ATOMIC STRUCTURE EFFECTS ON BULK AND SURFACE PROPERTIES OF MIXED METAL OXIDES FROM FIRST PRINCIPLES SIMULATIONS

By

BEVERLY BROOKS HINOJOSA

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

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To my husband Bebo
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<tr>
<td>$\delta$</td>
<td>displacement magnitude</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>dielectric permittivity of free space</td>
</tr>
<tr>
<td>$\varepsilon_i$</td>
<td>eigenvalue for modified Hamiltonian</td>
</tr>
<tr>
<td>$\varepsilon_r$</td>
<td>relative dielectric permittivity</td>
</tr>
<tr>
<td>$\eta$</td>
<td>electron density</td>
</tr>
<tr>
<td>$\psi_i$</td>
<td>single-electron wave-function</td>
</tr>
<tr>
<td>$\Psi_n$</td>
<td>set of eigenstates</td>
</tr>
<tr>
<td>$\nu_0$</td>
<td>pre-exponential factor for rate constants</td>
</tr>
<tr>
<td>$a$</td>
<td>number of cations</td>
</tr>
<tr>
<td>$B$</td>
<td>bond valence sum constant</td>
</tr>
<tr>
<td>$d_{(A-X)}$</td>
<td>bond length between cation “A” and anion “X”</td>
</tr>
<tr>
<td>$E_{\text{ads}}$</td>
<td>adsorption energy</td>
</tr>
<tr>
<td>$E_{\text{A}_2\text{O}'}$</td>
<td>energy of isolated $\text{A}_2\text{O}'$ sub-network</td>
</tr>
<tr>
<td>$E_{\text{B}_2\text{O}_6}$</td>
<td>energy of isolated $\text{B}_2\text{O}_6$ sub-network</td>
</tr>
<tr>
<td>$E_{\text{H}_2\text{O, gas}}$</td>
<td>energy of isolated water molecule</td>
</tr>
<tr>
<td>$E_{\text{H}_2\text{O, slab}}$</td>
<td>total energy of water adsorbed on SrTiO$_3$ slab</td>
</tr>
<tr>
<td>$E_{\text{interaction}}$</td>
<td>energy of interaction between $\text{A}_2\text{O}'$ and $\text{B}_2\text{O}_6$ sub-networks</td>
</tr>
<tr>
<td>$E_n$</td>
<td>set of eigenvalues</td>
</tr>
<tr>
<td>$E_{\text{slab}}$</td>
<td>total energy of relaxed bare SrTiO$_3$ surface or slab</td>
</tr>
<tr>
<td>$E_{\text{total}}$</td>
<td>energy of total $\text{A}_2\text{B}_2\text{O}_7$ lattice</td>
</tr>
<tr>
<td>$e\text{V}$</td>
<td>electron volts</td>
</tr>
<tr>
<td>$H$</td>
<td>Hamiltonian operator</td>
</tr>
<tr>
<td>$k_i$</td>
<td>coordination number of cation “i”</td>
</tr>
<tr>
<td>$m_e$</td>
<td>mass of an electron</td>
</tr>
</tbody>
</table>
\begin{align*}
M & \quad \text{mass of nucleus} \\
n & \quad \text{number of molecules} \\
n_i & \quad \text{charge of cation \textquotedblleft}i\text{\textquotedblright} \\
N & \quad \text{total number of electrons} \\
P & \quad \text{polarization} \\
r & \quad \text{spatial position of an electron} \\
R & \quad \text{spatial position of nucleus} \\
R_{ij} & \quad \text{bond length of each bond} \\
R_0 & \quad \text{bond valence sum reference bond length} \\
s_i & \quad \text{bond strength of cation \textquotedblleft}i\text{\textquotedblright} \\
S_{ij} & \quad \text{bond valence of each bond} \\
T_m & \quad \text{temperature of maximum dielectric permittivity} \\
T_p & \quad \text{desorption temperature} \\
V_{\text{Bi}} & \quad \text{vacancy on Bi site} \\
V_{\text{eff}} & \quad \text{effective potential} \\
V_{\text{ext}} & \quad \text{external potential} \\
V_{\text{Hartree}} & \quad \text{Hartree potential} \\
V_i & \quad \text{valence of ion \textquotedblleft}i\text{\textquotedblright} \text{ from bond valance sums} \\
V_{O'} & \quad \text{vacancy on O' site} \\
V_{\text{XC}} & \quad \text{exchange-correlation potential} \\
x & \quad \text{oxygen positional parameter} \\
z_j & \quad \text{ionic charge of anion \textquotedblleft}j\text{\textquotedblright} \\
Z & \quad \text{charge of nucleus}
\end{align*}
<table>
<thead>
<tr>
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<tr>
<td>BMN</td>
<td>(Bi₁.₅Mg₀.₅)(Mg₀.₅Ta₁.₅)O₇</td>
</tr>
<tr>
<td>BMT</td>
<td>(Bi₁.₅Mg₀.₅)(Mg₀.₅Ta₁.₅)O₇</td>
</tr>
<tr>
<td>BVS</td>
<td>bond valence sum</td>
</tr>
<tr>
<td>BZN</td>
<td>(Bi₁.₅Zn₀.₅)(Zn₀.₅Nb₁.₅)O₇</td>
</tr>
<tr>
<td>BZS</td>
<td>(Bi₁.₅Zn₀.₅)(Zn₀.₅Sb₁.₅)O₇</td>
</tr>
<tr>
<td>BZT</td>
<td>(Bi₁.₅Zn₀.₅)(Zn₀.₅Ta₁.₅)O₇</td>
</tr>
<tr>
<td>CG</td>
<td>conjugate gradient</td>
</tr>
<tr>
<td>CTN</td>
<td>(Ca₁.₅Ti₀.₅)(Ti₁.₀Nb₁.₀)O₇</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>ELF</td>
<td>electron localization function</td>
</tr>
<tr>
<td>EXAFS</td>
<td>extended X-ray absorption fine structure</td>
</tr>
<tr>
<td>GGA</td>
<td>generalized gradient approximation</td>
</tr>
<tr>
<td>GULP</td>
<td>Generalized Utility Lattice Program</td>
</tr>
<tr>
<td>HF</td>
<td>Hartree-Fock</td>
</tr>
<tr>
<td>HREELS</td>
<td>high resolution electron energy loss spectroscopy</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>LCAO</td>
<td>linear combinations of atomic orbitals</td>
</tr>
<tr>
<td>LDA</td>
<td>local density approximation</td>
</tr>
<tr>
<td>LEED</td>
<td>low energy electron diffraction (LEED)</td>
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<tr>
<td>LMTO</td>
<td>linear muffin tin orbital</td>
</tr>
<tr>
<td>MD</td>
<td>molecular dynamics</td>
</tr>
<tr>
<td>ML</td>
<td>monolayer</td>
</tr>
<tr>
<td>NEB</td>
<td>nudged elastic band</td>
</tr>
<tr>
<td>NVT</td>
<td>canonical ensemble</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>$O_w$</td>
<td>oxygen within water molecule</td>
</tr>
<tr>
<td>$O_x$</td>
<td>oxygen within oxide</td>
</tr>
<tr>
<td>PAW</td>
<td>projector augmented wave</td>
</tr>
<tr>
<td>PBC</td>
<td>periodic boundary condition</td>
</tr>
<tr>
<td>PBE</td>
<td>Perdew-Burke-Emzerhof parameterization</td>
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<tr>
<td>pDOS</td>
<td>partial density of states</td>
</tr>
<tr>
<td>RPBE</td>
<td>revised Perdew-Burke-Emzerhof parameterization</td>
</tr>
<tr>
<td>RUM</td>
<td>rigid unit mode</td>
</tr>
<tr>
<td>STM</td>
<td>scanning tunneling microscopy</td>
</tr>
<tr>
<td>STO</td>
<td>SrTiO$_3$</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoemission spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>TPD</td>
<td>temperature programmed desorption</td>
</tr>
<tr>
<td>UHV</td>
<td>under ultra high vacuum</td>
</tr>
<tr>
<td>UPS</td>
<td>ultraviolet photoemission spectroscopy</td>
</tr>
<tr>
<td>VASP</td>
<td>Vienna <em>Ab-initio</em> Simulation Package</td>
</tr>
<tr>
<td>ZPC</td>
<td>zero point correction</td>
</tr>
</tbody>
</table>
Oxides are a class of materials that play a critical role in many applications, including both electronic and catalytic. The hundreds of different oxides that vary in structure or chemical composition offer the opportunity to tune these materials for specific applications but to rationally design these oxide materials requires understanding the structure-property relationships. This dissertation presents modeling work based on density functional theory (DFT) on two oxides to understand the structure-property relationships. The predominant work of the dissertation focuses on examining the role of atomic displacements, oxygen vacancies, and cation substitutions in bismuth based pyrochlores. The second project involves the study of surface chemistry on SrTiO$_3$ surfaces.

Pyrochlores have the chemical formula $A_2B_2O_7$ and the structure allows these materials to be tuned with different choices of cations on the A and B cation site. Bi-based pyrochlores have received attention over the past decade for use in capacitor and high-frequency filter applications with extensive work focused on tuning material properties through cation substitutions. However, the myriad of effects induced by
cation substitutions are still not entirely understood and the relationship between cation substitution and dielectric properties needs further elucidation. In this work, DFT simulations explore the link between atomic structure and atomic displacements in Bi pyrochlores.

A range of cubic Bi pyrochlores with no cation substitutions were explored and significant displacements were found only in Bi$_2$Ti$_2$O$_7$. By examining the electronic structure, the formation of lone pairs on the Bi cation was found to induce cation displacement in Bi$_2$Ti$_2$O$_7$. It is shown that oxygen vacancies induce cation displacement in bismuth ruthenate, resolving a discrepancy between oxygen-deficient experimental results and the DFT results of non-defective bismuth ruthenate. A relationship between DFT-derived cation displacement and experimentally measured dielectric constants was found in a range of cation substituted Bi pyrochlores, Bi$_{1.5}$M$_{2+}$B$_{5+}$O$_{7}$ (with M$_{2+}=$Zn or Mg and B=Nb or Ta). Finally, dielectric relaxation is determined by the ease of cation hopping between energetically degenerate positions within the pyrochlore structure. To explore this hopping process, a preliminary study was completed to identify transition states to cation hopping and associated energy barriers for Bi$_2$Ti$_2$O$_7$, Bi$_{1.5}$ZnNb$_{1.5}$O$_{7}$, and Ca$_{1.5}$Ti$_{1.5}$NbO$_7$. 
CHAPTER 1
INTRODUCTION

1.1 Motivation

Metal oxides play an important role in modern microelectronics, catalysis, and numerous other technologies. As a class of materials metal oxides are ubiquitous partly because of their diversity. Metal oxides can be found that are high-k insulators, metallic, semiconductors, ferromagnetic, piezoelectric, ferroelectric, ferroplastic, and multiferroic. This list is a subset of the range of material properties that oxides can have depending on their composition and structure. Mixed metal oxides, such as that found in the perovskite (ABO$_3$) and pyrochlore (A$_2$B$_2$O$_7$) structures, have even a broader range of tunable properties due to the larger parameter space associated with the combination of two or more cations. Mixed metal oxides can also show both covalent and ionic nature in the distinct metal-oxygen bonds. For instance, in SrTiO$_3$ the Sr-O bonds are mainly ionic, while the Ti-O bonds show significant covalent bonding [1]. The presence of this additional heterogeneity in mixed metal oxides provides the possibility to tune the macroscopic properties through the choice of cations. For example, within the ABO$_3$ perovskite structure family a proper choice of the A and B cation can lead to a material that is ferroelectric (e.g. PbTiO$_3$) versus paraelectric (e.g. SrTiO$_3$) at room temperature. This large difference in the material property between PbTiO$_3$ and SrTiO$_3$ can be attributed to the covalent nature of the Pb-O bond in PbTiO$_3$ versus the purely ionic Sr-O bond in SrTiO$_3$ [1,2]. As will be seen in the work presented in this dissertation, the choice of cations in mixed metal oxides and the interaction between the subnetworks in these oxide structures can dramatically affect the material behavior.
In this dissertation, \textit{ab initio} quantum based simulations are presented on two distinct projects to help elucidate the structure-property relationships in two classes of mixed metal oxide structure families: perovskites and pyrochlores. This dissertation will focus on the pyrochlore system with the details of the work on SrTiO$_3$ surfaces discussed in Chapter 8.

1.1.1 Motivation for the Study of Bismuth Pyrochlores

Pyrochlore oxides have received much attention the past 30 years due to their diverse physical properties, which allow for a broad range of applications. Recently pyrochlores have been considered for use in applications such as high-permittivity dielectrics \cite{3}, solid electrolytes in solid-oxide fuel cells \cite{4}, potential host materials for the immobilization of plutonium and nuclear waste \cite{5,6}, and thermal barrier coatings \cite{7-9}.

As will be discussed in further detail in Chapter 2, the ideal stoichiometric pyrochlores (A$_2$B$_2$O$_7$) are cubic with space group $Fd\bar{3}m$ (number 227). It is often described as two interpenetrating sub-networks of A$_4$O' tetrahedra and BO$_6$ octahedra \cite{10}. In fact, the overall formula is typically represented as A$_2$B$_2$O$_6$O' to distinguish the oxygen within the two networks. This representation is one of a multitude of perspectives of the pyrochlore structure found in the literature (see Ref. [10-14] for more extensive discussion on pyrochlore structure in addition to Chapter 2).

The various representations of the structure are a reflection of the general complexity of pyrochlores, and the most helpful representation is often dependent on the particular property of interest. The complexity of the pyrochlore structure is also central to the great diversity in properties that make these materials so interesting.
Extensive experimental work on the synthesis and structural characterization of cubic pyrochlores have established stability fields for allowable substitution into the A and B cation site based on simple measures such as the ratio of the cation radii size and the cation electronegativity [12,15]. The typical A (B) cation radii is around 1 (0.6) Å, but variations of up to 0.2 Å for both cations have been stabilized. As the cation radii shift away from the typical values noted, the range of A/B substitutions that can stabilize into a stoichiometric cubic structure decreases sharply [15]. Recently, it has been shown that the stability field of allowable cation radii ratios can be extended, but these structures incorporate atomic displacements, while still retaining the cubic symmetry macroscopically. Both experimental and theoretical work has focused on finding optimal A/B combinations for particular applications. For example, a recent extensive computational study focused on the affect of A and B cations on the thermal conductivity of the pyrochlores to develop optimal TBCs [9].

While ideal (or simple) cubic pyrochlores are important, there has been a growing interest in more complex pyrochlores involving substitutions on the A and B cation sites. Substitutions on the cation site allow for a much broader range of stable cubic pyrochlores, and a considerable number of novel complex pyrochlores have been synthesized and studied experimentally. The Bi$_{1.5}$ZnNb$_{1.5}$O$_7$ (BZN) system is one key example of these substituted pyrochlore compounds that has been studied extensively due to a high dielectric constant, relatively low dielectric losses, compositionally tunable temperature coefficient of capacitance, and a sintering temperature of less than 950°C [13]. These properties are ideal for applications such as capacitors and high-frequency filter application [16]. The dielectric properties of such materials are of particular
technological interest [3,16]. Some background on the behavior of dielectrics is presented below in Section 1.1.2 with further details provided in Ref. [17,18].

1.1.2 Dielectric Behavior in Bismuth Pyrochlores

The dielectric behavior of an insulator is dictated by the response of the material to concentrate an applied electric field within itself by redistributing charges within the atoms or molecules of the material. This response has four contributions: atomic (electronic), ionic, dipolar, and space charge polarization as illustrated in Figure 1-1 [11,18]. The total dielectric permittivity ($\varepsilon$) is often scaled by the dielectric permittivity of free space ($\varepsilon_0$) to define the relative dielectric permittivity (often simply called the dielectric constant) which is written as $\varepsilon_r$ or $k'$. Each of the four polarization processes present in a material will contribute to the total dielectric permittivity. Since the mechanism of charge rearrangement for each process varies in both their length and time scales, these four mechanisms will be discussed in more detail from the smallest to largest length scales.

In the atomic, or electronic, polarization process, the spherical electron cloud surrounding an atom under zero electric field conditions displaces relative to the positive nucleus creating the elongated cloud illustrated in Figure 1-1. The atomic mechanism is not sensitive to temperature variations. Since this mechanism is dependent on only the movement of electrons, atomic polarization occurs at frequencies up to $\sim 10^{15} – 10^{17}$ Hz in all gases, liquids, and solids. Therefore this mechanism is expected to play a role within the bismuth pyrochlores. The atomic mechanism occurs at the highest frequencies of the four types, so at frequencies above $\sim 10^{18}$ Hz the dielectric permittivity of any material should equal the dielectric permittivity of free space [17].
The ionic mechanism occurs in materials with some ionic character where the ions are bound elastically to equilibrium positions. Under an applied electric field, the anions and cations displace towards the positive and negative electrodes, respectively. The displaced positions of the ions are not equilibrium positions; therefore, following the removal of the electric field, the ions will return to their original equilibrium positions. The ionic mechanism is also independent of temperature. Due to the larger length scale of the ions versus electrons, the ionic mechanism drops off at lower frequencies than the atomic (electronic) mechanism. The ionic mechanism occurs up to frequencies $\sim 10^{12}$ –
$10^{13}$ Hz and at frequencies above this the ionic contribution to the relative dielectric permittivity goes to 1 [17]. The ionic mechanism is expected to occur in bismuth pyrochlores.

The dipolar mechanism will only occur in materials with equivalent positions separated by an energy barrier that the ions may occupy with equal probability in the absence on an electric field. The ferroelectric tetragonal PbTiO$_3$ is an example of such a material, where the Ti cation is shifted up or down with respect to the center position. With the Ti cation in either the up or the down position, a dipole moment is created with respect to its six oxygen anions neighbors. Either the up or down position is equally occupied in the absence of an applied field, but when an electric field is applied the Ti cation will shift preferentially to have the dipole moments align with the electric field wherever possible. As illustrated in Figure 1-1, not every dipole moment will align based on the structure of the system and the location of equivalent positions with respect to the applied electric field. The dipolar mechanism occurs at low frequencies and typically drops off between $\sim 10^8 - 10^9$ Hz. Materials that have dipolar mechanism typically exhibit relative dielectric constants in the hundreds [17]. Unlike either the electronic or ionic mechanism, the dipolar mechanism will depend on temperature since increasing temperature increases randomness. Increasing the temperature is expected to decrease the dipolar contribution to the static relative dielectric constant [17]. As will be seen in Section 3.3.2 and 6.4.2, atomic displacement in bismuth based pyrochlores leads to energetically degenerate positions for both the cations and anions. The dipolar mechanism is therefore expected to contribute to the dielectric permittivity in bismuth pyrochlores. As will be discussed in Section 7.3.2, the temperature dependence of the
dipolar mechanism will allow for the approximation of the energy barrier separating the equivalent positions in BZN.

