three (or four) for Ca$_2$CaWO$_6$.

Region II is where the external libration lattice modes and internal oxygen bending modes ($\nu_5$) are anticipated to appear. No libration modes are observed for Sr$_2$ZnWO$_6$, four are observed for Sr$_2$CdWO$_6$, and five for Ca$_2$MgWO$_6$. Lentz reported modes in this area in his study of Sr$_2$ZnWO$_6$, but were extremely weak, thus explaining the absence of libration modes observed for this perovskite.$^{18}$ Only two libration modes are observed for Sr$_2$CaWO$_6$. As seen in Tables 2.6 and 2.7, the octahedral distortion angles are similar for Sr$_2$CdWO$_6$, Ca$_2$MgWO$_6$, and Sr$_2$CaWO$_6$, as is expected due to their somewhat similar tolerance factors. It could be predicted that Sr$_2$CaWO$_6$ would have a similar number of libration modes observed, but this is not the case. Perhaps these additional modes are of such low intensity that it is not possible to see these peaks in a
normal polycrystalline Raman spectrum. However, all six of these libration lattice modes are apparent in the Ca$_2$CaWO$_6$ spectrum, if the mode at 207 cm$^{-1}$ is labeled as a libration mode.

Ca$_2$CaWO$_6$ is an interesting perovskite to study with Raman scattering. It has a tolerance factor of 0.867, which is almost too low to sustain a perovskite structure in general, but also has a slightly distorted calcium octahedra, $\Delta_d = 1.16 \times 10^{-4}$. As lattice vibrations are more sensitive to distortions within the perovskite, it is possible that the large number of libration peaks, as compared to other tungsten based perovskites in this study, is due to either the slightly distorted calcium octahedron or the larger octahedral tilt of Ca$_2$CaWO$_6$ at 141° (Table 2.7). Since libration modes are considered external, and modes due to the octahedra itself are considered internal, it is safe to argue that the number of libration peaks observed is due to the increase in octahedral tilting, as this distortion is considered external from a Raman standpoint.

The internal oxygen bending motion, $\nu_5$, is also expected in Region II, and is found between 430 and 470 cm$^{-1}$ (Table 2.8). It is expected that this $\nu_5$ mode splits into a doublet, but the degree of the octahedral tilt distortion can affect how much splitting of this mode is observed. As shown in Figure 2.8, the $\nu_5$ mode is split only in the cases of Sr$_2$ZnWO$_6$ and Ca$_2$CaWO$_6$. While the doublet $\nu_5$ is not surprising for Ca$_2$CaWO$_6$ by any means, it is surprising that this band is split for Sr$_2$ZnWO$_6$ and not the rest of perovskites. As Sr$_2$ZnWO$_6$ has the highest tolerance factor of the series and is the least distorted, it would be anticipated that if a doublet Sr$_2$ZnWO$_6$ $\nu_5$ band is observed, that doublet bands would be observed for the remainder of the P2$_1$/n tungsten perovskite series as well. This
doublet is not caused by the secondary scheelite phase, as there are no scheelite Raman peaks at these frequencies (Figure 2.12). This Sr$_2$ZnWO$_6$ doublet mode was also observed by Lentz.\textsuperscript{18} Polarized Raman studies are needed to determine the source of the splitting in Sr$_2$ZnWO$_6$. It is interesting to note that the $v_5$ mode is slightly shifted to higher frequencies when the A cation is calcium versus the heavier and larger strontium. Although it is not expected that the A cation should play a factor in this internal oxygen bending mode, it does appear that the mass and size of the A cation can affect this mode.

The oxygen asymmetric stretching mode, $v_2$, is expected to occur in Region III and is found between 550 and 600 cm$^{-1}$. Due to the complete ordering of these tungsten perovskites, this $v_2$ peak is extremely weak and almost undetectable. For this reason, it is impossible to detect splitting of this band in these compounds without polarized Raman data.