The space charge mechanism shown in Figure 1-1 involves the rearrangement of charges within isolated regions of the material. This mechanism requires two phases within the material and will result in the accumulation of charges at the interface(s) of these regions. The space charge mechanism occurs at low frequencies, dropping off above $\sim 10^2$ Hz. Space charge is often identified in materials with dielectric constants in the thousands, such as BaTiO$_3$ where a static relative dielectric constant is reported of 3000 [17]. Based on the dielectric data reported on bismuth pyrochlore, the space charge mechanism is not expected to contribute to the relative dielectric permittivity.

The dielectric properties are linked to the mechanism of rearrangement, which in turn depends on the atomic structure. Therefore, correlating atomic structure and dynamics to observed dielectric behavior is a critical step in realizing the promise of pyrochlores in next-generation electroceramic materials.

The structure can be probed through experimental methods (see Section 1.2 for a survey of these efforts), but computational modeling can provide an inexpensive and effective form of investigating these materials at the atomic level. The goal of the work outlined here is to expand the understanding of the structure-property relationships for Bi-based pyrochlores through simulations. The modeling will use first-principles calculations, which may probe the role of electronic structure and allow predictive simulations of Bi-based pyrochlores. The fundamentals of these simulations are discussed in Section 1.3. The computational modeling will be an important complement to on-going experimental work in this area.
1.2 Literature Review

A brief survey of the experimental work examining Bi-pyrochlores along with efforts to model pyrochlores is present here. Ideal bismuth pyrochlores’ structural and electronic properties have been studied experimentally over the past three decades [15,19-28]. These pyrochlores have seen deviations from the ideal A₂B₂O₇ structure with Bi and O’ deficiencies and Bi and O’ displacements. The known simple bismuth pyrochlores are bismuth ruthenate (Bi₂₋ₓRu₂O₇₋ᵧ) [19-22,24], bismuth rhodate (Bi₁.₉₅Rh₂O₆.₈₃) [27], bismuth platinate (Bi₂Pt₂O₇) [15,29], bismuth iridate (Bi₁.₉Ir₂O₆.₈) [21,26], bismuth osmate (Bi₂Os₂O₇) [15], and bismuth titanate (Bi₂₋ₓTi₂O₇₋ᵧ) [23,25,28]. It is known that bismuth ruthenate exists is a non-stoichiometric ideal pyrochlore Bi₂₋ₓRu₂O₇₋ᵧ [20-22,24] and forms stoichiometric solid solution pyrochlore with the general formula A₂(Ru₂₋ₓAx)O₇ [19] or Bi₂₋ₓMₓRu₂O₇₋ᵧ [20] and has therefore been studied extensively.

There have been computational studies of the pyrochlore system for various A and B cations mainly focused in the area of interatomic potentials fitted to experimental lattice parameters [6,9,30-33]. The lanthanum and yttrium family of pyrochlores were studied using DFT recently to identify the structural, elastic and bonding properties of these systems [34] and results compared well with available studies. A complete study of bismuth stannate, a distorted pyrochlore, included a joint experimental and theoretical approach to understanding the bonding and lone pair activity in the material [35]. Due to the bismuth displacement and deficiency in bismuth titanate, it has been proposed as a model system to understand the properties of bismuth pyrochlores [14]. A linear muffin-tin orbital (LMTO) study was performed examining the density of states and the valence electron localization function (ELF) to clarify the bonding within the Bi₂O’ network. One
The other LMTO study involved bismuth ruthenate pyrochlore which has also been studied extensively since the compound allows for substitution on either the A [20] or the B [19] site and shows potential application in solid oxide fuel cells (SOFCs) [36]. The combined experimental and computational study in Ref. [20] proposes that the bismuth displacement is due to the lone pair’s stereochemical activity on the bismuth. Gaining an understanding of the simple pyrochlores in particular the role of the displacement of the bismuth cation will be important in understanding their complex multi-site substituted counterparts, but predictive computational work in this area has been limited.

The complex bismuth based substituted pyrochlores have been extensively studied experimentally, due to their ideal combination of characteristics for capacitors and high-frequency filter applications [3]. In the interest of time, this section will not present an exhaustive description of all experimental work, but will focus on those of pertinence to this dissertation. One system of particular interest is Bi$_{1.5}$ZnNb$_{1.5}$O$_7$ (BZN) which has zinc substituted equally on both the A and B site in the pyrochlore structure. BZN has been shown to be both zinc and oxygen deficient and to have disordered displacement on both the A and O’ site [13]. Experimental studies have used both X-ray and neutron powder diffraction techniques to determine the structural properties of these complex compounds [13,37] and recently, a more precise stoichiometry for BZN was determined to be Bi$_{1.5}$Zn$_{0.92}$Nb$_{1.5}$O$_{6.92}$ (BZN) [13]. Though BZN has received much attention, it is certainly not the only bismuth based complex pyrochlore to be studied. Other compounds include Bi$_{3/2}$ZnTa$_{3/2}$O$_7$ (BZT), Bi$_{3/2}$MgNb$_{3/2}$O$_7$ (BMN), Bi$_{3/2}$MgTa$_{3/2}$O$_7$ (BMT), and Bi$_{3/2}$ZnSb$_{3/2}$O$_7$ (BZS) to name a few [37,38]. The dielectric properties of ten of these types of compounds have been examined [3] and the phonon modes for BZN,
BZT, BMN and BMT have been determined [38]. Based on neutron diffraction data of BZN, short range ordering of metal ions and strain induced relaxation has been proposed [10]. The increased accuracy of structure resolution of complex pyrochlores in the last decade along with extensive spectroscopic studies have greatly increased the atomic-level understanding of these pyrochlores and the combination of these probes with predictive atomistic simulations should assist in the ultimate goal of understanding and predicting structure-property relationships for complex pyrochlores. This section is concluded by noting that there is a recent trend towards exploring complex pyrochlores with multiple substitutions such as $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Ti}_{1.5}\text{Nb}_{0.5})\text{O}_7$ (BZNT) [39], which reinforces the need for dependable predictive simulations of these materials to examine the large parameter space.

### 1.3 Simulation Methods

With the initial goal of performing multi-scale modeling, the simulation techniques to be used were density functional theory (DFT) and molecular dynamics (MD). The DFT calculations were to provide an accurate basis for constructing interatomic potentials for the MD simulations. The DFT calculations proved more elaborate and provided more information about these materials than initially expected and therefore are the only calculations discussed in this work. Future efforts on the development of the interatomic potentials will be discussed in Chapter 9. DFT is quantum mechanical calculations that approximately solve the Schrödinger equation without requiring any experimental input. The commercially available program called Vienna *Ab-initio* Simulation Package (VASP) was implemented in order to complete these calculations.
1.3.1 Periodic Boundary Conditions

Within VASP, periodic boundary conditions (PBC) are applied in all three directions; therefore, calculations that replicate a large structure may be performed with the smallest unit of symmetry repeated infinitely in all directions. Figure 1-2 shows a two dimensional schematic of the application of PBCs. The central box is the actual simulation cell that is inputted by the user. Following PBCs, the eight additional cells are created around the central cell. Each element within the central box is repeated in each additional image and these replicated elements are used when the atomic forces are calculated for each element within the original unit cell.

![Diagram of PBCs](image)

Figure 1-2. Two dimensional schematic illustrating periodic boundary conditions. The application of PBCs leads to the circle element translating from one corner of the simulation box to another, as illustrated by the arrows. (Reproduced from Ref. [40].)

As illustrated by the arrows in Figure 1-2, an element translated within the original cell to reduce the forces is moved within all images. Additionally, if the translation involves the element crossing one or more of the simulation boundaries that element’s
image will translate into the simulation box from the other side, as illustrated by the circles and arrows in Figure 1-2. See Ref. [40] for additional details regarding PBCs.

The PBC approach works very well for structures with repeating units of symmetry such as bulk materials, highly ordered surfaces (assuming an appropriate amount of vacuum space is included between the top and bottom of the slabs in the surface normal direction), and even in straight polymers without cross-linking. The introduction of cross-linking in polymers or even polymer folding onto itself leads to a break in symmetry which would require larger base unit cells to describe the structure. As DFT is the focus of this work, a summary of the fundamentals will be discussed below in Section 1.3.2. A practical introduction to DFT that is ideal for beginners or experimentalists can be found in Ref. [41] and a more detailed discussion is presented in Ref. [42].

**1.3.2 Fundamentals of Density Functional Theory**

One of the benefits of DFT is the variation principle which states that a total energy cannot be found that is lower than the true ground state; therefore, the true ground state energy cannot be undershot [43]. While it should be noted, this principle does not guarantee that the current lowest energy state is the global minimum it does provide the basis to compare configurations. Thus, this principle allows users to compare the energies for different configurations of the same atoms to make predictions about the most stable state that is likely to be present in an experimental apparatus. This implies a key component of DFT calculations is determining the energy associated with a particular structure. The details of how these calculations are completed are detailed in the sections to follow below.
1.3.2.1 Schrödinger equation

The basis of these calculations begins with the time-independent Schrödinger equation (Equation 1-1) and following a few approximations the problem is computationally solvable for solid-state systems [41].

\[ \hat{H}\psi = E\psi \]  \hspace{1cm} (1.1)

The Schrödinger equation is an eigenvalue problem where \( \hat{H} \) is the Hamiltonian operator, and \( \psi \) is a set of eigenstates (solution) with a particular set of eigenvalues \( E_n \) associated with a particular solution, \( \psi_n \). For a many-body problem with multiple electrons and nuclei, the Hamiltonian operator is quite complex and is defined in Equation (1.2).

\[ \hat{H} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{n_e} \nabla_i^2 + \sum_{i=1}^{n_e} \sum_{i \neq j}^{n_e} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^{n_e} \sum_{j=1}^{n_a} \frac{Z_i e^2}{|\mathbf{R}_i - \mathbf{R}_j|} + \frac{1}{2} \sum_{i=1}^{n_e} \nabla_i^2 + \frac{1}{2} \sum_{i=1}^{n_e} \sum_{j=1}^{n_a} \frac{Z_i Z_j e^2}{|\mathbf{R}_i - \mathbf{R}_j|} \]  \hspace{1cm} (1.2)

In Equation (1.2), lower (upper) case variables and subscripts are used for electrons (nuclei), and \( m_e (M) \) is the mass, \( \mathbf{r}(\mathbf{R}) \) is the spatial position of an electron (nucleus), and \( Z \) is the charge of a nucleus. The five terms on the right hand side of Equation (1.2) are the kinetic energy of each electron, interaction between each electron and nucleus, the electron-electron interaction, the kinetic energy of each nucleus, and the nucleus-nucleus interaction, respectively [42].

It is known that the mass of an electron \( (m_e) \) is 1800 times smaller than the mass of a nucleus \( (M) \) and therefore an electron will respond to changes in its surroundings much faster than a nucleus. This is the basis of the Born-Oppenheimer approximation [41]. This approximation allows for the separation of the electron and nucleus movements, which separates the mathematical solutions. The ground state of the electrons is solved for a fixed nuclei structure and the corresponding simpler Hamiltonian operator is
defined in Equation (1.3). The “external” potential, $V_{\text{ext}}$, includes the effect of the nuclei on the electrons.

$$
\hat{H} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i} V_{\text{ext}}(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} \phi^2_{|\mathbf{r}_i - \mathbf{r}_j|} 
$$

(1.3)

The proof of two theorems by Hohenberg and Kohn lead to the formulation of DFT used today [41]. It was first confirmed that all properties of a quantum many-body system, including the ground state energy, are unique functionals of the corresponding ground-state electron density. This lead to the replacement of the wave function, which is a function of $3N$ variables (where $N$ is the total number of electrons in the system), with the electron density, which is a function of only three variables (the spatial variables). This is especially important when considering the number of electrons including in the calculations presented within this work. For the bismuth pyrochlores the number of electrons exceeds 700, so this theorem reduces the dimensions from 21,000 to 3.

The second theorem proves total ground state energy cannot be underestimated. An electron density cannot be found that is different than the ground state electron density and results in a lower ground state energy. Therefore, if the true functional form of the electron density were known, the exact solution to the Schrödinger equation could be found by varying the electron density until the ground state energy was minimized. Instead, this variational principle is combined with approximate forms of the functional leading to approximate solutions to the Schrödinger equation.

1.3.2.2 Kohn-Sham equations

The calculations presented within this dissertation are based on the formulation of DFT presented by Kohn and Sham shortly after the proof of the two theorems detailed
in Section 1.3.2.1. The Kohn-Sham equations, of the form shown in Equation 1.4, express the electron density in terms of a set of equations where each equation involves a single electron.

\[
\left[-\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}}(r)\right] \psi_i(r) = \varepsilon_i \psi_i(r) \tag{1.4}
\]

These equations break the operator into two components, the first is the kinetic energy of the electrons and the second is the effective potential defined in Equation 1.5. The effective potential combines the external potential \(V_{\text{ext}}\), which was defined in Section 1.3.2.1, with the Hartree potential \(V_{\text{Hartree}}\) and the exchange-correlation potential \(V_{\text{XC}}\) \[41\].

\[
V_{\text{eff}}(r) = V_{\text{ext}}(r) + V_{\text{Hartree}}[\eta(r)] + V_{\text{XC}}[\eta(r)] \tag{1.5}
\]

For each Kohn-Sham equation, the Hartree potential defines the Coulomb repulsion between the single electron involved in the “current” Kohn-Sham equation and the total electron density dependent on all the electrons within the system. Since the electron being examined in the “current” Kohn-Sham equation contributes to the total electron density, the Hartree potential includes the repulsion between the electron in the “current” Kohn-Sham equation and itself within the total electron density. This “self-interaction” effect is unrealistic and is therefore corrected within the exchange-correlation potential \[41\]. The exchange-correlation will be discussed in more detail in Section 1.3.2.4.

**1.3.2.3 Iterative approach to find solutions to Kohn-Sham equations**

As may be obvious, the solution to the Kohn-Sham equations is not as simple as a set of \(N\) independent eigenvalue problems. To solve the Kohn-Sham equations the complete operator, seen in Equation (1.4), must be known. However, the \(V_{\text{Hartree}}\)
potential depends on the electron density (defined in Equation 1.6), which is found after solving the Kohn-Sham equations for the single-electron wave-functions ($\psi_i$). To overcome the circular nature of these equations, the iterative approach outlined in Figure 1-3 is taken in this work [41].

$$\eta(r) = \sum_i |\psi_i(r)|^2$$  \hspace{1cm} (1.6)

The approach begins with the definition of the initial structure and user determined parameters to set the level of accuracy for the calculation. Then an initial or trial electron density is approximated and used to approximate the operator to solve the Kohn-Sham equations to find the wave functions, $\psi_i$. With the wave functions known, the new electron density is determined from Equation (1.6). The new electron density is compared with the old electron density to determine if they are the same, with respect to a difference parameter that the user defined. If they are the same, the iteration stops, and if not then the current and previous electron densities are combined to create new electron density for the next loop. Once a self-consistent electron density is found, the structure may be evaluated to determine the total lattice energy, the forces and stresses on the material. The atomic positions may be optimized to reduce the forces and the new structure would enter the electron density optimization loop, shown in the shaded dotted inner box of Figure 1-3 again. These two loops would be repeated until the force criteria assigned by the user was meet [42]. Once the force criteria is reached the simulation stops and the final structure as well as its associated properties are reported. This corresponds to exiting the dashed box illustrated in Figure 1-3.
1.3.2.4 Exchange-correlation functional

The exchange-correlation is a potential that corrects for two main components. First the exchange portion considers the energy change of the total system if two electrons with different coordinates are interchanged. Second the correlation portion considers that the electrons are no longer being described as point particles, but as...
electronic densities. If the electrons were treated as point particles and the position of one point particle changes a second point particle will also change its position since the two are interacting with each other. When the point particles are replaced with electron densities, changing the position of one density does not have a direct influence onto the position of the second density. The exchange-correlation potential compensates for these two components and an exchange-correlation functional is used to approximate the potential.

Though the exchange-correlation functional is guaranteed by the Hohenberg-Kohn theorem, the exact form is still not known [41]. In the implementation of DFT, various approximations for the exchange-correlation functional are available to allow for the determination of an approximate solution to the Schrödinger equation. The exchange-correlation functional has been derived for uniform electron gas and is therefore the starting point of the approximations. For the calculations on the pyrochlore system presented in this dissertation, the local density approximation (LDA) has been used. For this approximation, the exchange-correlation potential at each point is set equal to the known exchange-correlation potential from the uniform electron gas at that same point. The generalized gradient approximation (GGA) was implemented in this dissertation for the SrTiO$_3$ surface calculations. GGA differs from LDA since in addition to the exchange-correlation potential depending on the uniform gas electron density it also depends on the gradient of the uniform gas electron density [41]. While both of these approximations have been effectively applied to various materials, in general LDA is more accurate on uniform systems such as bulk metals and GGA describes systems such as molecules and surfaces [42]. Therefore, LDA is used for all pyrochlore
calculations, discussed in Chapter 3 through 7 and GGA is used for the examination of SrTiO$_3$ surfaces, discussed in Chapter 8.

1.3.3 Calculation Details

All of the calculations discussed within this dissertation were performed with Vienna *Ab-initio* Simulation Package (VASP) [44-47], a plane-wave DFT code, using the projector augmented wave (PAW) pseudopotentials provided in the VASP database [48,49]. There are several user-defined parameters within VASP to aid in examining the systems. While these parameters were kept relatively unchanged throughout this dissertation, there were some changes made between the various chemical systems examined. The parameters chosen for each system will be detailed here. If a parameter is not mentioned, the VASP default was used. The parameters that were varied for the results reported in this dissertation are summarized for each system in Table 1-1.

The DFT calculations were performed within the local density approximation (LDA) [50] for all pyrochlores systems. The generalized gradient approximation (GGA) with the parameterization of Perdew *et al.* [51] was used to examine surface chemistry on SrTiO$_3$, detailed in Chapter 8. The Bi(5d, 6s, 6p), Rh(4p, 4d, 5s) Ti(3s, 3p, 3d, 4s), Ru(4p, 4d, 5s), Os(5p, 5d, 6s), Ir(5d, 6s), Pt(5d, 6s), Nb(4p, 4d, 5s), Ta(5p, 5d, 6s), Zn(4s,3d), Mg(2p, 3s), Ca(3s, 3p, 4s), Sr (4s, 4p, 5s), O(2s, 2p), and S(3s, 3p) orbitals were included as the valence electrons.