An intense oxygen symmetric stretch band, $v_1$, is also found in Region III, around 810 – 840 cm$^{-1}$ for these materials. Liegeois-Duyckaerts and Tarte claimed that, although the oxygen symmetric stretch position is caused mainly by the B$^{6+}$O$_6$ octahedron, both the M$^{2+}$ and A cations can shift this band in one direction or another. They believed that the both cation size and bond lengths of the M$^{2+}$ cation could shift this particular mode, according to the following equation:

$$v_1 = \sqrt{E_1 + E_2}$$

where $E_1$ and $E_2$ are the of M$^{6+}$-O and M$^{2+}$-O bonding energies respectively and $E_2 \ll E_1$.\textsuperscript{15} Figure 2.10 shows the relationship between cation size for the P2$_1$/n tungsten perovskite series and a general trend is observed.
As the crystal radius of the $M^{2+}$ cation decreased, the frequency of the $v_1$ mode increases. On the other hand, Figure 2.11 shows the relationship between the frequency of the $v_1$ band to the average $M^{2+}$-O octahedral bond length and, again, a trend is noticed. As the average bond length is decreased, the frequency of the $v_1$ mode increases, with the exception of $Sr_2CdWO_6$. However, again, it should be noted that there is no neutron data available for $Sr_2CdWO_6$, thus the oxygen positions cannot be accurately determined.

When considering the influences of the $M^{2+}$ cation on the frequency of this $v_1$ mode, electronegativity should also be considered, in addition to bond length. Figure 2.10 shows that the Mg-O bond distance is similar to that of Zn-O, but as zinc is more electronegative than magnesium, the Zn-O bond is stronger, thus shifting the $Sr_2ZnWO_6$ $v_1$ mode by a greater amount than observed for $Ca_2MgWO_6$. Although the trends in
Figures 2.10 and 2.11 are not linear, this supports Liegeois-Duyckaerts and Tarte’s argument that the $M^{2+}$ cation can weakly affect the position of the $\nu_1$ band, and general trends are observed.$^{15}$

![Graph demonstrating relationship of the frequency of the $\nu_1$ band to the $M^{2+}$-O average bond length. Sr$_2$CdWO$_6$ does not have reported neutron data, thus bond lengths cannot be accurately determined.](image)

**Figure 2.11:** Graph demonstrating relationship of the frequency of the $\nu_1$ band to the $M^{2+}$-O average bond length. Sr$_2$CdWO$_6$ does not have reported neutron data, thus bond lengths cannot be accurately determined.

The secondary scheelite impurity phases did not affect the Raman spectra of these compounds to a great degree. However, Manoun et. al. performed high pressure Raman studies on Sr$_2$CaWO$_6$ and assigned each observed mode, some of which were impurity peaks. Manoun et. al. stated that the peak at 922 cm$^{-1}$ can “unambiguously” be assigned to the W-O bond movements. This peak, as well as their reported peak at 339 cm$^{-1}$, is not present in the Sr$_2$CaWO$_6$ Raman spectra is this study because these peaks belong to the scheelite phase, $M^{2+}$WO$_6$.$^{19}$ The peaks at approximately 920 and 335 cm$^{-1}$ are the two
strongest scheelite Raman peaks, as shown in Figure 2.12. Additionally, the peak Manoun et. al. assigned as an overtone of the 922 and 152 cm\(^{-1}\) peaks is not present in the Raman spectra of this study because, again, these peaks are due to two different phases. Thus, it is not an overtone peak. Despite these few inaccuracies, all other assignments by Manoun et. al. agree with the assignments in this study.\(^{19}\)

![Figure 2.12: Raman spectra of the scheelite impurity phases.](image)

## 2.4 Conclusions

Several tungsten-based perovskites were synthesized and studied with Raman scattering spectroscopy. All observed Raman peaks for all tungsten perovskites in this
chapter were successfully assigned according to group theory rules. While not all 24 anticipated Raman peaks could be found for the P2₁/n perovskites in this study, some notable trends were discussed. The frequency of the characteristic $\nu_1$ mode shifted according to the $M^{2+}$-O and $M^{2+}$ cation size (Figures 2.10 and 2.11), with a couple of anomalies. The Raman spectrum for Ca$_2$CaWO$_6$ had the largest number of observed libration lattice peaks that is most likely due to the considerable octahedral tilt of the perovskite. While polarized, single crystal Raman data is necessary to observe all expected peaks and definitely assign the lattice peaks to either translational or librational, the Raman assignments in this study are in agreement with previously reported studies on similar materials.
Chapter 3

Raman Studies of Ordering and Octahedral Tilting of $A_2M^{3+}\text{TaO}_6$ ($A = \text{Ba}, \text{Sr, Ca}; M^{3+} = \text{Sc, Y, Al}$) Perovskites

3.1 Overview

Tantalum-based perovskites, $A_2M^{3+}\text{TaO}_6$, can be ordered, partially ordered, or disordered, depending on the size difference of the $M^{3+}$ cation. When the B cations are yttrium and tantalum, the large size difference between the two ions results in a fully ordered perovskite, but when the $M^{3+}$ cation is either scandium or aluminum, the size difference alone is not large enough for complete ordering. In such cases, B site order also depends on annealing temperature, as will be shown with $\text{Sr}_2\text{AlTaO}_6$ and $\text{Ba}_2\text{ScTaO}_6$ in this study. X-ray diffraction studies are performed on all perovskites in this chapter to determine the order parameter, and interesting effects and patterns will be discussed. Raman scattering studies have not been reported for $\text{Ba}_2\text{ScTaO}_6$ or $\text{Ca}_2\text{YTaO}_6$ to the best of our knowledge.
3.2 Synthesis

Conventional solid state synthesis was performed by grinding stoichiometric amounts of high purity (>99% starting materials BaCO$_3$, SrCO$_3$, CaCO$_3$, Ta$_2$O$_5$, Al$_2$O$_3$, Sc$_2$O$_3$, and Y$_2$O$_3$ in an agate mortar and pestle and heating in a ceramic crucible for 12 – 24 hours. Ba$_2$ScTaO$_6$ and Ba$_2$YTaO$_6$ were obtained using ScTaO$_4$ and YTaO$_4$ precursors respectively, which were also synthesized by conventional solid state synthesis and heated at 900 – 1000 °C. Multiple heating cycles were necessary for some materials to obtain pure phase. Sr$_2$AlTaO$_6$ was synthesized via the flux method, in which the starting materials were first ground and heated at 900 °C in a ceramic crucible for 2.5 hours. SrCl$_2$ was then added in a 2:1 ratio of SrCl$_2$ to starting material and heated at 900 °C for 12 hours, melting the SrCl$_2$ and thus facilitating the reaction process. Once the heating cycle was complete, the SrCl$_2$ flux was washed away with dilute acid and the desired material was dried overnight. The perovskite was then annealed for 10 hours. Order variation in Sr$_2$AlTaO$_6$ and Ba$_2$ScTaO$_6$ was obtained by annealing at different temperatures after a pure phase perovskite had been obtained. Table 3.1 summarizes the synthesis parameters for the perovskites in this chapter.
<table>
<thead>
<tr>
<th>Composition</th>
<th>Space Group</th>
<th>Final Annealing Temperature (°C)</th>
<th>Tolerance Factor (τ)</th>
<th>Order Parameter</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba$_2$YTaO$_6$</td>
<td>Fm3m</td>
<td>1600</td>
<td>0.981</td>
<td>100%</td>
<td>2.8% Y$_2$O$_3$</td>
</tr>
<tr>
<td>Ca$_2$YTaO$_6$</td>
<td>P2$_1$/n</td>
<td>900</td>
<td>0.873</td>
<td>100%</td>
<td>5.7% Y$_2$O$_3$</td>
</tr>
<tr>
<td>Sr$_2$AlTaO$_6$</td>
<td>Fm3m</td>
<td>1200 - 1600</td>
<td>1.018</td>
<td>45 – 77%</td>
<td>-</td>
</tr>
<tr>
<td>Ca$_2$AlTaO$_6$</td>
<td>P2$_1$/n</td>
<td>1600</td>
<td>0.963</td>
<td>92%</td>
<td>-</td>
</tr>
<tr>
<td>Ba$_2$ScTaO$_6$</td>
<td>Fm3m</td>
<td>1250 - 1600</td>
<td>1.020</td>
<td>69 – 96%</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 3.1: Synthesis parameters for perovskites in this study.