All calculations were performed at fixed volume and shape, while the atoms were relaxed until the forces were less than 0.03 eV/Å. For some of the calculations, the force was reduced even further to less than 0.001 eV/Å. However, after testing it was determined that forces as low as 0.03 eV/Å could reproduce the structure properties
within the accuracy reported here and the total energy accuracy for the calculations are equivalent, as seen in Table 1-1.

Though all atoms are free to relax in these optimized structures the crystal lattice or shape is fixed. For the simple bismuth pyrochlores, the cubic lattice constant is optimized by performing several fixed volume calculations with varying lattice constant and determining the corresponding energy versus volume profile. When compared with experimentally determined lattice constants, the DFT values are within 1 %. Once the optimized lattice constant is identified, all subsequent calculations are fixed to this value. This process was repeated after atomic displacement was identified to determine if any lattice expansion occurred.

For the complex bismuth pyrochlores, the lattice constant was fixed to the experimentally determined lattice constant at the lowest temperature reported in the literature. These lattice constants were 10.55668 Å [13] for Bi$_{1.5}$ZnNb$_{1.5}$O$_7$ (BZN), 10.54075 Å for Bi$_{1.5}$ZnTa$_{1.5}$O$_7$ (BZT), 10.5525 Å for Bi$_{1.5}$MgNb$_{1.5}$O$_7$ (BMN), and 10.529 Å for Bi$_{1.5}$MgTa$_{1.5}$O$_7$ (BMT) and 10.2301 Å for Ca$_{1.5}$Ti$_{1.5}$Nb$_{1.0}$O$_7$ (CTN) [52]. For the SrTiO$_3$, the cubic lattice constant was optimized for the bulk structure then the (100) surfaces were created based on the optimized bulk structure.

Electronic relaxation was performed with the conjugate gradient (CG) method accelerated using Methfessel-Paxton Fermi-level smearing with a Gaussian width of 0.1 eV [53] for the pyrochlores. For SrTiO$_3$, electronic relaxation was performed with a block Davidson iteration method accelerated using Fermi-level smearing with a Gaussian width of 0.1 eV [53]. A plane wave cutoff energy of 400 eV was used for all systems.
Table 1-1. Calculation details for the various simulations discussed throughout dissertation.

<table>
<thead>
<tr>
<th>System</th>
<th>Energy Cut-Off</th>
<th>Force Criteria</th>
<th>Pseudo-Potential</th>
<th>$k$-Mesh</th>
<th>Total Energy Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple pyrochlores in ideal structure (Ch. 3)</td>
<td>400 eV</td>
<td>0.001 eV/Å</td>
<td>LDA</td>
<td>6×6×6</td>
<td>0.02 eV</td>
</tr>
<tr>
<td>Simple pyrochlores in displaced structure (Ch. 3, 4, 7)</td>
<td>400 eV</td>
<td>0.001 eV/Å</td>
<td>LDA</td>
<td>3×3×3</td>
<td>0.01 eV</td>
</tr>
<tr>
<td>Simulated Annealing (Ch. 3, 4, 5, 7)</td>
<td>400 eV</td>
<td>500 steps</td>
<td>LDA</td>
<td>1×1×1</td>
<td>0.02 eV</td>
</tr>
<tr>
<td>Deficient simple pyrochlores (Ch. 5)</td>
<td>400 eV</td>
<td>0.005 eV/Å</td>
<td>LDA</td>
<td>3×3×3</td>
<td>0.02 eV</td>
</tr>
<tr>
<td>Complex Pyrochlores (Ch. 6, 7)</td>
<td>400 eV</td>
<td>0.03 eV/Å</td>
<td>LDA</td>
<td>1×1×1</td>
<td>0.02 eV</td>
</tr>
<tr>
<td>Ion Hopping (Ch. 7)</td>
<td>400 eV</td>
<td>0.05 eV/Å</td>
<td>LDA</td>
<td>3×3×3 (Bi$_2$Ti$_2$O$_7$) 1×1×1 (BZN/CTN)</td>
<td>0.02 eV</td>
</tr>
<tr>
<td>Surface Chemistry of SrTiO$_3$ (Ch. 8)</td>
<td>400 eV</td>
<td>0.03 eV/Å</td>
<td>GGA-PBE</td>
<td>8×8×1</td>
<td>0.01 eV</td>
</tr>
</tbody>
</table>
For the simple pyrochlores reported in Chapter 3, 4, 5 and 7 a 3×3×3 Monkhorst-Pack [54] mesh was used. For the complex pyrochlores reported in Chapter 6 and 7 there were a large number of configurations explored therefore only the Γ-point (1×1×1) was used for the k-mesh. A 3×3×3 k-mesh was tested for the BZN system and there was no difference among the results within accuracy reported.

These parameters were tested by performing additional calculations with higher cut-off energies (450 eV, 500 eV), finer k-mesh grids (3×3×3 for BZN, 4×4×4, 6×6×6, 8×8×8 for simple pyrochlores) and resulted in differences less than 0.02 eV in the total energy. Several calculations were performed to confirm that spin-polarization does not affect any of the results; therefore, all data reported are without spin-polarization. The generalized gradient approximation (GGA) with the parameterization of Perdew et al. [51] was tested for the pyrochlore systems and provided qualitative agreement with the results reported in Chapter 3-7. It was confirmed that the favorability of atomic displacement and lone pair formation does not depend on the functionals. For the SrTiO₃ system, the effects of the functional on the accuracy of the DFT calculations will be discussed in Section 8.2.3.4.1.

1.3.4 DFT Tools and Analysis Techniques

Additional simulation techniques will be implemented in the DFT calculations to aid in investigating these materials. These methods include simulated annealing and nudged elastic band method. In order to aid in understanding the results from these calculations throughout the dissertation, details on the techniques are provided in here. Additionally, details are provided for Bader charges and electron localization functions, which are two of the analysis tools that are used to interpret the calculations.
1.3.4.1 Simulated Annealing

Since there is no guarantee that DFT is capturing the global minima, simulated annealing was performed to probe for lower energy states that exhibit displacements of cations from their high symmetry sites. Simulated annealing is a two step process where the system is provided thermal energy for a given amount of steps and then the structure is quenched by removing all thermal energy and optimizing the structure to the final state. Both steps of the simulated annealing calculations were performed under fixed crystal shape and volume. The initial heating step was performed using *ab initio* molecular dynamics (MD) [44-47] with the relaxed ideal pyrochlore structures as the initial structures.

The MD simulations were conducted with only the Γ point (1×1×1 k-mesh) within the canonical (NVT) ensemble, with fixed number of atoms, volume, and temperature. The Nosé thermostat was used to control temperature variation from 1000 K to 300 K over 500 MD steps with a time step of 0.5 femtoseconds. Though these temperatures are not exact, by providing thermal energy to the system the atoms may sample new spatial positions and potentially overcome any energy barriers separating a local minimum from the global minimum. Unlike any other type of calculation discussed, this step is performed for only a specific number of steps and not until a force criteria is met.

After MD simulation, the system was minimized using the same approach as outlined above in Section 1.3.3 (3×3×3 mesh, CG method, etc.) and the equilibrium lattice parameter was reevaluated for the cation displaced structure. While the MD simulation is over extremely short times, it was confirmed that increasing the simulation length does not affect the final fully relaxed structure.
1.3.4.2 Nudged Elastic Band

As will be discussed in Chapter 7 and 8, it is often of interest to understand reaction pathways or minimum energy pathways between previously determined minima. DFT has been used in combination with nudged elastic band (NEB) method [55-57] to successfully identify transition states in proton transfer [58], surface diffusion [59], and surface chemistry, such as in the water gas shift reaction on copper [60]. In this dissertation NEB is used to examine the minimum energy pathway between pyrochlores with different displacement patterns in Chapter 7 and reactions intermediates in water dissociation on SrTiO$_3$ in Chapter 8.

The NEB calculations involve connecting two (previously determined) minima by a discrete number of structures, or images. These images are created by interpolating the structures between the two minima with the goal of mapping out the structural intermediates joining these stable minima along a reaction pathway. Figure 1-4 was reproduced from Ref [57] and shows a schematic of a potential energy profile between two minima, labeled initial and final. The path proposed by the interpolated structure intermediates is labeled NEB and the actual minimum energy pathway is labeled MEP.

During the NEB calculation, the two minima are fixed and each image minimizes the total energy while maintaining equal spacing along the reaction coordinate between its neighbors. This is accomplished by introducing spring forces along the band between neighboring images. The forces are detailed in the insert of Figure 1-4. The component of force perpendicular to the band is projected and minimized. This minimization should pull the initial path (labeled NEB in Figure 1-4) towards the actual MEP between the two minima.
Figure 1-4. Figure 1 from Ref [57] showing the potential energy profile between two minima labeled “initial” and “final”. The minimum energy path (MEP) as well as the nudged elastic band (NEB) path are shown between the two minima. The insert details the two components that make up the NEB force $F_{\text{NEB}}$: the spring force $F_{\parallel}$, along the tangent $\hat{t}_i$, and the perpendicular force due to the potential $F_{\perp}$. The unprojected force due to the potential $F_{\perp}$ is also shown for completeness.

One analogy to help illustrate this technique is to imagine two people by a mountain in two different valleys. A rope may be thrown from one person to the other across the mountain. The two people may slide the rope along the mountain to find the easiest path connecting them but neither person may move and the rope can stretch but will not break.

Since the images (structure intermediates) are equally spaced with respect to the reaction coordinate, the regular NEB method does not require the identification of a local saddle point. In fact, often if an even number of images is used, the saddle point will not be identified. Therefore, after the minimum energy pathway is mapped out with the regular NEB method, the climbing image approach is applied where the image with the highest energy is pushed towards the local saddle point. The saddle point or transition state structure minimizes its energy in all direction except along the elastic band. This type of minimization results in the loss of equal spacing along the reaction
pathway between neighboring images. Due to this loss of equally spaced images, it is recommended that the climbing image approach start from a converged regular NEB calculation.

1.3.4.3 Bader Charges

One of the direct benefits of using DFT to examine oxides is the prediction of the ground state electron density. Many details may be extracted from the electron density to aid in describing the nature of bonding within the oxide and the nature of bonding will impact macroscopic observation such as insulating or metallic properties.

It is known that within oxides covalent bonding may occur which would result in the sharing of electrons between cations and anions. While formal charges may be assumed for each atom type, Bader proposed a method of evaluating the electron density to assign charge density at each atom [61]. Bader identified in most molecules the charge density between atoms reaches a minimum at some distance from each atom. This results in the occurrence of a two-dimensional zero-flux surface which has the charge density minimum perpendicular to the surface. By identifying these zero-flux surfaces the method allows one to assign a Bader volume for each atom and split the charge density between two atoms [61]. This provides a way to approximate the total electronic charge of an atom by assigning the charges within the atom's Bader volume to each atom. The code of Henkelman et al. [62] was used throughout this dissertation to identify both the Bader volumes and Bader charges in various oxides.

Within DFT, atoms are assigned a specific number of electrons based on the user-defined pseudopotential. The Bader determined electronic charge may be compared with the number of electrons assigned from the pseudopotentials in order to determine the Bader charge on each atom. The deviation between the atomic Bader charges and
the formal ionic charge indicates the degree of covalency and can provide insight into the bonding nature within oxides.

1.3.4.4 Electron Localization Function

The properties observed in bismuth pyrochlores have often been connected to the highly polarizable bismuth cation with $6s^2$ lone pair of electrons on the A site [13,20,37,52,63,64]. One technique of visualizing these lone pairs is through the electron localization function (ELF), which was introduced by Becke and Edgecombe as a real space technique of mapping electrons into core, shell, bonding, and lone pair electrons based on the Pauli exclusion principle. The technique has been advanced by Savin and Silvi in an effort to provide a more quantitative description of the chemical bond [65,66]. The ELF function maps the probable distribution of electrons graphically, where a fully localized (delocalized) electron has an ELF value of 1 (0).

1.4 Objectives of Dissertation

As detailed above in Section 1.1 and 1.2, this dissertation objective is to help connect the atomic-level structure of mixed metal oxides with the macroscopically observable properties through ab initio simulations. In order to begin examining these oxides with DFT simulations, a thorough understanding of the atomic structure is necessary and outlined in Chapter 2. The pyrochlores are the main focus of this dissertation and will be detailed exclusively in Chapters 3 through 7 with the perovskite SrTiO$_3$ discussion reserved for Chapter 8. In Chapter 3 the occurrence of atomic displacements is isolated for cubic bismuth pyrochlores without cation substitution. The electronic interactions that drive atomic displacement in Bi$_2$Ti$_2$O$_7$ are further explored in Chapter 4 where sulfur is substituted on the O and O’ site to perturb the Bi-O’ and Bi-O bonding. The role of both cation and anion vacancies on the A$_2$O’ network of bismuth
ruthenate is presented in Chapter 5. Atomic displacement and cation substitutional ordering is explored in four complex pyrochlores in Chapter 6. Preliminary efforts to connect DFT simulations with dielectric relaxation in complex pyrochlores by identifying cation hopping mechanisms between equivalent lattice positions is presented in Chapter 7. The key observations from this work as well as expected future directions are summarized in Chapter 9. Background on lone pair formation is summarized in Appendix A. Additional details for the pyrochlore system not included in the body of the dissertation are discussed in Appendix B.
CHAPTER 2
CRYSTALLOGRAPHY OF PEROVSKITE AND PYROCHLORE MATERIALS

A detailed understanding of the structure, in particular the crystallographic language used to describe these structures, is critical in understanding the results presented in this dissertation. As seen in Section 1.3, understanding and generating a reasonable initial structure is also the first step for the DFT calculations. Therefore, this chapter will present a detailed introduction of the two bulk crystal structures of the materials examined in this dissertation. Given the complexity of the pyrochlore system, the simpler perovskite (SrTiO₃) system will be presented first. The examination of the perovskite bulk structure here will be useful when the surface chemistry of SrTiO₃(100) is discussed in Chapter 8.

2.1 Structure of Strontium Titanate

SrTiO₃ (STO) is a perovskite material with space group Pm₃m (number 221). The cubic bulk lattice constant is reported to be 3.90 Å from experiment [67] and 3.94 Å from DFT calculations [68]. Within the cubic structure, the eight Sr²⁺ ions occupy the cube corners, six O²⁻ ions are centered in each cube face, and one Ti⁴⁺ ion is in the body centered position, as shown in Figure 2-1.

Figure 2-1. Bulk unit cell of SrTiO₃ shown near the <100> direction.
From Figure 2-1, it can be seen that the Ti$^{4+}$ ions are octahedrally coordinated to the six O$^{2-}$ on the faces. These TiO$_6$ octahedra are aligned in the cubic structure; however, there are some reports of antiferroelectric octahedra tilting [69-71] at low temperature. Figure 2-2 shows an alternative view with the Sr$^{2+}$ centered and the twelve Sr-O bonds illustrated. Additionally, the Ti ions at the corners of the unit cell are shown in the center of each octahedron.

![Figure 2-2](image)

Figure 2-2. Sr centered bulk unit cell of SrTiO$_3$ shown near the <100> direction.

2.2 Structure of Bismuth Pyrochlores

2.2.1 Crystallography and Visualization of the Pyrochlore Structure

Ideal stoichiometric pyrochlores (A$_2$B$_2$O$_7$) are cubic with space group Fd$\overline{3}$m (number 227) and can be described as two interpenetrating networks of corner sharing BO$_6$ octahedra and corner sharing A$_4$O’ tetrahedra [10], as shown in Figure 2-3. In fact, the overall formula is typically represented as A$_2$B$_2$O$_6$O’ to distinguish the oxygen within the two networks. Figure 2-3 represents one of a multitude of perspectives of the pyrochlore structure found in the literature (see Ref. [10-14] for more extensive discussion on pyrochlore structure).
The ideal cubic pyrochlore structure has 88 atoms in its unit cell and is highly symmetric with four distinct crystallographic sites occupied by A (site 16d), B (site 16c), O (site 48f), and O’ (site 8b) atoms. The selection of these sites and differences between them will be discussed in detail below. Only two parameters are needed to completely describe an ideal pyrochlore, the lattice constant and the $x$ positional parameter of the oxygen in 48f. When defects and deficiencies are introduced further parameters are needed to describe the system.

### 2.2.1.1 Origin and cation centering in Fd3m space group

As mentioned above, ideal pyrochlores usually adopt the Fd3m space group, which has two possible origin choices at either the 8a site (origin choice 1) or the 16c.
site (origin choice 2) [72]. Origin choice 2 is more commonly used in the literature and used exclusively within this work. Within origin choice 2, the ideal sites occupied are the 16d site (0.5,0.5,0.5), 16c site (0,0,0), O anion at 48f site (x,0.125,0.125), and O’ anion at either the 8a site (0.125,0.125,0.125) or 8b site (0.375,0.375,0.375). If the larger A\(^{3+}\) cation is in the 16d (0.5,0.5,0.5) site, the configuration is termed B-centered with the smaller B\(^{4+}\) cation occupying site 16c (0,0,0) and the O’ anion at 8b (0.375,0.375,0.375).

Alternatively, in the A-centered configuration, the A cation occupies the 16c site (0,0,0) with the B cation at site 16d (0.5,0.5,0.5) and the O’ anion at 8a (0.125,0.125,0.125). Unless otherwise noted, the B-centered configuration is used in this work and, where needed, experimental works are converted to this configuration for comparison. By symmetry, only the 48f O atoms experience unbalanced forces and will therefore relax in the ideal cubic pyrochlores with the parameter x used to characterize the oxygen position. The value of x depends on the occupant of site 16c (0,0,0) and the relationship between the A- and B-centered configurations is \(x(A) = 0.75 - x(B)\) [72]. There are known bounds observed in the value of x based on the oxygen polyhedral coordination at the 48f site surrounding the A and B cations. If the oxygen ions form a regular octahedron (cube), the resulting value for x(B) would be 0.3125 (0.375).

### 2.2.1.2 Wyckoff positions in Fd\(\overline{3}\)m space group

The spatial positions termed 16d, 16c, 8b and 48f that the four ions within the pyrochlore are located are called Wyckoff positions. While Wyckoff positions are used in all space groups to aid in describing the structure, the particular labels, i.e. 16d, are unique for each space group. To further explain, the 8b site within the Fd\(\overline{3}\)m space group does not necessarily match the 8b site within space group Fd\(\overline{3}\)c. To understand
the location and particular symmetry associated with each Wyckoff position, the reader should refer to Volume A: Space group symmetry within the International Tables for Crystallography, which is available online at http://it.iucr.org/A/. The Wyckoff position labeling can immediately tell the reader the multiplicity of the site based on the number component. For example, the site 16d has a multiplicity of 16, which means by defining a single point in the crystal lattice, 15 additional equivalent sites are defined by symmetry. Therefore, based on the sites occupied in the ideal pyrochlore there are 16 Bi and 16 B cations in addition to 8 O’ and 48 O anions, thus creating the 88 atom unit cell.