### 3.3 X-ray Diffraction Results

Powder X-ray diffraction was performed on all perovskites to determine phase purity and B site ordering. The diffraction patterns are shown in Figure 3.1. The order parameter for perovskites was determined by analyzing the super structure (odd-odd-odd) peaks in the X-ray diffraction pattern, with the exception of Sr$_2$AlTaO$_6$ and Ba$_2$ScTaO$_6$. The super structure peaks for these two perovskites were too broad to obtain a good fit with a Rietveld refinement. Instead, a calibration curve was created using GSAS.$^{21}$ Theoretical diffraction patterns with varying degrees of ordering were created with GSAS and the ratio of the area of the 111 and 022 $hkl$ peaks was analyzed to create the calibration curve. Using the ratio of the areas of the 111 and 022 peaks in the real diffraction patterns, the order parameter was determined. The order parameter is calculated from the refined occupancy ($x$) by the following equation:

$$\text{Order Parameter} = 1 - 2(1 - x)$$
Figure 3.1: X-ray diffraction spectra of the tantalum-based perovskites in this study with space groups of Fm$\bar{3}$m and P2$_1$/n.
Table 3.2: Perovskite lattice parameter and β angle refinements as compared to literature values.

Refined lattice parameters were accurate within 0.01 Å and β angles were accurate within 0.01 degrees of the literature values, as shown in Table 3.2. Ba$_2$YTaO$_6$ and Ca$_2$YTaO$_6$ contained a small Y$_2$O$_3$ impurity which does not affect the study. Based on this refinement data, all materials were synthesized correctly and were pure phase products. Table 3.3 shows the Rietveld refinement parameters and atomic positions for Ca$_2$YTaO$_6$ and Ca$_2$AlTaO$_6$, while Figures 3.3 and 3.4 depict the observed versus calculated XRD spectrum for each respectively. Table 3.4 shows the octahedral tilt angles.
for Ca$_2$YTaO$_6$ and Ca$_2$AlTaO$_6$, both with a P2$_1$/n space group. The smaller calcium cation results in a tilting distortion of the octahedra, thus lowering the space group from cubic, and it is seen in Table 3.4 that Ca$_2$YTaO$_6$ has a greater octahedral tilting distortion than Ca$_2$AlTaO$_6$. As neutron data could not be found for these two perovskites, angles shown in Table 3.4 were obtained from refined X-ray diffraction data in this study. As noted previously, X-ray diffraction cannot accurately determine oxygen positions, thus powder neutron diffraction is needed to accurately locate the oxygen positions in these perovskites. Distortion indices were not calculated for these perovskites due to lack of available neutron data for the P2$_1$/n perovskites in the chapter.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff Position</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>Occupancy</th>
<th>B$_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaYTaO$<em>6$, $R</em>{wp} = 28.935$, $\chi^2 = 1.489$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Ca</td>
<td>4e</td>
<td>0.5107(6)</td>
<td>0.5546(8)</td>
<td>0.2535(3)</td>
<td>1</td>
<td>-0.086(6)</td>
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<tr>
<td>Ta</td>
<td>2c</td>
<td>0</td>
<td>0.5</td>
<td>0</td>
<td>1</td>
<td>0.334(6)</td>
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<tr>
<td>Y</td>
<td>2d</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.334(6)</td>
</tr>
<tr>
<td>O1</td>
<td>4e</td>
<td>0.2074(9)</td>
<td>0.1836(3)</td>
<td>-0.0439(3)</td>
<td>1</td>
<td>0.103(3)</td>
</tr>
<tr>
<td>O2</td>
<td>4e</td>
<td>0.3215(7)</td>
<td>0.7098(6)</td>
<td>-0.0629(5)</td>
<td>1</td>
<td>0.103(3)</td>
</tr>
<tr>
<td>O3</td>
<td>4e</td>
<td>0.3850(7)</td>
<td>-0.0484(8)</td>
<td>0.2362(8)</td>
<td>1</td>
<td>0.103(3)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff Position</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>Occupancy</th>
<th>B$_{eq}$</th>
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<tr>
<td>CaAlTaO$<em>6$, $R</em>{wp} = 22.771$, $\chi^2 = 1.166$</td>
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<tr>
<td>Ca</td>
<td>4e</td>
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<td>0.0295(7)</td>
<td>0.7534(5)</td>
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<tr>
<td>Al(1)</td>
<td>2c</td>
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<td>0.5</td>
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<td>0.962(9)</td>
<td>0.282(3)</td>
</tr>
<tr>
<td>Ta(1)</td>
<td>2c</td>
<td>0</td>
<td>0.5</td>
<td>0</td>
<td>0.037(1)</td>
<td>0.282(3)</td>
</tr>
<tr>
<td>Al(2)</td>
<td>2d</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>0.037(1)</td>
<td>0.282(3)</td>
</tr>
<tr>
<td>Ta(2)</td>
<td>2d</td>
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<td>0</td>
<td>0</td>
<td>0.962(9)</td>
<td>0.282(3)</td>
</tr>
<tr>
<td>O1</td>
<td>4e</td>
<td>0.2719(9)</td>
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<td>0.071(2)</td>
</tr>
<tr>
<td>O2</td>
<td>4e</td>
<td>0.3007(7)</td>
<td>0.2933(5)</td>
<td>0.5343(2)</td>
<td>1</td>
<td>0.071(2)</td>
</tr>
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<td>0.9236(8)</td>
<td>0.4879(2)</td>
<td>0.7518(7)</td>
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**Table 3.3:** Atomic positions for Ca$_2$AlTaO$_6$ and Ca$_2$YTaO$_6$ obtained from powder X-ray diffraction.
Figure 3.2: Rietveld refinement data for Ca$_2$YTaO$_6$. The green bars represent the Y$_2$O$_3$ impurity.
Figure 3.3: Rietveld refinement data for Ca$_2$AlTaO$_6$. 
Table 3.4: Relevant bond lengths and octahedral tilt angles for Ca$_2$YTaO$_6$ and Ca$_2$AlTaO$_6$.