2.2.1.3 Sub-network interactions in ideal pyrochlores

As mentioned above, often the pyrochlore structure is thought of as two separate sub-networks (A2O’ and B2O6); however, the two networks are not isolated from each other since the A cation is bound to oxygen ions within both networks. Within the 16d site, the larger A3+ cation is coordinated to two O’ and six O ions. Alternatively, the smaller B4+ cation is coordinated to six O ions when occupying the 16c site. The ratio of the total energy of the pyrochlore system for compositions without cation substitution is shown in Table 2-1. It can be seen that up to 17 percent of the total lattice energy is due to the interaction between the two sub-networks.

These percentages were determined by taking the total equilibrium structure and performing a single point calculation, i.e. no atomic movement was allowed, for the two sub-networks isolated from each other to provide the total energy for each sub-network. The energy due to interaction was calculated from Equation 2-1, where $E_{\text{interaction}}$, $E_{\text{total}}$, $E_{A_2O'}$, and $E_{B_2O_6}$ are the energy associated with the interaction between the two
networks, the total lattice energy, the energy of the $A_2O'$ and $B_2O_6$ sub-networks, respectively. Each energy type was scaled by the system's total lattice energy in order to determine the percent contribution.

$$E_{interaction} = \left[ \left( E_{total} \right) - \left( E_{A_2O'} + E_{B_2O_6} \right) \right]$$

Table 2-1. The percent of total lattice energy due to the $A_2O'$ and $B_2O_6$ networks, and the interaction between the two sub-networks for the six simple bismuth pyrochlores.

<table>
<thead>
<tr>
<th>% of Total Energy</th>
<th>$Bi_2Ir_2O_7$</th>
<th>$Bi_2Os_2O_7$</th>
<th>$Bi_2Pt_2O_7$</th>
<th>$Bi_2Rh_2O_7$</th>
<th>$Bi_2Ru_2O_7$</th>
<th>$Bi_2Ti_2O_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_2O'$ network</td>
<td>17%</td>
<td>16%</td>
<td>19%</td>
<td>18%</td>
<td>17%</td>
<td>15%</td>
</tr>
<tr>
<td>$B_2O_6$ network</td>
<td>69%</td>
<td>75%</td>
<td>64%</td>
<td>65%</td>
<td>70%</td>
<td>68%</td>
</tr>
<tr>
<td>Network interaction</td>
<td>14%</td>
<td>10%</td>
<td>17%</td>
<td>17%</td>
<td>13%</td>
<td>17%</td>
</tr>
</tbody>
</table>

The local structure is depicted in Figure 2-4 to help illustrate the structural effect leading to the $E_{interaction}$. In Figure 2-4a the isolated Bi and B cation environments are viewed along the [111] direction. This direction corresponds to the $O'$-$Bi$-$O'$ bonding axis. By rotating normal to this direction the same local structure is shown along the [112] direction in Figure 2-4b. This direction aids in understanding how the $Bi_2O'$ sub-network extends through the open spaces created within the $B_2O_6$ sub-network. To help visualize the system, the $Bi_4O'$ tetrahedra are shown as open, empty frames instead of filled tetrahedra, as was shown in Figure 2-3. Additionally, the $O'$ and $O$ ions are shown in orange and red, respectively. The $O$ ions that are linking the corner sharing $BO_6$ octahedra in Figure 2-4a are the six $O$ ions coordinated to the central Bi cation. The positional parameter $x$ discussed above for this Wyckoff site $(48f)$ defines the tilting of the octahedra seen in Figure 2-4b. Since the $Bi$-$O'$ bond lengths are shorter than the $Bi$-$O$ bond lengths the coordination of Bi is sometimes referred to as $2+6$. The longer $Bi$-$O$
bond lengths are necessary to satisfy the bond valence for each ion within the structure. This will be discussed further in Section 2.2.3.

(a) ![Figure 2-4. Local structure of Bi and B cations within ideal pyrochlore structure, viewed along the (a) [111] and (b) [112] direction. The key indicates each atom type and the Bi cations above and below the plane of BO₆ octahedra are distinguished for visual aid.](image)

**2.2.2 Site Symmetry**

As discussed in Section 2.2.1.2, within the Fd\̅m space group there are specific spatial positions that may be occupied by the various constituent atoms termed Wyckoff positions. The symmetry of a particular Wyckoff site helps interpret subtle changes in the overall structure due to significant changes to the local environment. This is particularly true for the case of bismuth pyrochlores. As will be discussed throughout this dissertation, atomic displacement within this material is prevalent. The site symmetry of the ideally occupied positions will be discussed here.

In the ideal position, the Bi cations have \(\bar{3}m\) symmetry, which means that along the cubic primary direction, the \(<100>\) family, there is no symmetry. There is three fold inversion symmetry along the secondary direction, the \(<111>\) family, and along the
tertiary direction, the <110> family, the Bi ions have a mirror plane. To aid in visualizing the three fold inversion the two overlapping tetrahedra in Figure 2-4 are isolated in Figure 2-5. Though a local area is isolated the three fold inversion can be visualized using the Bi ions shown in Figures 2-5a and 2-5b. Any n-fold inversion symmetry operation can be broken down into two components.

(a)  
(b)  

Figure 2-5. Site symmetry of Bi cations within ideal pyrochlore structure, viewed along the (a) [111] and (b) [112] direction.

The first component involves a counter-clockwise rotation about the axis of symmetry by 360°/n and the second is a reflection through the origin. In this case, if the ion labeled 1 is selected and rotated 120° about the [111] direction, the atom labeled 2 would be created. This component is shown as the solid (black) arrow in Figure 2-5. Then the rotation is followed by an inversion about the origin. In Figure 2-5, the center Bi may be used as a visual aid of the inversion point and this inversion is illustrated further by the dotted (green) line in Figure 2-5. Though the inversion point not
technically correct since the Bi cations are not located at the origin, inversion through the center Bi point is equivalent (visually) to inversion through the origin. Following this inversion, the Bi ion labeled 3 would be created. The selection of the first Bi ion, i.e. the Bi ion labeled 1 in Figure 2-5, is irrelevant; each Bi ion illustrated in Figure 2-5 is reproduced following this symmetry operation.

To help visualize the mirror planes along the tertiary direction (the <110> family), one plane is shown in Figure 2-5a as the dashed (blue) line. From this mirror plane the Bi ion labeled 1 would be reflected to the Bi ion labeled 2. There are two other mirror planes in Figure 2-5a that are not indicated to minimize confusion. The two additional mirrors planes would correspond to the blue line shown in Figure 2-5a rotated counterclockwise by 60° twice.

The B$^{4+}$ cations have $\bar{3}m$ site symmetry, which is the same site symmetry as the Bi cations. This should not be unexpected since above it is discussed that the selection of either a B-centered (chosen here) or A-centered configuration is possible. The origin was not altered between these two configurations, merely which ion would occupy the 16c Wyckoff position located at the origin.

The O' site symmetry is 4$\bar{3}m$ which means there is four fold inversion along the cubic primary direction, the <100> family, there is three fold rotation along the secondary direction, the <111> family, and along the tertiary direction, the <110> family, the O' ions have a mirror plane.

The O ions in the 48f site have 2.mm site symmetry which means that along the cubic primary direction, the <100> family, there is two fold rotation. There is no
symmetry along the secondary direction, the \(<111>\) family, and along the tertiary
direction, the \(<110>\) family, the O anions have a two perpendicular mirror planes.

2.2.3 Bi\(_2\)O Network

Though the entire Bi\(_2\)O’ network is not illustrated, the symmetry explain in Section
2.2.2 would extend to reproduce the full network. The Bi\(_2\)O’ network is made of corner
sharing tetrahedra and each tetrahedron is connected along the O’-Bi-O’ bonding axis,
which correspond to a direction within the \(<111>\) family.

The Bi\(_2\)O’ network is often referred to as an anti-cristobalite structure. This is
because it is structurally similar to the SiO\(_2\) \(\beta\)-cristobalite structure, which is composed
of Si centered, corner sharing SiO\(_4\) tetrahedra. In contrast, the Bi\(_2\)O’ network is
constructed by O’ centered, corner-sharing Bi\(_4\)O’ tetrahedra and is thus termed “anti”-
cristobalite. In fact, the two compounds have the same symmetry with the anions and
cations inverted, i.e. the Bi cation has the same symmetry as the O ion in the SiO\(_2\)

One benefit of the relationship between these structures is the fact that SiO\(_2\) has
been extensively studied in order to understand the dynamic disorder of the silica
tetrahedra that has been reported. It has been determined that while each tetrahedron
remains relatively regular, the corner atoms are displaced from the ideal high symmetry
sites. This type of displacement occurs due to low frequency phonons which are
referred to as rigid unit modes [73-76]. Additionally, it has been observed that the
displacements that occur in bismuth pyrochlores have been related to the dynamic
disorder observed in silica. Namely, the displacement of the Bi and O’ atoms in the
pyrochlore structure have shown similar concerted displacement as that observed in
silica, which has been termed \(\beta\)-cristobalite type displacive disorder [77].
this type of correlation is illustrated in Figure 2-6. This type of correlation is observed for some of the pyrochlores reported in this dissertation as will be discussed in Chapter 3, 5, 6 and 7.

![Figure 2-6. Local structure illustrating the $\beta$-cristobalite type displacive disorder. The Bi (tetrahedron corner) and O' (tetrahedron center) atoms are in their ideal position with the black arrows indicating direction of displacement.](image)

2.2.4 Bond Valence Model and its Application in Bismuth Pyrochlores

Often bond valence theory is used to help examine how and why ions within pyrochlore materials exhibit atomic displacement and the concept of bond valence will be used in interpreting the DFT results in both the simple and complex pyrochlores.

Bond valance model stems from Linus Pauling’s rules for ionic compounds. The first rule is that each cation within an ionic material will be surrounded by a polyhedron of anions and the shape of the polyhedron is based on the ratio of the cation to anion radii. For a complete list of critical ratios and the corresponding anion coordination, see Figure 2.21 in Ref. [78]. Pauling’s second rule says that within ionic structures, the ionic charge of each anion ($z_j$), defined in Eq. 2.2, will be (nearly) equal and opposite in charge to the sum of each cation’s (a) its bond strength ($s_i$) [79]. Where a cation’s bond
strength \( s_i \) is defined in Eq. 2.2 as its charge \( n_i \) divided by its coordination number \( k_i \) [79].

\[
z_j \approx \sum_{i=1}^{n} s_i = \sum_{i=1}^{n} \frac{n_i}{k_i} \tag{2.2}
\]

Pauling’s third and fourth rule pertain to the linking of neighboring polyhedral. Two linked polyhedral may be corner, edge, or face sharing. The most unstable is face sharing with decreased stability for cation with large charge and low coordination number. All linked polyhedral in the pyrochlore structure are corner sharing; therefore instabilities associated with face sharing are not a concern. Rule four addresses the presence of different types of cations in an ionic material. Polyhedral around cations with large charge and low coordination tend to avoid linking to other polyhedral.

The extension to bond valence sum comes from Pauling’s second law and was identified and refined by Brown [80]. The bond valence \( S_{ij} \) associated with each bond is related the bond length \( R_{ij} \) with respect to predefined constants \( R_0 \) and \( B \), which may be found in Appendix 1 of Ref. [80]. The valence \( V_i \) of an ion is equal to the sum of all bond valences associated with that ion, as defined in Eq. (2.3).

\[
V_i = \sum_{j} S_{ij} = \exp \left( \frac{R_0 - R_{ij}}{B} \right) \tag{2.3}
\]

The bond valence sum \( V_i \) should be close to the expected valence of the ion. For example, within the pyrochlore structure, the O anion in the O’ site are coordinated to four A site cations. Within ideal or simple pyrochlores without cation substitution, the A site is occupied by Bi cations. If the Bi cations and O’ anion form a perfect tetrahedron then each O’-Bi bond will contribute one quarter of the total bond valence sum for the O’ anion. As will be reported in Section 5.4.1.2, in ideal \( \text{Bi}_2\text{Ru}_2\text{O}_7 \) without atomic displacement, the Bi-O’ bond length is 2.21 Å and results in a O’ bond valence of 2.93.
which is considerably larger than the expected value of 2, this could indicate the occurrence of atomic displacements. The bond valence of the Bi cations is 3.42 which again indicates an over bonding of the Bi and O’ atoms. However, within the Ru$_2$O$_6$ network, the bond valence of the O and Ru atoms are 2.01 and 4.08, respectively, which is close to their expected valence of 2 and 4.
CHAPTER 3
FIRST-PRINCIPLES STUDY OF CUBIC BISMUTH PYROCHLORES


3.1 Introduction

As discussed in Section 2.2, ideal stoichiometric pyrochlores (A$_2$B$_2$O$_7$) are cubic with space group Fd$ar{3}$m and often described as two interpenetrating networks of B$_2$O$_6$ octahedra and A$_2$O' tetrahedra [10,15], as shown in Figure 3-1. The overall formula is typically represented as A$_2$B$_2$O$_6$O' to distinguish the oxygen within the two networks. Figure 3-1 represents one of a multitude of perspectives of the pyrochlore structure found in the literature (see Ref. [10-14] for more extensive discussion on pyrochlore structure). From extensive experimental work on the synthesis and structural characterization of cubic pyrochlores, stability fields have been proposed for allowable substitution into the A and B cation site based on simple measures such as the ratio of the cation radii size and the cation electronegativity [12,15]. The typical A (B) cation radii is around 1 (0.6) Å, but compounds with variations of up to 0.2 Å for both cations are stabilized. As the cation radii shift away from the typical values noted, the range of A/B substitutions that stabilize into a stoichiometric cubic structure decreases sharply [15]. Recent experimental work extended the stability field of allowable cation radii ratios with structures that incorporate large static atomic displacements and retain the cubic symmetry macroscopically [20,23,28]. For an excellent but somewhat dated survey of known cubic pyrochlores see Ref. [15].
Figure 3-1. The (a) ideal $A_2B_2O_6O'$ pyrochlore structure and the two interpenetrating sub-networks (b) $A_2O'$ tetrahedra and (c) $B_2O_6$ octahedra.

Recent attention is focused on bismuth based pyrochlores, where the $Bi^{3+}$ cation resides in the A site, for their potential use in capacitor and high-frequency filter applications [13,14,37]. Bismuth has a lone pair of electrons and the cation radius is 1.17 Å [81], making it one of the larger A cations found in the pyrochlore family and results in a relatively small region of stability in the structure field map [15]. In the past decade, experimental work extended this stability region, with the synthesis of
numerous complex Bi pyrochlores that incorporate substitutions of small cations in both the A and the B site. The most extensively studied of these materials is Bi$_{3/2}$Zn$_{0.92}$Nb$_{1.5}$O$_{6.92}$ (BZN) [3,10,13,16,39,82-85]. Structure and spectroscopic probes reveal a large amount of displacive disorder on both the A and O’ ions that led Withers et al. [10] to propose several ordering principles on the A$_2$O’ network for these materials based on X-ray diffraction (XRD) studies. The large displacements of the ions in BZN and other complex bismuth-based pyrochlores, such as Bi$_{3/2}$ZnTa$_{3/2}$O$_7$, Bi$_{3/2}$MgNb$_{3/2}$O$_7$, and Bi$_{3/2}$MgTa$_{3/2}$O$_7$, are critical to the observed high dielectric permittivity [38]. There is still a need to better understanding the nature of the cation displacements. Interestingly, some of the more simple bismuth pyrochlores (i.e. without cation substitution) are reported to have cation displacements. In particular, large cation displacements are reported for Bi$_2$Ru$_2$O$_7$ [20] and Bi$_2$Ti$_2$O$_7$ in both the stoichiometric [23] and defective form [28]. The simple bismuth pyrochlores are of interest from a technological viewpoint [86-88], but also allow for examining the role of cation displacements without the influence of substitutions on the cation sites.

The majority of the work on A-site bismuth pyrochlores is experimental with only a few recent density functional theory (DFT) studies of Bi$_2$Sn$_2$O$_7$ [35], Bi$_2$Ti$_2$O$_7$ [14], and Bi$_2$Ru$_2$O$_7$ [20]. The DFT work on bismuth pyrochlores is restricted to its ideal cubic structure except for the work by Walsh et al. [35] examining the low temperature, monoclinic phase of Bi$_2$Sn$_2$O$_7$. DFT can be an invaluable tool in systematically exploring and providing insight into the role of structure, composition, and atomic relaxation on the properties of pyrochlores. While the experimental work provided details of the structure of several bismuth pyrochlores, synthesis of these materials is non-trivial and often
results in O deficiencies. The density and nature of these O deficiencies can vary and sometimes were not identified in early experimental work. The presence of O deficiencies introduces additional complexities, since their influence on deviations from the cubic pyrochlores is not well understood. Comparisons between experiment and DFT calculations of ideal defect-free pyrochlores will identify deviations due to the presence of deficiencies. DFT can also help to establish connections between the electronic structure and observed structural behavior in the Bi pyrochlores. Of particular interest is the role of the Bi lone pair in the experimentally reported large cation displacement in some bismuth pyrochlores [14,20,23,28]. The lone pair of Bi is believed to create stereochemical constriction leading to more distorted structures that deviate from the ideal cubic form found in other families of pyrochlores. The reduction of this lone pair nature due to mixing of orbitals between the Bi and B-site cations is proposed to explain the lack of distorted structures in the bismuth metallic pyrochlores [26,27,89]. A systematic study of the differences in electronic structure of various bismuth pyrochlores, including insulating versus metallic, will be important in clarifying the role of lone pairs in bismuth pyrochlores.

This chapter reports DFT calculations on a range of simple cubic bismuth containing pyrochlores Bi$_2$B$_2$O$_6$O' (B = Ti, Ru, Rh, Ir, Os, Pt) that have been synthesized experimentally [15,20,23,26-28]. The above bismuth pyrochlores were initially examined within the ideal cubic pyrochlores structure. Subsequently, the potential role of cation displacements in stabilizing the cubic bismuth pyrochlores was investigated.