<table>
<thead>
<tr>
<th>Bond Lengths and Octahedral Tilt Angles</th>
<th>Ca$_2$YTaO$_6$</th>
<th>Ca$_2$AlTaO$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M$^{3+}$ - O1 – M$^{3+}$ (deg)</td>
<td>148.67(8)</td>
<td>162.27(5)</td>
</tr>
<tr>
<td>M$^{3+}$ - O2 – M$^{5+}$ (deg)</td>
<td>142.71(6)</td>
<td>154.50(2)</td>
</tr>
<tr>
<td>M$^{3+}$ - O3 – M$^{5+}$ (deg)</td>
<td>141.48(7)</td>
<td>155.40(6)</td>
</tr>
<tr>
<td>M$^{3+}$ - O1</td>
<td>2 x 2.204(1)</td>
<td>2 x 1.844(7)</td>
</tr>
<tr>
<td>M$^{4+}$ - O2</td>
<td>2 x 2.226(9)</td>
<td>2 x 1.914(4)</td>
</tr>
<tr>
<td>M$^{3+}$ - O2</td>
<td>2 x 2.235(9)</td>
<td>2 x 1.939(7)</td>
</tr>
<tr>
<td>Ta$^{5+}$ - O1</td>
<td>2 x 1.978(9)</td>
<td>2 x 2.017(4)</td>
</tr>
<tr>
<td>Ta$^{5+}$ - O2</td>
<td>2 x 2.026(2)</td>
<td>2 x 1.995(9)</td>
</tr>
<tr>
<td>Ta$^{5+}$ - O3</td>
<td>2 x 2.026(2)</td>
<td>2 x 1.962(1)</td>
</tr>
</tbody>
</table>

3.4 Effects of Disorder in the Raman Spectrum

In a normal Raman scattering experiment, the spectra is obtained from the center of the Brillouin zone. When B site disorder is present, the Raman selection rules are no longer valid, and contributions to the Raman spectrum can come from the entire Brillouin zone. Thus, interesting effects can be seen in the Raman spectra of disordered perovskites, such as band broadening and peak shifts. Additionally, Raman forbidden peaks may become present in these types of spectra, as will be discussed with the case of Ba$_2$ScTaO$_6$. Recalling from previous chapters, the irreducible representation for an Fm$ar{3}$m perovskites is:

$$\Gamma = T(F_{2g}) + v_1(A_{1g}) + v_2(E_g) + v_5(F_{2g})$$

where $T$, $v_1$, $v_2$, $v_5$ correspond to the translational lattice, oxygen symmetric stretch, oxygen asymmetric stretch, and oxygen bending vibrations respectively.
Sr$_2$AlTaO$_6$ is a partially disordered cubic Fm$ar{3}$m perovskite. By annealing at differing temperatures, varying degrees of B site ordering was obtained for this perovskite. Figure 3.4 shows the Sr$_2$AlTaO$_6$ Raman spectra with the expected four bands. The bands at approximately 149, 464, 571, 865 cm$^{-1}$ can be assigned to $T$, $v_1$, $v_2$, and $v_5$ respectively. These assignments are in agreement with the spectra reported by Tao et. al.$^{27}$ However, there is an additional feature at 130 cm$^{-1}$, exhibited as a shoulder of the $T$ mode, in all Sr$_2$AlTaO$_6$ perovskites in this study and a weak feature at approximately 660 cm$^{-1}$ in the perovskites with order parameters up to 70%. These additional features are most likely caused by the disorder in the sample. As previously stated, a typical Raman spectrum is obtained from the center of the Brillouin zone, but when disorder is present, selection rules are broken and contributions can occur from other areas of the Brillouin zone.$^{27}$ This allows for additional, Raman forbidden peaks to appear within a vibrational spectrum. The 660 cm$^{-1}$ peak disappears in the perovskites with a higher order parameter, but the lattice mode at 130 cm$^{-1}$ does not. It should be noted that the 130 cm$^{-1}$ mode appears with a 630 nm laser as well, so it is not a figment of the laser. This is because lattice modes are sensitive to distortions within the perovskite, and the highest order parameter obtained for Sr$_2$AlTaO$_6$ is only 77%. It is possible that this additional lattice mode would disappear with a completely ordered perovskite.
The location and width of the $\nu_1$ Raman band can be predictive of ordering in perovskites and some interesting trends have been noted in the literature. Zheng et. al. studied the effect of disorder on the $\nu_1$ mode, stating that a broad peak indicates more short range order present in the material, while a narrow peak indicates long range order.\textsuperscript{28} If this comparison is performed for the varying degrees of B site ordering for Sr$_2$AlTaO$_6$, a nearly linear trend is observed (Figure 3.5). As the order parameter increases, the $\nu_1$ peak narrows, as also observed by Zheng et. al.\textsuperscript{28} The broadening effect in this mode with lower ordered perovskites is due to short range order, whereas a
narrow, sharp $\nu_1$ mode corresponds to long range order in the material. The exact position of the $\nu_1$ mode shifts slightly as well with ordering, as shown in Figure 3.6. Again, the relationship is close to linear with a slight frequency downshift occurring in perovskites with a lower amount of B site ordering. These comparisons reinforce the claim by Zheng et. al. that the $\nu_1$ mode is sensitive to B site ordering and can be indicative of both long range and short range order.  

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.5.png}
\caption{Graph depicting the full-width half-max (FWHM) of the $\nu_1$ peak as compared to the order parameter for Sr$_2$AlTaO$_6$.}
\end{figure}
Figure 3.6: Comparison of the location of the $\nu_1$ mode and the order parameter for Sr$_2$AlTaO$_6$.

When the A cation is replaced with a smaller calcium ion, the space group is lowered to P2$_1$/n and octahedral tilting occurs to accommodate the size difference. Ca$_2$AlTaO$_6$ is a partially ordered perovskite with an order parameter of 92%. Group theory predicts 24 Raman active bands for a P2$_1$/n perovskite:

$$\Gamma = 6T(3A_g + 3B_g) + 6L(3A_g + 3B_g) + 2\nu_1(A_g + B_g) + 4\nu_2(2A_g + 2B_g) + 6\nu_5(3A_g + 3B_g)$$

In the equation above, $\nu_1$, $\nu_2$, $\nu_5$, $T$, and $L$ are the symmetric oxygen stretch, asymmetric oxygen stretch, oxygen bending, translational lattice, and libration lattice modes respectively. The external lattice modes tend to be most sensitive to distortions within the perovskite and it was shown in Chapter 2 that the greater the distortion, the more lattice peaks observed. Figure 3.7 shows the Raman spectra for Ca$_2$AlTaO$_6$, where thirteen
peaks are observed for Ca$_2$AlTaO$_6$. It is common in a non-polarized Raman spectrum for lower symmetry materials to not observe all anticipated peaks. This can be caused by several factors which were discussed in earlier chapters.