3.2 Calculation Details

First-principles calculations were performed with Vienna Ab-initio Simulation Package (VASP) [44-47], a plane-wave DFT code, using the projector augmented wave
(PAW) pseudopotentials provided in the VASP database [48,49]. The Bi(5d, 6s, 6p), O(2s, 2p), Rh(4p, 4d, 5s) Ti(3s, 3p, 3d, 4s), Ru(4p, 4d, 5s), Os(5p, 5d, 6s), Ir(5d, 6s), and Pt(5d, 6s) orbitals were included as the valence electrons. The DFT calculations were performed within the local density approximation (LDA) [50]. The LDA is expected to underestimate lattice constants and overestimate the strength of bonding, but has been found to be more accurate than the GGA functionals for many metal oxides [90,91] and La and Y-based pyrochlores [34]. The generalized gradient approximation (GGA) with the parameterization of Perdew et al. [51] was tested and provided qualitative agreement with the results reported in this chapter. Electronic relaxation was performed with the conjugate gradient (CG) method accelerated using Methfessel-Paxton Fermi-level smearing with a Gaussian width of 0.1 eV [53]. The ideal Fd\(\bar{3}\)m space group symmetry was tested and the bismuth pyrochlores examined in this work retain the ideal structure. Therefore, all calculations were performed at fixed volume and shape, while the atoms were relaxed until the forces were less than 0.001 eV/Å. A plane wave cutoff energy of 400 eV was used along with a 6\(\times\)6\(\times\)6 Monkhorst-Pack [54] mesh, resulting in 10 irreducible \(k\)-points. Test calculations done with a cutoff energy of 450 eV and an 8\(\times\)8\(\times\)8 mesh result in differences less than 0.02 eV/88-atom cell in the total energy, well within the error for the results presented in this chapter. Several test calculations were performed to confirm that spin-polarization does not effect any of the results; therefore, all data reported in this chapter are without spin-polarization.

As discussed in Section 2.2.1.1, pyrochlores may be defined structurally using one of two origins and with different centering options based on the selected origin. Unless otherwise noted, the B-centered configuration at origin choice 2 (see Section 2.2.1.1 for
more detail) is used in this chapter and, where needed, experimental work is converted to this configuration for comparison. By symmetry, only the 48f O atoms can relax in the ideal cubic pyrochlores, and therefore the entire structure is explained by two parameters: the cubic lattice constant and the oxygen positional parameter ($x$). The role of displacing the cations and O’ atoms from their high symmetry positions was examined and the details of these calculations are presented in Section 3.3.2.

3.3 Results and Discussion

3.3.1 Ideal Bismuth Pyrochlores

For each of the bismuth pyrochlores ($\text{Bi}_2\text{B}_2\text{O}_6\text{O}'$, $\text{B}=\text{Ti}, \text{Ru}, \text{Rh}, \text{Ir}, \text{Os}, \text{Pt}$) the equilibrium lattice parameter was determined by generating energy versus volume curves. These relaxed structures retain the ideal pyrochlore structure discussed in Section 3.2. The key structural parameters (lattice parameter and oxygen positional parameter) for the relaxed structures of all the simple pyrochlores examined are reported, along with experimental data as a function of B cation radius in Figs. 3-2 and 3-3 and in Table 3-1. The B cation radii, taken from Ref. [81] were useful in defining stability field maps for simple pyrochlores [15]. In several families of pyrochlores, the B cation radii were shown to correlate with structural, mechanical, and thermal properties when examined using empirical potentials [6,9,33,92]. Figure 3-2a shows that these DFT results for the lattice constants are within ~1% of the experimental values. Considering that LDA underestimates lattice constants, this level of accuracy is excellent and on par with previous DFT studies [34]. The lattice parameter of the $\text{Bi}_2\text{Ti}_2\text{O}_7$ system shows the largest deviation and is underestimated by 1.2%. The oxygen positional parameter shown in Figure 3-2b are within ~0.5 % of the experimental data except for $\text{Bi}_2\text{Ti}_2\text{O}_7$, which shows an error of nearly 2% overestimation.
Table 3-1. The cubic lattice constant \((a)\), oxygen positional parameter \((x)\), Bi-O’ \((d_{(A-O')})\) length, Bi-O48f \((d_{(A-O48f)})\) length, B-O48f \((d_{(B-O48f)})\) length, and B-O-B angle in order of cation radius for Bi2Rh2O7, Bi2Ti2O7, Bi2Ru2O7, Bi2Ir2O7, Bi2Pt2O7, and Bi2Os2O7. Italics represent average values, while + and * denote experimental studies conducted at room temperature and low temperature (≤12 K).

<table>
<thead>
<tr>
<th></th>
<th>(a) (Å)</th>
<th>(x) (Å/Å)</th>
<th>(d_{(A-O')}) (Å)</th>
<th>(d_{(A-O48f)}) (Å)</th>
<th>(d_{(B-O48f)}) (Å)</th>
<th>B-O-B (°)</th>
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<tr>
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<td>0.332</td>
<td>2.206</td>
<td>2.485</td>
<td>1.986</td>
<td>130.2</td>
</tr>
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<td>Experimental Bi(1.95)Rh(2)O(6.83)(+)(a)</td>
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<td>0.3317</td>
<td>2.2249</td>
<td>2.508</td>
<td>2.001</td>
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<tr>
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<td></td>
</tr>
<tr>
<td>This Work</td>
<td>10.230</td>
<td>0.3244</td>
<td>2.213</td>
<td>2.547</td>
<td>1.96</td>
<td>134</td>
</tr>
<tr>
<td>Experimental Bi(2)Ti(2)O(7)(+)(b)</td>
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<td>0.3187</td>
<td>2.289</td>
<td>2.559</td>
<td>1.964</td>
<td>137.5</td>
</tr>
<tr>
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<td>0.3187</td>
<td>2.277</td>
<td>2.637</td>
<td>1.9655</td>
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<td></td>
</tr>
<tr>
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<td>2.209</td>
<td>2.509</td>
<td>1.977</td>
<td>131.8</td>
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<td>2.55</td>
<td>1.98</td>
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</tr>
<tr>
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<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>This Work</td>
<td>10.250</td>
<td>0.3312</td>
<td>2.219</td>
<td>2.505</td>
<td>1.994</td>
<td>130.6</td>
</tr>
<tr>
<td>Experimental Bi(1.9)Ir(2)O(6.8)(+)(e)</td>
<td>10.3256</td>
<td>0.3299</td>
<td>2.236</td>
<td>2.534</td>
<td>2.003</td>
<td>131.4</td>
</tr>
<tr>
<td><strong>Bi2Pt2O7</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>2.239</td>
<td>2.519</td>
<td>2.018</td>
<td>129.9</td>
</tr>
<tr>
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<td></td>
<td></td>
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</tr>
<tr>
<td><strong>Bi2Os2O7</strong></td>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
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<td>0.3268</td>
<td>2.219</td>
<td>2.536</td>
<td>1.976</td>
<td>133</td>
</tr>
<tr>
<td>Experimental Bi(2)Os(2)O(7)(f)</td>
<td>10.338</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

\(a\)Ref. [27]; \(b\)Ref. [23]; \(c\)Ref. [28]; \(d\)Ref. [20]; \(e\)Ref. [26]; \(f\)Ref. [15]
Bi$_2$Ti$_2$O$_7$ falls outside the stability field predicted based on the ratio of cation radius, but was recently synthesized with and without O’ defects [23,28]. Diffraction studies showed that bismuth and the O’ atoms displace in the Bi$_2$Ti$_2$O$_7$ pyrochlore [23,28]. The differences in the structural parameters between these DFT calculations and experimental results for Bi$_2$Ti$_2$O$_7$ were attributed to the Bi cation displacement.

Figure 3-2. The dependence of the (a) cubic lattice constant and (b) the oxygen positional parameter on the B$^{4+}$ cation radius as determined by DFT (square) and experiment (triangle) for Rh [27], Ti [23,28], Ru [20], Ir [26], Pt [15], and Os [15]. The A-centered configuration oxygen positional parameter values reported for Bi$_2$Ti$_2$O$_7$ [23,28] are converted to the B-centered configuration value (see Section 3.2. for discussion on A versus B-centered configuration). The dashed lines drawn between the DFT values included as a visual aid. Note that Ir and Pt have the same ionic radius of 0.625 Å.

A recent study of defective Bi$_2$Ru$_2$O$_7$ [20] also reported Bi displacements with small displacement of the oxygen in the 8b site. For Bi$_2$Ru$_2$O$_7$, a large deviation for either the lattice parameter or the x positional parameter was not found between the DFT results with no cation displacements and the experimentally reported structure with cation displacements [20]. The role of Bi cation displacement in the bismuth pyrochlores is examined directly in Section 3.3.2.
Excluding Bi$_2$Ti$_2$O$_7$, the DFT results for both lattice parameter and oxygen displacement parameter do not show any systematic correlation to B cation radii. It is important to stress the DFT results follow the same trends as the experimental data. Barker et al. found that $x$ increases with increasing B$^{4+}$ cation radius for various pyrochlores [93]. As shown in Figure 3-2a, this simple relationship does not hold over the entire range of bismuth pyrochlores, since the oxygen positional parameters for Rh and Os have an inverse relationship with respect to the B cation radii. A relationship between the B cation radii and cubic lattice constant has not been explicitly noted in literature, but Minervini et al. observed a strong linear relationship between lattice parameter and A cation radii for several families of B cation pyrochlores [92]. A similar trend observed for some of the bismuth pyrochlores (see Figure 3-2a), has some clear contradictions. Ir and Pt have the same cation radii but different lattice constants and the Os system has exactly the same lattice constant as Ir despite the larger cation radii. The structural parameters were plotted with electronegativity and other definitions of the cation radius with no simple trends observed, indicating the bonding in the bismuth based pyrochlores may be more complex than other pyrochlore families. As will be shown in Section 3.3.3, when the electronic structure of these pyrochlores is examined, there is a large degree of B cation dependent covalency in the bismuth pyrochlores. The lack of a relationship between structure and cation radii can be attributed to the covalent interactions and a similar observation was made in a recent DFT study of lanthanum and yttrium based pyrochlores involving the polarizable Sn cation [34]. It is worthwhile to note that the lattice constant for Bi$_2$Ti$_2$O$_7$ falls in a similar region to the other bismuth pyrochlores with corresponding cation radii. Kennedy noted the larger lattice constants
associated with the insulator (Ti and Sn) versus metal (Rh, Ru, and Ir) bismuth pyrochlores [27]. The “ideal” DFT calculations (i.e. no cation displacements) indicate that the larger lattice constant of the insulating bismuth pyrochlores (Ti and Sn) is related to the inclusion of cation displacements within these structures. As is discussed in the next section, the inclusion of atomic displacement dramatically changes the lattice constant of Bi$_2$Ti$_2$O$_7$.

The relevant bond lengths for the pyrochlore structure from DFT and experiment are presented in Figure 3-3. Overall both Bi-O and Bi-O’ bond lengths compare well with experimental data, but as with the lattice constant and oxygen positional parameter there is a larger difference in the Bi$_2$Ti$_2$O$_7$ system. For the Bi$_2$Ti$_2$O$_7$ system, the average experimental Bi-O$_{48}$ bond length compares very well, even with the exclusion of bismuth displacement. In the experimental study, the Bi-O’ bond length for Bi$_2$Ti$_2$O$_7$ is slightly larger than that observed in other bismuth pyrochlores. Since the Bi displacement is perpendicular to the O’-Bi-O’ chains, the Bi-O’ bond length lengthens by this displacement. The values for the bond lengths of B-O$_{48}$ compare well with experimental data for all the systems considered.

Though not shown in Figure 3-3, the bond angles in all six bismuth pyrochlores compare well to experimental values, but once again Bi$_2$Ti$_2$O$_7$ shows the largest deviation. The B cation to O to B cation bond angles are reported in Table 3-1 and compared with available experimental data. Overall, the structural parameters shown in Figs. 3-2 and 3-3 compare well with available experimentally data indicating that DFT accurately captures the structural relaxation in the simple bismuth pyrochlore systems, at least for systems without large cation displacements observed.
3.3.2 Bismuth Pyrochlores with Atomic Displacement

The role of cation displacements must be examined to address the issue of the large deviations observed for Bi$_2$Ti$_2$O$_7$ relative to the other bismuth pyrochlores. Experimentally, it is known that the bismuth ions displace from their ideal crystallographic site for some simple bismuth pyrochlores [20,23,28]. Due to the symmetry of the initial structure, the Bi atoms cannot displace during relaxation; only the O48f atoms have non-zero forces at the initial structure. Therefore, it is possible that all of the relaxations are actually sitting on a saddle point with respect to displacements of the Bi atoms. Ideally, the phonon modes in the pyrochlore structure would be explored to identify any soft modes, but with the large unit cell these calculations are computationally expensive. Instead, a simpler approach was used to investigate the role of bismuth displacement within these pyrochlores. For each Bi pyrochlores, simulated

![Figure 3-3. Bond lengths for Bi-O', Bi-O48f, and B-O48f as a function of cation radius as determined by DFT (dark blue) and experiment (light orange) for Rh [27], Ti [23,28], Ru [20], Ir [26], Pt [15], and Os [15]. The lines drawn between the values included as a visual aid. Note that Ir and Pt have the same ionic radius of 0.625Å.](image-url)
annealing was performed, beginning with the relaxed structures found in Section 3.3.1, with the volume fixed using \textit{ab initio} molecular dynamics (MD) \cite{44-47} (see Section 1.3.4.1 for additional details). This approach forces the Bi, B cations, and O’ ions out of their zero-force crystallographic sites. The simulated annealing consisted of MD simulations within the canonical (NVT) ensemble, with fixed number of atoms, volume, and temperature. The Nosé thermostat was used to control the temperature variation from 1000 K to 300 K over 500 MD steps with a time step of 0.5 femtoseconds. While the simulated annealing procedure is over extremely short times, after 100 MD steps the atoms displace from their high symmetry sites indicating that the number of steps is sufficient to accomplish the primary goal. Due to the loss of symmetry within these displaced configurations, the \textit{ab initio} MD was performed with only the $\Gamma$ point for the \textit{k}-mesh. After simulated annealing, the system was minimized using the same approach as outlined in Section 3.2 except a $3\times3\times3$ \textit{k}-mesh (14 irreducible \textit{k}-points) was used in place of the $6\times6\times6$ \textit{k}-mesh. Comparisons made in this section between displaced and undisplaced structures are from calculations using the $3\times3\times3$ mesh and the decrease in \textit{k}-mesh was confirmed not to affect any of the conclusions.

Table 3-2 shows the energy change due to cation displacement and the average atomic displacements from the ideal positions of the Fd\textbar3$m$ cubic pyrochlore structure for all the bismuth pyrochlores examined. Similar values for the atomic displacement reported from experimental studies of $\text{Bi}_2\text{Ti}_2\text{O}_7$ and $\text{Bi}_2\text{Ru}_2\text{O}_7$ are also included in Table 3-2. In these calculations, only one system, $\text{Bi}_2\text{Ti}_2\text{O}_7$, showed cation displacement improved the thermodynamic favorability by an appreciable amount of energy (0.097 eV/Bi cation). The initial simulated annealing step outlined above is performed at the
equilibrium volume identified for the ideal pyrochlore structure, but the cation
displacement may be coupled to the system volume. To ensure the identification of a
global minimum energy structure, the volume of the structure incorporating the cation
displacement was reoptimized by examining energy versus volume curves for the
displaced structure. The volume optimization was performed for only the Bi$_2$Ti$_2$O$_7$, since
it is the only structure that shows any significant cation displacement. An increase in
lattice parameter from 10.23 to 10.34 Å was found and improved thermodynamic
favorability by 0.028 eV/Bi atom. With the optimized displaced structure, the DFT lattice
parameter of 10.34 Å for Bi$_2$Ti$_2$O$_7$ compares well with experimental values of ~10.36 Å.
The volume increase corresponding with the asymmetric structure of the displaced
Bi$_2$Ti$_2$O$_7$ is due to the steric effects of the lone pair. Similar increases in volume occur
for the transition of rocksalt to litharge for PbO and SnO [94]. The total energy change
from the ideal configuration to the volume optimized displaced structure for Bi$_2$Ti$_2$O$_7$ is
0.125 eV/Bi atom. This magnitude of energy change due to cation displacement in
Bi$_2$Ti$_2$O$_7$ is on par with the energy change of 0.27 eV/Bi atom reported by Walsh et al.
for Bi$_2$Sn$_2$O$_7$ to change from the ideal cubic pyrochlore to the monoclinic ground state
structure [35].

The bismuth pyrochlores examined in this chapter were confirmed to retain the
ideal cubic structure in agreement with all the experimental evidence. The similarity
between the energy associated with cation displacement in Bi$_2$Ti$_2$O$_7$ versus a change in
structure in Bi$_2$Sn$_2$O$_7$ indicates that both are feasible mechanisms for Bi-based
pyrochlores to reduce the stereochemical effects of the Bi lone pair. The more complex
structural change observed in Bi$_2$Sn$_2$O$_7$ is likely due to additional stereochemical effects
from the Sn atom in the B site. The other bismuth pyrochlores have a different mechanism in reducing the lone pair nature of the Bi cation based on the hybridization between the Bi 6s and B cation d orbitals. The details of the electronic structure differences between the metal bismuth pyrochlores and Bi₂Ti₂O₇ discussed in Section 3.3.3.

Table 3-2. The energy change and average displacement magnitudes of simple pyrochlores after simulated annealing with respect to the ideal structure is shown. (Positive value of energy corresponds to increasing thermodynamic favorability.) Systems ordered in increasing energy with the lattice constant and oxygen positional parameter included. Bi₂Ti₂O₇ with volume optimized represents average values from ten different configurations.