**Figure 3.7**: Raman spectrum of Ca$_2$AlTaO$_6$.

Table 3.5 shows the mode assignments for Ca$_2$AlTaO$_6$, which are consistent with the assignments of the tungsten perovskites in Chapter 2 (Table 2.7). Three translation lattice modes are observed, and six libration modes are observed, if it is assumed that there are no extraneous peaks present due to disorder, as will be discussed in the case of

53
Ba$_2$ScTaO$_6$. Raman studies were reported by Runka et. al. for Ca$_2$AlTaO$_6$, but lattice modes were not extensively analyzed in the paper. However, the spectrum obtained in this study is similar to that reported by Runka et. al. It is expected that the $\nu_2$ mode would split into a doublet, while the $\nu_5$ mode would split into a triplet. However, a doublet is observed for $\nu_5$ and a single, broad peak for $\nu_2$. The lack of expected splitting is likely due to convoluted peaks.

<table>
<thead>
<tr>
<th>$\nu$ Ca$_2$AlTaO$_6$</th>
<th>Assignment</th>
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<tbody>
<tr>
<td>155</td>
<td>$T$</td>
</tr>
<tr>
<td>184</td>
<td>$T$</td>
</tr>
<tr>
<td>216</td>
<td>$T$</td>
</tr>
<tr>
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<td>$L$</td>
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<td>864</td>
<td>$\nu_1$</td>
</tr>
</tbody>
</table>

Table 3.5: Raman mode assignments for Ca$_2$AlTaO$_6$.

Another example of a partially ordered cubic Fm$\overline{3}$m perovskite is Ba$_2$ScTaO$_6$. Again, only four peaks are expected, but as shown in Figure 3.8, there are many additional features present, which are due to disorder effects. The expected bands at approximately 120, 410, 540, and 810 cm$^{-1}$ can be assigned to $T$, $\nu_1$, $\nu_2$, and $\nu_5$ respectively. Specific locations of the modes vary by a couple wavenumbers depending on the ordering of the perovskite. It is interesting to note that the additional, unanticipated modes become less prominent as the order parameter of the perovskite is increased. This
is particularly striking in the band at 730 cm$^{-1}$. In the 69% ordered perovskite, this band is prominent, but almost disappears completely in the material with an order parameter of 96%. It also appears as though there is some peak splitting occurring in the $\nu_1$ mode of the 96% ordered perovskite, as a definitive shoulder is now present. Although some peak asymmetry of this mode is observed in the lower ordered perovskites, it is likely that the narrowing of the $\nu_1$ mode (Figure 3.9) resulted in a peak separation here. The same $\nu_1$ trends were observed for this perovskite as were observed in Sr$_2$AlTaO$_6$ where the $\nu_1$ mode narrows and shifts to higher frequencies as the order parameter increases (Figures 3.9 and 3.10). The peaks widths for Ba$_2$ScTaO$_6$ were determined by curve-fitting the $\nu_1$ mode with multiple peaks, choosing the center peak as the symmetric oxygen stretch. The peak widths of the $\nu_1$ mode of the tungsten perovskites from Chapter 2 are typically in the 10 – 20 cm$^{-1}$ range.
Figure 3.8: Raman spectra of Ba$_2$ScTaO$_6$ with different ordering parameters. Spectra have been offset for clarity.
Figure 3.9: Graph depicting the full-width half-max (FWHM) of the \( \nu_1 \) peak as compared to the order parameter for \( \text{Ba}_2\text{ScTaO}_6 \). The peak was defined using a curve fitting application.
Figure 3.10: Comparison of the location of the $\nu_1$ mode and the order parameter for Ba$_2$ScTaO$_6$. 
Ba$_2$YTaO$_6$ (Figure 3.10) is a fully ordered perovskites due to the size difference between the yttrium and tantalum ions. Dr. Wolfgang Windl and coworkers performed theoretical Raman calculations on this perovskite using density functional theory (DFT). DFT predicts bands to occur at 95, 372, 589, and 832 cm$^{-1}$, which closely match the features at 104, 387, 547/574, and 839 cm$^{-1}$ in the spectrum above. These modes can be assigned to the $T$, $v_1$, $v_2$, $v_5$ vibrations respectively. The asymmetric oxygen stretching vibration, $v_2$, is unexpectedly split in the case of Ba$_2$YTaO$_6$, accounting for the two features at 547 and 574 cm$^{-1}$. Several authors have assigned the prominent feature present at 761 to the $u_2$ Raman vibration, but DFT calculations suggest otherwise.$^{30,31,32}$
Assigning the $\nu_2$ mode at 761 cm$^{-1}$ is also inconsistent with the typical location of this band in these type of perovskites. As seen in the highly ordered tungsten-based perovskites in the previous chapter, it is common for the asymmetric stretching vibration in fully ordered perovskite to be weak or absent altogether. Every other perovskite in this study shows the asymmetric stretch mode in the 500-650 cm$^{-1}$ region of the Raman spectra, which is consistent the DFT predictions.