<table>
<thead>
<tr>
<th></th>
<th>Energy Change</th>
<th>Lattice Constant</th>
<th>Average Displacements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(eV/Bi)</td>
<td>(Å)</td>
<td>Bi (Å)</td>
</tr>
<tr>
<td>Bi₂Pt₂O₇</td>
<td>9.5E-04</td>
<td>10.345</td>
<td>0.332</td>
</tr>
<tr>
<td>Bi₂Rh₂O₇</td>
<td>9.5E-04</td>
<td>10.190</td>
<td>0.332</td>
</tr>
<tr>
<td>Bi₂Os₂O₇</td>
<td>9.5E-04</td>
<td>10.250</td>
<td>0.327</td>
</tr>
<tr>
<td>Bi₂Ru₂O₇</td>
<td>0.001</td>
<td>10.205</td>
<td>0.329</td>
</tr>
<tr>
<td>Bi₂Ir₂O₇</td>
<td>0.002</td>
<td>10.250</td>
<td>0.331</td>
</tr>
<tr>
<td>Bi₂Ti₂O₇</td>
<td>0.097</td>
<td>10.230</td>
<td>0.324</td>
</tr>
<tr>
<td>volume</td>
<td>0.146 ± 0.009</td>
<td>10.340</td>
<td>0.324</td>
</tr>
<tr>
<td>optimized</td>
<td>Bi₂Ti₂O₇</td>
<td></td>
<td>0.38</td>
</tr>
<tr>
<td>Bi₁.₈₇Ru₂O₆.₉₀₃&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-</td>
<td>10.27</td>
<td>0.327</td>
</tr>
<tr>
<td>Bi₂Ti₂O₇&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-</td>
<td>10.359</td>
<td>0.431</td>
</tr>
<tr>
<td>Bi₁.₇₄Ti₂O₆.₆₂&lt;sup&gt;c&lt;/sup&gt;</td>
<td>-</td>
<td>10.357</td>
<td>0.431</td>
</tr>
</tbody>
</table>

<sup>a</sup>Ref. [20]; <sup>b</sup>Ref. [23]; <sup>c</sup>Ref. [28]

Table 3-2 also shows that although there is displacement in all six of the bismuth pyrochlores, with the exception of Bi₂Ti₂O₇, the average magnitude of these displacements are less than ∼0.05Å. This result agrees with available experimental observations except for Bi₂Ru₂O₇, where a Bi displacement of 0.16 Å has been reported.
The differences between DFT and experiment for the Bi$_2$Ru$_2$O$_7$ system are addressed in Section 3.3.2.2. While the general features of the displacements found in Bi$_2$Ti$_2$O$_7$ are similar to experiment, there are important differences which are discussed in detail below.

3.3.2.1 Atomic displacement in Bi$_2$Ti$_2$O$_7$

Two experimental studies of Bi$_2$Ti$_2$O$_7$ have been reported, with their main results for the structure reproduced in Table 3-2 [23,28]. The earlier study synthesized Bi$_2$Ti$_2$O$_7$ with A$_2$O’ network deficiency [28], but subsequently Hector et al. demonstrated that Bi$_2$Ti$_2$O$_7$ can be synthesized in stoichiometric cubic form [23]. These two studies will be referred to as deficient and stoichiometric. Both studies analyzed the structure with X-ray and neutron powder diffraction and confirmed to be cubic pyrochlores in the Fd$ar{3}$m space group. The experimental work on stoichiometric Bi$_2$Ti$_2$O$_7$ reports structural details from X-ray diffraction at both room temperature and 2 K. Since the DFT calculations are at 0 K, the low temperature experimental data is used for comparison. Initial attempts to fit the diffraction data using the ideal pyrochlores structure resulted in large thermal parameters in both the stoichiometric and deficient studies, which indicates static displacements in the system [23,28]. Both studies saw the (422) reflection within the X-ray diffraction data collected, which is not possible in the ideal pyrochlore structure with isotropic atoms occupying the ideal $a$, $b$, $c$, $d$, or $f$ sites of the space group and only becomes possible if the atoms are anisotropic or occupy the $e$, $g$, $h$, or $i$ positions [13]. Incorporation of static displacements of Bi dramatically improved the fit to the diffraction data and reduced the thermal parameters to plausible values [23,28]. Hector et al. still found high O’ thermal parameters in the stoichiometric system, which were reduced by
the incorporation of static displacements in a fraction of the O’ atoms. Both studies reported no significant static displacements in the B2O6 network. Below the three main features of the Bi2Ti2O7 structure (Bi cation displacement, O’ displacement, and the B2O6 network) will be discussed in detail and compared with the two experimental studies.

While both experimental studies find large Bi cation displacement, they differ in the details of the resulting displaced structure. Moreover, the stoichiometric system requires the additional O’ displacement discussed above. It is important to stress that establishing the details of the static displacements experimentally is non-trivial and multiple possibilities may be indistinguishable. DFT results can assist in determining the significance of the particular displacements reported in the experiments. A comparison between the DFT results and the experiment indicates the same general features of large Bi cation displacement and smaller displacements in the other atoms. Before the details of the Bi cation displacement are discussed it is helpful to examine the ideal local environment around the Bi cation shown in Figure 3-4. Two views of the bonding network are shown, one perpendicular to and one along the O’-Bi-O’ chains. The Bi cation is in a scalenohedral cage with two O’ atoms and six O48f atoms at the edges. The six O48f atoms form a puckered ring around the Bi cation outlined in black in Figure 3-4, with three slightly above and three slightly below the Bi atom.

Both experimental studies examined several different possible Bi cation displacements. The best fit to the diffraction data for the stoichiometric and deficient Bi2Ti2O7 was Bi in the 96g and 96h crystallographic site, respectively [23,28]. There are six equivalent positions around the Bi cation for both the 96g (x, x, z) and 96h (0, y, -y)
sites as illustrated in Figure 3-4. The assumption is that the Bi cation displaces randomly to one of these six equivalent sites, which when averaged over the bulk material results in an average ideal bulk pyrochlore structure.

(a)  
(b)

Figure 3-4. The ideal puckered ring (outlined in black) created by the six O48f (labeled O) atoms surrounding Bi (green) at site 16c with O’ (tan) at 8a shown: (a) perpendicular to and (b) along the O’-Bi-O’ chains. Dark red is used to distinguish the O48f atoms slightly below Bi. Small ions represent the six 96g(x, x, z) sites (light gray) and the six 96h(y, -y, 0) sites (dark blue) for Bi atom displacement.

The 96g(x, x, z) site brings the Bi closer to one of the six O48f atoms within the pucker ring and the displacement occurs along the direction of the Bi-O48f bond (see Figure 3-4b), while the 96h(0, y, -y) site involves a displacement between two of the six Bi-O48f bonds. Hector et al. note that the fitting quality between the 96g and 96h sites results in only a small difference and these two sites may be indistinguishable within the diffraction data.
Figure 3-5. The Bi bonding networks for the two experimental studies with the six O48f (red) atoms surrounding the Bi sites for the stoichiometric case at 96g(x, x, z) (light gray) [23] and the deficient case at 96h(y, -y, 0) (dark blue) [28], and O' (tan) at 8b shown: (a) perpendicular to and (b) along the O'-Bi-O' chains. Only one of the six equivalent sites shown for both 96g and 96h along with the bond lengths in Å (light gray for 96g and dark blue for 96h) between these two sites and the six O48f and the two O'. Dark red used to distinguish the O48f atoms slightly below Bi.

The main differences between Bi occupying 96g and 96h Wyckoff sites can be seen within the altered Bi-O48f and Bi-O' bonding networks shown in Figure 3-5. The ideal Bi-O48f bonding network, seen in Figure 3-4, has six equal bond lengths. For the ideal Bi$_2$Ti$_2$O$_7$ structure determined with DFT (see Section 3.3.1), a lattice constant of 10.23 Å and an oxygen positional parameter of 0.324 was found, which corresponds to a Bi-O48f bond length of 2.55 Å. There will be four or three unique Bi-O48f bond lengths if the Bi occupies the 96g or 96h site respectively, as seen in Figure 3-5b.

Here, Figure 3-5b shows the bonding network along the O'-Bi-O' chains for both the stoichiometric and deficient experimental structures [23,28]. Additionally, the site 96h displaces the Bi perpendicular to the O'-Bi-O' chains resulting in equal Bi-O' bond lengths, while the 96g site is not directly perpendicular resulting in two different bond lengths.
lengths as illustrated in Figure 3-5a. The details of the refined crystallographic parameters for Bi$_2$Ti$_2$O$_7$ from the two experimental studies along with these DFT results are reported in Table 3-3.

Table 3-3. A comparison of the crystallographic parameters of Bi$_2$Ti$_2$O$_7$ obtained from two experimental studies [23,28] and the results from simulated annealing at a lattice constant of 10.34 Å. The experimental temperatures differed with + and * denoting room temperature and low temperature (≤12 K), respectively.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
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<th>$y/b$</th>
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</tr>
</thead>
<tbody>
<tr>
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<td>0.0167</td>
<td>-0.0357</td>
</tr>
<tr>
<td>Ti</td>
<td>16$d$</td>
<td>1/2</td>
<td>1/2</td>
<td>1/2</td>
</tr>
<tr>
<td>O</td>
<td>48$f$</td>
<td>1/8</td>
<td>1/8</td>
<td>0.43128</td>
</tr>
<tr>
<td>O'(1)</td>
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<td>1/8</td>
</tr>
<tr>
<td>O'(2)</td>
<td>32$e$</td>
<td>0.215</td>
<td>0.215</td>
<td>0.215</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>$x/a$</th>
<th>$y/b$</th>
<th>$z/c$</th>
</tr>
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<tbody>
<tr>
<td>Bi</td>
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<td>0.97255</td>
</tr>
<tr>
<td>Ti</td>
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<td>O</td>
<td>48$f$</td>
<td>1/8</td>
<td>1/8</td>
<td>0.43126</td>
</tr>
<tr>
<td>O'</td>
<td>8$a$</td>
<td>1/8</td>
<td>1/8</td>
<td>1/8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>$x/a$</th>
<th>$y/b$</th>
<th>$z/c$</th>
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</thead>
<tbody>
<tr>
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<td>0.97582</td>
</tr>
<tr>
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<td>0.01451</td>
<td>0.96615</td>
</tr>
<tr>
<td>Bi</td>
<td>192$i$</td>
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<td>0.01934</td>
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</tr>
<tr>
<td>Ti</td>
<td>192$i$</td>
<td>0.49275</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>O</td>
<td>48$f$</td>
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<td>1/8</td>
<td>0.4256</td>
</tr>
<tr>
<td>O'</td>
<td>192$i$</td>
<td>1/8</td>
<td>0.12984</td>
<td>0.13467</td>
</tr>
</tbody>
</table>

Comparisons between experiment and the DFT results for displaced Bi$_2$Ti$_2$O$_7$ must be qualified due to the restricted system size in the DFT calculations. The DFT calculations are performed on one unit cell with periodic boundary conditions and therefore will not include the full set of all possible displacements sampled in a real crystal. To ensure the conclusions about Bi cation displacement from DFT are valid, ten
distinct simulated annealing and/or relaxation runs were performed at the optimized Bi$_2$Ti$_2$O$_7$ lattice parameter of 10.34 Å. In addition to annealing from the ideal structure with Bi at site 16c, similar runs were performed on structures with small random initial displacements (-0.005 Å to 0.005 Å) on the Bi cations. Obviously, ten runs will not result in the appearance of all possible displacements, but as discussed below the observed displacements in the DFT calculations can be grouped into specific site types.

The relaxed Bi$_2$Ti$_2$O$_7$ structures were modified by shifting Bi atoms into other equivalent displacement sites and reoptimized the structure. Stability of such structures gives confidence the site types identified in these DFT calculations are fully occupied. For example, if Bi relaxing to a 96g site is observed, then occupation of all six possible displacements into a 96g site in the real crystal is expected. Differences between the energy of the 10 optimized structures are negligible (less than 0.003 eV/Bi cation). The similarity in energy between the relaxed structures and the ability to identify additional equivalent displacements indicates that if a large number of simulations were performed or at a larger system size, all the equivalent sites would appear with equal probability. Correlation among the atomic displacements in Bi$_2$Ti$_2$O$_7$ is discussed at the end of this section.

From the ten DFT simulations an average Bi cation displacement of ~0.38 ± 0.02 Å is found, which again is in good agreement with the experimental values of 0.43 (0.38) Å in the stoichiometric (deficient) system (see Table 3-2) [23,28]. Within the DFT study it is found that the bismuth cation displaces to both the 96g and the 96h sites in addition to the 192i(x, y, z) site (see Table 3-3). The displacements were determined by comparing the final relaxed positions for bismuth in each simulation with the initial ideal
configuration and binned the displacement magnitudes in 0.05 Å intervals. Figure 3-6 illustrates each of the three sites observed in these DFT calculations for the Bi displacement, including the six equivalent 96\(h\) sites in Figure 3-6a, the six 96\(g\) sites in Figure 3-6b, and the twelve 192\(i\) sites in Figure 3-6c.

![Diagram of Bi displacement sites](image)

Figure 3-6. The (a) 96\(h\), (b) 96\(g\), and (c) 192\(i\) displacement sites of the Bi cations observed from simulated annealing DFT of Bi\(_2\)Ti\(_2\)O\(_7\). The two O’ atoms included for orientation and all equivalent Bi displacement sites shown with one labeled.

The DFT results present a different scenario for Bi displacement than both the stoichiometric and deficient experimental results. Both experimental studies note that the 96\(g\) and 96\(h\) sites may be indistinguishable since they overlap to a great extent. The fitting quality to the experimental diffraction data in switching between the 96\(g\) and 96\(h\) sites was reported to be minimal with a \(\chi^2\) of 4.83 and 4.86 for the 96\(g\) and 96\(h\) sites, respectively [23]. DFT was used to probe whether there is a detectable difference between the two experimental models. Beginning with the experimentally determined crystallographic structures, the energetics of the two experimental structures were examining at the experimental lattice constants using the structure optimization method detailed in Section 3.2. There was no discernible difference in the energetics of the two
starting structures, which further indicates that these two crystallographic sites are likely both occupied in the real Bi$_2$Ti$_2$O$_7$ crystal. From the literature, neither experimental study examined the possibility of multiple displacement sites. It would be worthwhile to revisit the experimental data and evaluate the fit to the diffraction data for a model incorporating the 96g, 96h, and 192i displacement sites as predicted by DFT. It is suspected that the quality of the fit between the two experimental models and the DFT prediction will be indistinguishable with the diffraction data, and other more precise probes of the Bi$_2$Ti$_2$O$_7$ system will be needed to resolve this issue. Specifically, the use of infrared spectroscopy could identify any mode splitting of the Bi-O' mode, as seen in complex bismuth-based pyrochlore [38].

The issue of O' displacement is now addressed, where there is also a substantial difference between the two experimental studies. The deficient structure study fixed the O' occupation and therefore the O' anions do not undergo any displacement. Although the isotropic thermal parameter for O' was larger than that of the other atoms, it remained reasonable at 0.02 Å$^2$ [28]. In the stoichiometric case, Hector et al. present a structural model with less than 100% occupation at the ideal site. They confirmed there were no O' deficiencies and the initial model with no O' displacement resulted in a relatively large isotropic thermal parameter at ~0.05 Å$^2$ indicating disorder on this site [23]. Instead they found the best fit to the diffraction data when the O' occupied one of two sites; the ideal 8a site at 90% site occupancy and the 32e (x, x, x) at 10% site occupancy. Displacement to the 32e (x, x, x) site would cause the O' to move from its center position between four Bi cations toward two and simultaneously away from two of the Bi cations, resulting in two different bond lengths. The magnitude of the O'
displacement, for the 10% of O' atoms that displace, determined was quite large at 0.15 Å (see Table 3-2 for details of the structure). While the displacement of only 10% of the O' atoms in the stoichiometric system was selected based on ideal site occupation, and it is difficult to find a plausible driving force for such a selective mechanism. Though it is assumed that they examined models with 100% displacement of O', they did not report the quality of such models [23]. Similar to the stoichiometric system, O' ion displacement was observed in the DFT calculations, though the average magnitude of displacement was smaller at 0.11 ± 0.01 Å as compared to 0.15 Å [23] and the displacement occurred at every O' site unlike the 10% reported in the experimental study. In a single unit cell there are eight O' atoms and within each of the ten simulations, the initial position was at the ideal 8b site. Within this chapter, every O' ion displaces by approximately the same magnitude and in the same direction within one simulation. In the DFT relaxed structures, the displaced O' do not occupy the 32e site seen within the stoichiometric study. Instead, all of the displacement vectors of the O' atoms belong to the < 0.1, 0.05, 0.0 > family, resulting in O' occupying the 192i site (see Table 3-3). To illustrate the single displacement vector of all eight O' ions within the unit cell of one simulation, the relaxed O' ions are shown in Figure 3-7 with Bi displacement sites identified along with the 16c and 8b ideal sites. With the [110] direction indicated in Figure 3-7, it can be seen that the O' displaced ions follow the same vector within one unit cell and there appears to be a relationship between the O' and Bi displacements further discussed below. This O' directional displacement is consistent with other complex bismuth-based pyrochlores refinement, but in those systems the O' displacement is along the [110] direction [13].
The occurrence of O’ anion displacement coincides with Bi cation displacement in Bi₂Sn₂O₇ [95], Bi₂Ru₂O₇ [20], and Bi₂Ti₂O₇ [23]. The difference in nature and magnitude of O’ displacement between these structures depends on the B₂O₆ network. Even though the O’ displacement within this work differs from the experimental works for simple bismuth pyrochlores, the identification follows the coupling of O’ displacement and Bi cation displacement.

![Figure 3-7. The Bi-O’ bonding network with the 8a site (tan), the displaced O’ (dark red), the 16c site (light blue) and the 96g, 96h, and 192i Bi displacement sites (dark green) determined in all ten simulated annealings. The bonding network direction provided indicates the displaced sites appear correlated along the [110] direction, with an alternating of the orientation with respect to the ideal site, either in front of or behind.](image)

The discussion on the structure of Bi₂Ti₂O₇ is concluded with the B₂O₆ network. In both experimental studies the oxygen at the 48f site was unaffected, and both determined an oxygen positional parameter of 0.3187. Since there was no change in the oxygen positional parameter and Ti atoms were at site 16d in the experimental
models, the Ti-O\textsubscript{48f} bonding remained completely unaffected by the Bi cation displacement. By contrast, within this chapter the Ti atoms showed displacement with an average of 0.07 ± 0.02 Å, but did not have a significant effect on the average Ti-O\textsubscript{48f} bond length found at 1.965 Å, matching both experimental studies. Although the average bond length found in this study was unaffected by displacement, the distribution of Ti-O\textsubscript{48f} bond lengths observed within each TiO\textsubscript{6} octahedron ranged from 1.88 to 2.07 Å, with the average in each octahedron equal to 1.965 Å. The small average magnitude of the Ti displacement seen in this study may indicate that these displacements could be absorbed by the thermal parameters experimentally and without direct probing may be overlooked.

Based on the observations made within this study, reexamination of the experimental structural parameters with emphasis paid on the site(s) of Bi and any potential displacement of the Ti cations could provide further insight into this system. Since this study identified multiple Wyckoff sites occupied by displaced Bi cations, it would be beneficial to determine if this is also observed within the experimental crystal and if there is any short range ordering of displacement sites. The DFT results indicate that the multiple displacement positions around the ideal Bi site are energetically equivalent, but the barriers to hop among these displacement sites have not been addressed in this chapter (see Chapter 7 for details). This hopping mechanism has been proposed in bismuth-based pyrochlores by Nino et al.[96], Levin et al.[13], Vanderah et al.[12], and Somphon et al. [77] for other pyrochlore compounds exhibiting cation displacement. Future DFT studies probing the potential energy surface of
bismuth cation hopping between these displacement sites will assist in understanding of the dielectric properties of these materials.

Up to this point, the structure of Bi$_2$Ti$_2$O$_7$ has concentrated on terms of an average structure where it is assumed that the displacements discussed occur randomly but with equal probability. The experimental studies could not probe any correlation within the atom displacements in Bi$_2$Ti$_2$O$_7$, since they only have information on the average structure. Bismuth- based pyrochlores have recently been studied as “spin-ice” pyrochlores, where the tetrahedron bonding of O’ ions around the central Bi cation are compared to the ice equivalent of oxygen- centered tetrahedrons with two hydrogen ions covalently bonded at a smaller length and two more distantly bonded by hydrogen bonding [14]. Structural analysis of these complex pyrochlores has shown short-range order [10]. Such characteristics are mirrored within the observed displacements of bismuth in Bi$_2$Ti$_2$O$_7$. Both the Bi displacement and O’ displacement seen within this study follow the “two-long, two-short” bonds, resulting in each tetrahedron of BiO’$_4$ comprised of, on average, two bonds at 2.2 Å and two bonds at 2.3 Å. A relationship between the Bi displacement sites can be seen in Figure 3-7 with the displacement site alternating between in front of or behind the ideal 16c site along the [110] direction. It is found that within any given simulation these two alternating sites belong to two of the three Wyckoff sites identified for Bi displacement (i.e. 96g, 96h, 192i), occurring in pairs of either (96g and 96h) or (96g and 192i). It is stressed that for no individual simulation of a unit cell are all three Bi displacements observed, indicating there is a strong correlation between the Bi cation displacements.
Previous studies have investigated the displacement within bismuth-based pyrochlores to identify any correlation with results depending on the cation(s) occupying the B site [14]. In the case of Bi$_2$InNbO$_7$, the observation of diffuse streaking at particular Bragg reflections in electron diffraction patterns indicates the occurrence of $\beta$-cristobalite-type displacive disorder in the Bi$_2$O$'$ sub-structure [77]. In this structure along with Bi$_{1.89}$Fe$_{1.16}$Nb$_{0.95}$O$_{6.95}$, displacement within the BiO$'$ tetrahedron network is highly correlated and believed to be related to the dielectric properties [10,63,96,97]. Similar correlation between Bi displacements are observed within this study of Bi$_2$Ti$_2$O$_7$ (Figure 3-7) and within the electronic structure detailed in Section 3.3.3. Although electron diffraction patterns from experimental studies of this system are not known, it would be of interest to investigate the presence of similar indicators of displacive disorder within such patterns.

### 3.3.2.2 Atomic displacement in Bi$_2$Ru$_2$O$_7$

Experimentally, Bi$_2$Ti$_2$O$_7$ is not the only simple bismuth pyrochlore that exhibits Bi cation displacement. Avdeev et al. report a bismuth displacement of 0.16 Å [20] in Bi$_2$Ru$_2$O$_{7-\delta}$. In their investigation, it is determined that Bi occupies the 96$h$ site and O$'$ occupies the 32$e$ site. The displacement of the O$'$ ions is relatively small at 0.01 Å. However, despite multiple attempts with simulated annealing including at various volumes no substantial bismuth displacements is observed for the Bi$_2$Ru$_2$O$_7$ system. The energetics and magnitude of cation displacement are both negligible in this investigation, with only 0.006 eV/Bi cation associated with an average Bi displacement of only 0.05 Å. Similar to Bi$_2$Ti$_2$O$_7$, calculations were performed on the experimentally reported displaced structure, with the experimental structure found to be less stable by
1.8 eV/Bi cation when compared to the ideal undisplaced structure that is reported in Section 3.3.1. When compared to the energy change in the titante system, the magnitude indicates that the experimental structure is highly unfavorable. Since the lattice constant may be coupled to the Bi displacement, the volume was varied within the experimental structure, but it remains less favorable than the ideal undisplaced system by 1.7 eV/Bi. Recently, Goodwin et al. have examined the defective Bi$_2$Ru$_2$O$_{7-\delta}$ using diffuse electron diffraction [98]. They find a structural model involving beta-cristobalite type displacement for Bi cations best fits the diffraction features. Also DFT calculations were performed using the structural model of Goodwin et al. [98], and again cation displacement is not favored. Cation displacement was again not favorable with the consideration of spin polarization for both the simulated annealing of the ideal configuration and in the atomic relaxation of the experimental structure.

Between the simulated annealing runs performed on both the ideal starting structure and the experimentally determined displaced structure, the DFT results suggest that cation displacement is not critical to stabilize the Bi$_2$Ru$_2$O$_7$ system. As shown in the next section, based on the electronic structure of the metallic bismuth pyrochlores, there is no indication that Bi$_2$Ru$_2$O$_7$ should behave dramatically different than the other metallic bismuth pyrochlores. The source of the discrepancies between DFT and the recent experimental studies is not currently clear. The Bi$_2$Ru$_2$O$_{7-\delta}$ in the experiments is defective in O’ and Bi, possible triggering the observed bismuth cation displacement, but the role of O’ vacancies on the structure of the bismuth pyrochlores was not probed in this chapter. Both experimental studies assumed that the vacancies do not play a significant role in the observed cation displacements. Goodwin et al. find a
good fit to the diffraction patterns without the O’ vacancies, which gives support to this assumption [98]. From the literature, there is no experimental study of stoichiometric Bi$_2$Ru$_2$O$_7$. Future DFT and experimental studies are needed to clarify the role of O’ vacancies and may assist in resolving the conflict between DFT and experimental results. The role of O’ vacancies is directly examined using DFT in Chapter 5.

### 3.3.3 Electronic Structure

To shed light on the observation of large cation displacements solely in the Bi$_2$Ti$_2$O$_7$ system, the electronic structure was examined for the simple bismuth pyrochlores and the displaced Bi$_2$Ti$_2$O$_7$. Structure distortions in Bi and Pb based oxides are quite common [35,94] and are usually attributed to the sterochemical activity of the lone pair on the cation. Recently, electronic structure calculations of SnO, PbO and Bi$_2$O$_3$ oxides have shown that the classical picture of lone pair formation due to the hybridization of s and p orbitals of the metal cation is not correct [94,99,100]. Instead, they found that the asymmetric electronic structure in these materials is due to interactions between the metal cation s and p and O 2p states, and it is these interactions that stabilize the distorted structure [94,99,100]. The Bi pyrochlores are more complex since there are two cations and the above understanding in the oxides does not shed light directly on why only the Bi$_2$Ti$_2$O$_7$ shows appreciable distortions.

Below details the electronic structure obtained from the DFT results using Bader atomic charges, total and partial electronic density of states (DOS and pDOS), and the electron localization function (ELF) for each of the bismuth-based pyrochlores. It is found that the atomic displacements in Bi$_2$Ti$_2$O$_7$ are favored due to the Bi s and p orbitals interactions with the O’ p orbital in a manner similar to that reported by Walsh et al. for distorted PbO, SnO, and Bi$_2$Sn$_2$O$_7$ [94,99,101]. The metallic bismuth pyrochlores do not show
displacement due to weaker Bi-O’ interactions combined with stronger Bi-O interactions at the Fermi level. These differences in bonding between Bi-O’ are sufficient to suppress the formation of the lone pair upon cation displacement and therefore large cation displacement is not favored in the metallic bismuth pyrochlores. An examination of the ELF of the distorted Bi$_2$Ti$_2$O$_7$ with Bi cation displacement clearly displays the asymmetric electronic distribution around the Bi cation indicative of a lone pair and alters the bonding network.

The distribution of charges within the system of the ions aids in characterizing the bonding between atoms. The atomic charges were determined based on the Bader criteria for decomposing the electron density [61] using the code of Henkelman et al. [62]. Figure 3-8 presents the Bader charges for all the Bi pyrochlores in this study plotted against the B cation radius. The values for the various ions are comparable to values seen in a recent DFT investigation of La- and Y-based pyrochlores [34]. The trends of the Bader charges versus the cation radius were examined, shown in Figure 3-8, but similar to the bond lengths (see Section 3.3.1) a simple trend was not found.

The deviation between the atomic Bader charges and the formal ionic charge indicates the degree of covalency. All ions deviate from their formal charge values, indicating the importance of covalency in these systems. The smallest difference between the DFT atomic charge and the formal charge is found in the Bi$_2$Ti$_2$O$_7$ system, indicating that the Ti-O bond is less covalent than the B-O bond in the metallic pyrochlores.

The degree of covalency of the cation-O bonds in bismuth pyrochlores was previously explored using electronegativity values of the ions [102]. The larger the
difference in electronegativity between the two bonded atoms, the more ionic the bond. Based on this relationship, Wang et al. determined that the B-O bond should be least covalent in Bi$_2$Ti$_2$O$_7$, which matches the conclusion from the DFT atomic charges. Therefore, in systems that do not show large cation displacements the B-O bonds are more covalent. Figure 3-8 also indicates the change in atomic charges in Bi$_2$Ti$_2$O$_7$ due to atomic displacement. Though dramatic changes were not seen in the charge values, but Bi and O' atoms undergo the greatest change due to increased Bi-O' interaction after displacement.

Figure 3-8. Bader atomic charges in units of e for the Bi, B, O$_4$ and O' ion presented for each of the bismuth pyrochlores. The charges within the Bi$_2$O' network are darker while the charges associated with the B$_2$O$_6$ network are lighter colored. Lines are drawn as a visual aid, solid for the cations and dashed for the oxygen ions. Averaged Bader charges for the Bi$_2$Ti$_2$O$_7$ displaced system at 10.34 Å are indicated by the stars.

The DOS of each system was examined to identify electronic structure characteristics. Figure 3-9 presents the DOS for some of the bismuth pyrochlores without cation displacement. The known metallic bismuth pyrochlores of Bi$_2$Ru$_2$O$_7$, Bi$_2$Rh$_2$O$_7$, Bi$_2$Ir$_2$O$_7$, Bi$_2$Pt$_2$O$_7$, Bi$_2$Os$_2$O$_7$.
Bi$_2$Ir$_2$O$_7$, Bi$_2$Rh$_2$O$_7$, and Bi$_2$Os$_2$O$_7$ all have qualitatively similar DOS that indicate metallic behavior; therefore, Figure 3-9a shows only the Bi$_2$Ru$_2$O$_7$ DOS. As seen in Figure 3-9b, the DOS for Bi$_2$Pt$_2$O$_7$ is slightly different from the other transition metal bismuth pyrochlores and shows a small band gap of 0.5 eV. Experimental work identified Bi$_2$Pt$_2$O$_7$ as a semi-metal [15] but did not provide information on the band gap. It is known experimentally that Bi$_2$Ti$_2$O$_7$ behaves as an insulator and Figure 3-9c shows the DFT results predict a band gap of 1.8 eV compared with the value of 2.95 estimated from UV-Vis adsorption spectrum by Yao et al. [103]. In general DFT is known to underestimate band gaps, and the value determined here is comparable to a value of 2 eV determined by Seshadri [14] from linear muffin-tin orbital calculations.

![Figure 3-9](image_url)

**Figure 3-9.** Density of states in arbitrary units for (a) Bi$_2$Ru$_2$O$_7$, (b) Bi$_2$Pt$_2$O$_7$, and (c) Bi$_2$Ti$_2$O$_7$ in the ideal cubic pyrochlores structure with no cation displacement. The zero energy value represents the Fermi level.
The pDOS is shown for undistorted and distorted Bi$_2$Ti$_2$O$_7$ and Bi$_2$Ru$_2$O$_7$ in Figure 3-10. Again only the Bi$_2$Ru$_2$O$_7$ pDOS is shown, but the other metallic bismuth pyrochlores have essentially the same features. Similar mixing of states qualitatively matched prior DFT studies of Bi$_2$Ru$_2$O$_7$ and undistorted Bi$_2$Ti$_2$O$_7$ [14,20]. The Bi 6s and 6p, B cation d, and the O 2p states appear in the conduction and valence bands. The discussion is initially focused on the main features that impact the observed cation displacement in Bi$_2$Ti$_2$O$_7$.

A comparison of the pDOS of undistorted Bi$_2$Ti$_2$O$_7$ with recently reported studies of PbO, SnO, and Bi$_2$Sn$_2$O$_7$ [35,94,99], shows several sharp similarities. Bi s states show mixing with O’ p states in the lower part of the valence band (-10 to -8 eV) and near the Fermi level at the top of the valence band. The Bi s – O’ p mixing near the Fermi level observed in undistorted Bi$_2$Ti$_2$O$_7$ (Figure 3-10a) has been reported in PbO, SnO, and Bi$_2$Sn$_2$O$_7$, and is associated with antibonding interactions [35,94,99]. There is mixing between Bi p states with O’ p states in the top region of the valence band, which is further enhanced in the Bi$_2$Ti$_2$O$_7$ after cation displacement and volume optimization (see Figure 3-10a and 3-10b). The Bi s – O’ p mixing near the Fermi level is also enhanced by cation displacement.

A recent study by Walsh and Watson on the distorted $\alpha$-phase and undistorted cubic $\gamma$-phase of Bi$_2$Sn$_2$O$_7$ [101] shows similar differences in the Bi-O’ interactions as the undistorted and distorted Bi$_2$Ti$_2$O$_7$ pDOS. The Bi p – (Bi s – O’ p) interactions are associated with the asymmetric electron density of the lone pair and is the same mechanism observed in several other oxides that distort due to the presence of a lone pair [35,94,99,101].
Figure 3-10. Partial density of states in arbitrary units of Bi (6s), Bi (6p) and B (d) for the Bi$_2$Ti$_2$O$_7$ pyrochlore (a) before and (b) after displacement and volume optimization and the Bi$_2$Ru$_2$O$_7$ pyrochlore (c) undistorted and (d) with forced displacement.

Other oxides such as PbO and SnO do show a larger change in the degree of the mixing of Bi cation – O upon a change from high to low symmetry structures. Therefore, the formation of the lone pair is not due to direct Bi s–Bi p hybridization, but instead is a result of Bi s and p hybridization with O’ p states. There are interactions between Bi and
O\ p\ states\ in\ Bi_2Ti_2O_7,\ but\ the\ Bi\ s – O\ p\ interactions\ are\ less\ pronounced\ than\ the\ Bi\ s – O’\ p\ interactions\ and\ occur\ at\ an\ energy\ further\ down\ from\ the\ Fermi\ level.

As seen in a comparison of Figure 3-10a and 3-10c, there are many differences between the pDOS of the undistorted Bi_2Ti_2O_7 and the metallic bismuth pyrochlores (Bi_2Ru_2O_7). Bi_2Ru_2O_7 shows more overlap between Ru\ d\ and\ O\ p\ states\ over\ a\ broad\ range\ than\ found\ between\ Ti\ d\ and\ O\ p\ in\ Bi_2Ti_2O_7,\ which\ reinforces\ the\ conclusion from\ the\ Bader\ atomic\ charges\ that\ the\ B-O\ bond\ is\ more\ covalent\ in\ the\ metallic pyrochlores. The Bi\ s – O’\ p\ mixing\ in\ Bi_2Ru_2O_7\ is\ similar\ to\ Bi_2Ti_2O_7\ for\ the\ lower\ energy\ region\ in\ the\ valence\ band,\ but\ the\ Bi\ s\ and\ p\ mixing\ with\ O’\ p\ states\ at\ the\ top\ of\ the\ valence\ band\ shows\ several\ differences. Firstly, the Bi\ s – O’\ p\ interactions\ in\ Bi_2Ru_2O_7,\ similar\ to\ the\ antibonding\ interactions\ found\ in\ Bi_2Ti_2O_7,\ occur\ 2\ eV\ below\ the Fermi\ level. There\ is\ also\ mixing\ between\ the\ Bi\ s\ and\ p\ states\ with\ O48f\ across\ the Fermi\ level\ along\ with\ some\ mixing\ of\ the\ Bi\ s\ and\ O’\ p\ states. In\ general,\ there\ is\ more\ mixing\ between\ the\ Bi\ states\ and\ O48f\ p\ states\ in\ Bi_2Ti_2O_7\ and\ while\ additional\ mixing\ of\ the\ Bi\ s\ and\ O’\ p\ states\ is\ observed\ at\ the\ Fermi\ level\ it\ is\ much\ less\ pronounced than\ the\ Bi – O48f\ interactions. The net effect of the greater mixing of Ru\ d\ and\ O48f\ p\ states\ on\ the\ top\ of\ the\ valence\ band\ is\ a\ reduction\ of\ the\ Bi-O’\ interactions. This reduction is sufficient to eliminate the interactions that favor lone pair formation upon cation displacement in Bi_2Ru_2O_7. The pDOS for a displaced Bi_2Ru_2O_7 is shown in Figure 3-10d and as large an enhancement of Bi-O’ mixing that occurs in displaced Bi_2Ti_2O_7 is not found.

The ELF for the Bi_2Ti_2O_7 displaced system on the (111) and (\bar{1}11) plane is shown in Figure 3-11a and 3-11b, respectively. Figure 3-11a provides details of the Bi-O48f
environment, while Figure 3-11b highlights the interaction between the Bi-O’ network and the Ti-O48f network. Within Figure 3-11a, the Bi cation bonds strongly to three of the six O48f anions, leaving a small space between the remaining three O48f anions and the Bi cation.

Figure 3-11. The electron localization of the displaced Bi2Ti2O7 at 10.34 Å for the (a) (111) plane with Bi in the center and the (b) (111) plane with the Bi, Ti, O’, and O48f ions indicated. The ELF values range from 0 (light red) to 1 (dark purple), as shown by the scale.

A more strongly localized lobe of electron density, corresponding to the lone pair, partially occupies the space. Figure 3-11a indicates that the Bi cation displacement allows the lone pair on the Bi cation to occupy space that would be otherwise unavailable within the ideal configuration. A similar ELF structure has been observed for the bismuth-based SrBi2Ta2O9 by Seshadri [14], where the electrons preferentially localize to one half of the ion. Figure 3-11b illustrates the correlation with the Bi cation displacements explained in Section 3.3.2.1, with the Bi displacement simultaneously
alternating towards and away from the Ti-O48f networks. As mentioned in Section 3.3.2.1, Somphon et al. observed this correlated Bi displacement within the more complex Bi2InNbO7 and Bi2FeNbO7 compounds and indicated that it would affect the displacive disorder, and therefore the dielectric properties [77]. Though not shown here (included in Section B.4.1), the ELF for Bi2Ru2O7 provides no indication that atomic displacement is needed to stabilize the structure.