The additional bands present at 316 and 761 cm$^{-1}$ present a perplexing problem. These features are not unique to this study, as they are present in all reported Raman studies on this perovskite. The $Y_2O_3$ Raman modes do not correspond to these extraneous peaks (Appendix B). Although according to a Rietveld refinement $Ba_2YTaO_6$ is a fully ordered perovskite, there may still be a small amount of disorder present, on the order of a couple percentage points. It is also possible that, as there is a $Y_2O_3$ impurity present, there could be barium or tantalum vacancies to account for the charge difference. Thus, local defects or a minute degree of disorder may account for the unexpected features in the Raman spectrum.

Like $Ca_2AlTaO_6$, $Ca_2YTaO_6$ is a P2$_1$/n perovskite with an octahedral tilting distortion, and is fully ordered due to the large size difference between the yttrium and tantalum cations. The Raman spectrum for $Ca_2YTaO_6$ is shown in Figure 3.12 and the mode assignments are shown in Table 3.9. One translational and four librational lattice modes are observed. Although $\nu_2$ is broad, as was seen in $Ca_2AlTaO_6$, a faint amount of splitting is present, as is expected for this perovskite. The oxygen bending mode, $\nu_5$, which is expected to split into a triplet, is split into two peaks in this perovskite. This was
also observed in Ca$_2$AlTaO$_6$. The unanticipated peak at 710 cm$^{-1}$ is similar to the extraneous peak observed for Ba$_2$YTaO$_6$. Despite refinements showing that this is a fully ordered perovskite, there may still be a small amount of disorder present, accounting for this additional peak, as with Ba$_2$YTaO$_6$.

Figure 3.12: Raman spectrum of Ca$_2$YTaO$_6$. 
Table 3.6: Raman mode assignments for Ca$_2$YTaO$_6$.

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<tr>
<th>$\nu$ Ca$_2$YTaO$_6$</th>
<th>Assignment</th>
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<tbody>
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<td>793</td>
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3.5 Conclusion

Tantalum-based perovskites were synthesized with differing order parameters with and without an octahedral tilting distortion. Sr$_2$AlTaO$_6$ and Ba$_2$ScTaO$_6$ were synthesized with several degrees of B site ordering by using different annealing temperatures. Peaks that were predicted by group theory were assigned to vibrational modes, but there were additional, unexpected modes in perovskites with B site disorder present in the material. In Ba$_2$ScTaO$_6$, these additional modes became less intense or disappeared altogether with an increase in ordering. A few nearly linear trends were observed for the $\nu_1$ mode as compared to order parameter. There was a downshift in peak position of the symmetric oxygen stretch with increasing order parameter and narrower $\nu_1$ peaks were observed for materials with a higher order parameter (Figure 3.5 through 3.8). Overall, interesting observations and trends were noted when disorder effects can be attributed to the material.
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Appendix A: GSAS Order Parameter Calibration Curves

\[ y = 6.3972x^{-2.102} \]
\[ R^2 = 0.9988 \]

Sr$_2$AlTaO$_6$
$y = 16.469x^{-1.985}$

$R^2 = 1$
Appendix B: Raman Spectra of $\text{Y}_2\text{O}_3$