3.4 Summary

Using Density Functional Theory (DFT) calculations, a range of cubic Bi2B2O6O’ (B = Ti, Ru, Rh, Ir, Os, Pt) pyrochlores was examined and the structural parameters along with the electronic structure of the bismuth pyrochlores in their ideal cubic, defect-free structure are reported. The role of cation displacements within the cubic structure was investigated, with the identification of atomic displacement in the Bi2Ti2O7 compound. The atomic displacement stabilizes this structure with an energy change of similar magnitude to that of other bismuth-based pyrochlores. In Bi2Ti2O7, an average displacement of 0.38 Å for the Bi cation, 0.07 Å for the Ti cation, 0.11 Å for the O’ anion was found, and an energy change of ~0.15 eV/Bi atom. The Bi cation displacements appear to be correlated as seen in other more complex bismuth pyrochlores. Examination of the electronic structure shows the main difference between Bi2Ti2O7 and the metallic bismuth pyrochlores is the extent of Bi-O’ interactions. In Bi2Ti2O7, more overlap of Bi s and p states with O 2p states was observed similar to the reported electronic structure of Bi2Sn2O7, PbO and SnO [94,99], which leads to the asymmetric electronic structure around the Bi cation and the displacement of cations in Bi2Ti2O7. These DFT results match the general understanding from experimental studies, but underestimate the displacement in Bi2Ru2O7 compared with experimental results of
defective Bi$_2$Ru$_2$O$_{7.5}$ [20]. Work directly examining the role of vacancies may assist in resolving the differences between these DFT results and experimental work on Bi$_2$Ru$_2$O$_7$ and is discussed in Chapter 5.
CHAPTER 4
THE INFLUENCE OF SULFUR SUBSTITUTION ON THE ATOMIC DISPLACEMENT IN BISMUTH TITANATE

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4.1 Introduction

A general feature observed in all the Bi pyrochlores that show high dielectric permittivity is large ion displacement from the ideal Fd$\bar{3}$m sites of the cubic pyrochlore structure. This atomic displacement results in multiple energetically equivalent sites that facilitate cation hopping. Because compounds such as BZN incorporate cation substitutions onto both the A$_2$O’ and B$_2$O$_6$ networks it is difficult to fully separate the myriad of influences on cation displacement. In order to overcome this difficulty in Chapter 3, the investigation of a series of cubic bismuth pyrochlores without cation substitution (Bi$_2$B$_2$O$_6$O’, B= Ti, Ru, Rh, Os, Ir, Pt) [104] was discussed. Only Bi$_2$Ti$_2$O$_7$ showed a preference for atomic displacement and the magnitude from DFT matched the experimentally reported values [23,28]. Through the analysis of the electronic structure of Bi$_2$Ti$_2$O’O$_6$ (see Section 3.3.3), the atomic displacement was attributed to the development of a lone pair on the Bi cations. The lone pair does not form for the other bismuth pyrochlores examined confirming that the B$_2$O$_6$ network has some influence in the lone pair formation. In this chapter, the role of the B$_2$O$_6$ versus A$_2$O’ network in the formation of the lone pair in Bi$_2$Ti$_2$O’O$_6$ is further developed by examining the effect of sulfur substitution on the two networks.

Walsh and co-workers showed that substitution of sulfur for oxygen suppressed the formation of the lone pair observed in PbO [94,105,106]. This suppression of the
lone pair explains the difference in structure between PbO (litharge) and PbS (rocksalt). More importantly, the work on PbO and PbS shows that the lone pair formation is dependent on the cation-anion hybridization and not just due to hybridization of 6s and 6p orbitals of Pb [94]. Section 3.3.3 showed that the B2O6 network influences lone pair formation in Bi pyrochlores through a secondary effect. For the semi-metallic and metallic systems the Bi cations interact more strongly with the O anions within the B2O6 network [104]. This stronger Bi-O interactions weakens the Bi-O’ interactions, which in turn suppresses the formation of the lone pair. This model for lone pair formation essentially matches the conclusion from DFT studies of lead oxides and bismuth oxides by Walsh et al. [94,100,105,106]. Specifically, in lead oxides and bismuth oxides the nature of the cation-anion direct bonding is critical to induce lone pair formation, but in pyrochlores the B2O6 network can influence the primary Bi-O’ interactions.

In this chapter, a similar approach to Walsh and co-workers is employed to further elucidate the lone pair formation in Bi$_2$Ti$_2$O’O$_6$ through sulfur substitution. Though some pyrochlore compounds have been synthesized with S on the O’ site [15,107] the goal of this study is not to detail stable pyrochlore compounds with sulfur substitutions. Instead a purely theoretical approach is taken to provide further insight into the lone pair formation in Bi$_2$Ti$_2$O’O$_6$.

Sulfur may substitute onto either of the two sites occupied by oxygen, which are the 8b (X’) site within the A$_2$O’ network and 48f (X) site within the B$_2$O$_6$ network. Three configurations were created with sulfur substituted (i) only on the 8b (X’) site, (ii) only on the 48f (X) site and (iii) on both the 8b (X’) and 48f (X) sites with the molecular formulae of Bi$_2$Ti$_2$S’O$_6$, Bi$_2$Ti$_2$O’S$_6$ and Bi$_2$Ti$_2$S’S$_6$, respectively. It is found that S substitution only
on the O’ site can suppress cation displacement, confirming the primary importance of the Bi-O’ interactions. Comparisons of the electronic structure in Section 4.3.2 shows that the S substitution on the O’ site modifies the Bi-anion hybridization which suppresses the formation of the lone pair. Section 4.3.3 shows through S substitution on the B₂O₆ network of Bi₂Ru₂O₆O’, cation displacement and lone pair formation can be induced in the metallic Bi pyrochlores by disrupting the Bi-O interactions.

4.2 Calculation Details

First-principles calculations were performed with Vienna Ab-initio Simulation Package (VASP) [44-47], and details nearly match that reported in Section 3.2. The Bi(5d, 6s, 6p), Ti(3s, 3p, 3d, 4s), O(2s, 2p), and/or S(3s, 3p) orbitals were included as the valence electrons for the projector augmented wave (PAW) pseudopotentials. The DFT calculations were performed within the local density approximation (LDA) [50]. It was confirmed that the favorability of atomic displacement and lone pair formation does not depend on the functionals. All calculations were performed at fixed volume and shape, while the atoms were relaxed until the forces were less than 0.03 eV/Å. Though all atoms are free to relax in these optimized structures the crystal lattice is fixed to the cubic pyrochlore structure. A plane wave cutoff energy of 400 eV was used along with a 3×3×3 Monkhorst-Pack [54] mesh, resulting in 14 irreducible k-points. Test calculations done with 450 eV cutoff and a 4×4×4 mesh resulted in differences less than 0.01 eV/88-atom unit cell in the total energy, well within the error for the results presented in this chapter.

To probe minima associated with displaced cations, simulated annealing (see Section 1.3.4.1) calculations were performed under fixed crystal shape and volume using ab initio molecular dynamics (MD) [44-47] with the relaxed ideal pyrochlore
structures (from the above procedure) as the initial structures. The MD simulations were conducted with only the Γ point within the NVT ensemble starting at 1000 K and cooling to 300 K over 500 MD steps with a time step of 0.5 femtoseconds. After MD simulation, the system was minimized using the same approach as outlined above (3×3×3 mesh, CG method, etc.) and the equilibrium lattice parameter was reevaluated for the cation displaced structure. While the MD simulation is over extremely short times, it was confirmed that increasing the simulation length does not affect the final fully relaxed structure.

4.3 Results and Discussion

4.3.1 Structural Details

For each of the bismuth pyrochlores (Bi$_2$Ti$_2$X'X$_6$, X= O or S) the equilibrium lattice parameter was determined by generating energy versus volume curves. Table 4-1 contains the equilibrium lattice parameters for the Bi$_2$Ti$_2$O'O$_6$, Bi$_2$Ti$_2$S'O$_6$, Bi$_2$Ti$_2$O'S$_6$ and Bi$_2$Ti$_2$S'S$_6$ pyrochlore system. Though there is no experimental data available for comparison in the sulfur containing systems, in the Bi$_2$Ti$_2$O'O$_6$ system there is excellent agreement between the DFT value of 10.34 Å and the experimental values of 10.357 Å for Bi$_{1.74}$Ti$_2$O$_6.62$ [28] and 10.35907 Å for Bi$_2$Ti$_2$O$_7$ [23]. In the earlier study, DFT predicted lattice parameters for other Bi-based pyrochlores were within 1% of experimental values providing confidence in DFT’s ability to reproduce these structures [104].

Bi$_2$Ti$_2$S'O$_6$ has only 8 sulfur atoms per unit cell and shows the smallest lattice expansion from 10.23 Å to 10.65 Å. When the number of sulfur atoms is increased to 48 per unit cell in the Bi$_2$Ti$_2$O'S$_6$, a much larger lattice expansion to 12.0 Å is observed. In
the Bi$_2$Ti$_2$S’S$_6$, with sulfur on both the X’ (8b) and X (48f) sites, the lattice expands slightly more to an equilibrium lattice parameter of 12.3 Å.

Table 4-1. The cubic lattice parameter in Å and average bond lengths in Å of the ideal structure (before annealing) is shown for the Bi$_2$Ti$_2$X’X$_6$ and Bi$_2$Ru$_2$O’X$_6$ pyrochlore systems.

<table>
<thead>
<tr>
<th>System</th>
<th>Lattice Parameter (Å)</th>
<th>Expansion Percentage (%)</th>
<th>Bond Length (Å)</th>
<th>Bond Expansion Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_2$Ti$_2$O’O$_6$</td>
<td>10.23</td>
<td>–</td>
<td>2.21 2.55 1.96</td>
<td>–</td>
</tr>
<tr>
<td>Bi$_2$Ti$_2$S’O$_6$</td>
<td>10.65</td>
<td>4.1</td>
<td>2.31 2.69 2.02</td>
<td>4.5 5.5 3.1</td>
</tr>
<tr>
<td>Bi$_2$Ti$_2$O’S$_6$</td>
<td>12.00</td>
<td>17.3</td>
<td>2.59 2.91 2.35</td>
<td>17.2 14.1 19.9</td>
</tr>
<tr>
<td>Bi$_2$Ti$_2$S’S$_6$</td>
<td>12.30</td>
<td>20.2</td>
<td>2.66 3.03 2.38</td>
<td>20.4 18.8 21.4</td>
</tr>
<tr>
<td>Bi$_2$Ru$_2$O’O$_6$</td>
<td>10.205</td>
<td>–</td>
<td>2.21 2.51 1.98</td>
<td>–</td>
</tr>
<tr>
<td>Bi$_2$Ru$_2$O’S$_6$</td>
<td>11.75</td>
<td>15.1</td>
<td>2.54 2.88 2.28</td>
<td>15.1 14.8 15.2</td>
</tr>
</tbody>
</table>

It is well known that S anions are larger than O anions so the lattice expansion is not unexpected. In order to understand if the lattice expansion depended only on the incorporation of the larger sulfur anion on various lattice sites, the real space volume occupied by each atom was identified within the lattice. Utilizing the code of Henkelman et al. [62], the Bader volumes were determined based on the Bader criteria for decomposing the electron density [61]. Since the Bader volumes are calculated using the zero-flux surfaces in the electron density gradient, the sum of Bader volumes in a crystal will exactly equal the total cell volume. Therefore, each Bader volume will depend on the equilibrium lattice volume. To compare the atomic volume of an atom on a specific site between the various crystal systems examined, each Bader volume was scaled by its corresponding total unit cell volume. As expected, it was found that the scaled Bader volume of the Ti cation and O anion remain the same between the Bi$_2$Ti$_2$O’O$_6$ and the Bi$_2$Ti$_2$S’O$_6$ system. However, the scaled Bader volume of the Bi cation was reduced by 8% while the S increased the X’ (8b) site volume by 23%. In the
Bi$_2$Ti$_2$O’S$_6$ system the S anion increased the X (48f) site volume by 15% in comparison to the Bi$_2$Ti$_2$O’O$_6$ system. Between the Bi$_2$Ti$_2$O’O$_6$ and the Bi$_2$Ti$_2$O’S$_6$ systems, the Bi, Ti, and O’ atoms showed volume reductions of 27%, 24%, and 27%, respectively. Based on the variations in the Bader volumes, the equilibrium lattice parameter may not be determined \textit{a priori} with only the atomic volumes of the constituent atoms.

Table 4-1 also shows the Bi-X’, Bi-X, and B-X bond lengths, where X can represent either O or S atom. As expected, the lattice expansion increases all the bond lengths significantly. In the ideal pyrochlore structure only the O atom experiences non-zero forces and will undergo atomic relaxation to optimize both the Bi-O and Ti-O bond lengths. Therefore, the Bi-X’ bond length scales directly with the lattice parameter.

Some variations are observed when the bond lengths corresponding to the O site are examined. In the Bi$_2$Ti$_2$S’O$_6$ system, there is a 4.1% lattice expansion but the Ti-O bond only increases by 3.1%. This smaller Ti-O bond length indicates the Ti atom bonds more strongly to the O atoms and therefore pulls the O atoms in closer, which then elongates the Bi-O bond by 5.5%. In both the Bi$_2$Ti$_2$O’S$_6$ and Bi$_2$Ti$_2$S’S$_6$ systems, the Bi-S bond is reduced with respect to the lattice expansion and the Ti-S bond is elongated, indicating the Bi-S interactions are stronger than the Ti-S interactions.

Atomic displacement was probed for in the three materials by performing simulated annealing as discussed in Section 4.2, with the results summarized in Table 4-2. Since the lattice parameters vary considerably between the systems, both the average displacement magnitudes and these magnitudes scaled by the equilibrium lattice parameter are included in Table 4-2. In Bi$_2$Ti$_2$S’O$_6$, atomic displacement is not favored since no significant energy change or atomic displacement was observed.
Table 4-2. The cubic lattice parameter in Å, energy change in eV/Bi atom, and average displacement magnitudes in Å after simulated annealing with respect to the ideal structure with positive energy indicating an increase in thermodynamic favorability are shown for the Bi$_2$Ti$_2$O’O$_6$, Bi$_2$Ti$_2$S’O$_6$, Bi$_2$Ti$_2$O’S$_6$, and Bi$_2$Ru$_2$O’S$_6$ pyrochlore systems. The average bond lengths are provided in Å.

<table>
<thead>
<tr>
<th>Lattice Parameter (Å)</th>
<th>Energy Change (eV/Bi)</th>
<th>Displacement Magnitude (Å)</th>
<th>Bond Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>[Scaled by Lattice Parameter (Å/Å)]</td>
<td>Bi</td>
</tr>
<tr>
<td>Bi$_2$Ti$_2$O’O$_6$</td>
<td>10.34</td>
<td>0.146 ± 0.001</td>
<td>0.38 ± 0.02 [0.037 ± 0.002]</td>
</tr>
<tr>
<td>Bi$_2$Ti$_2$S’O$_6$</td>
<td>10.65</td>
<td>0.000</td>
<td>0.00 ± 0.00 [0.000 ± 0.000]</td>
</tr>
<tr>
<td>Bi$_2$Ti$_2$O’S$_6$</td>
<td>12.00</td>
<td>0.533</td>
<td>0.51 ± 0.14 [0.043 ± 0.012]</td>
</tr>
<tr>
<td>Bi$_2$Ru$_2$O’S$_6$</td>
<td>11.75</td>
<td>0.064</td>
<td>0.23 ± 0.03 [0.019 ± 0.002]</td>
</tr>
</tbody>
</table>
Additionally, atomic displacement was attempted by forcibly pushing the Bi cations out of the ideal $16d$ site and after atomic relaxation it was observed that $\text{Bi}_2\text{Ti}_2\text{S'}\text{O}_6$ does not retain the pyrochlore structure. The resulting structure is not energetically favorable with respect to the un-displaced pyrochlore structure; therefore, the ideal pyrochlore structure without cation displacement is taken as the preferred structure for the $\text{Bi}_2\text{Ti}_2\text{S'}\text{O}_6$ system.

Alternatively, atomic displacement is favored in the $\text{Bi}_2\text{Ti}_2\text{O'}\text{S}_6$ system with an energy change of 0.53 eV per Bi cation. When comparing this value with that reported in the $\text{Bi}_2\text{Ti}_2\text{O'}\text{O}_6$ system of 0.15 eV per Bi cation [104], the atomic displacement here is 3.5 times more favorable. This larger preference for the displaced structure is attributed to the disruption of the Bi-Ti$_2$O$_6$ interactions. The Bi cation interacts less with the Ti$_2$S$_6$ network than the Ti$_2$O$_6$ network, which in turn allows for stronger Bi-O’ hybridization. As will be discussed in more detail in Section 4.3.2, the Bi-O’ interactions leads to lone pair formation and corresponding atomic displacement. For $\text{Bi}_2\text{Ti}_2\text{O'}\text{S}_6$, these stronger Bi-O’ interactions make the asymmetric atomic displaced structure much more favorable over the ideal structure with no cation displacement.

In the $\text{Bi}_2\text{Ti}_2\text{O'}\text{O}_6$ system the Bi cation displaces on average 0.38 Å and in $\text{Bi}_2\text{Ti}_2\text{O'}\text{S}_6$ the Bi cations are displacing on average 0.51 Å. Additionally, in $\text{Bi}_2\text{Ti}_2\text{O'}\text{S}_6$ the 0.7 Å atomic displacement of the Ti atoms is more than four times that seen in the $\text{Bi}_2\text{Ti}_2\text{O'}\text{O}_6$ system. The average bond lengths are included in Table 4-2. The Bi displacement in the $\text{Bi}_2\text{Ti}_2\text{O'}\text{S}_6$ system reduces the Bi-O’ bond length from 2.59 Å to 2.33 Å and is comparable to the 2.26 Å bond length of $\text{Bi}_2\text{Ti}_2\text{O'}\text{O}_6$. Table 4-2 shows the averaged Ti-S bond length is not significantly altered by the large displacement of Ti.
However, within each of the Ti centered octahedron there are variations in the six local Ti-S bonds with up to a 0.2 Å variance of the Ti-S bond lengths within some of the octahedrons.

The simulated annealing of Bi$_2$Ti$_2$S’S$_6$ shows similar results to Bi$_2$Ti$_2$S’O$_6$ with minimal atomic displacement observed initially and lattice distortion upon forcible atomic displacement. Since atomic displacement in Bi$_2$Ti$_2$O’O$_6$ can be suppressed by S substitution on the O’ site, the Bi$_2$Ti$_2$S’S$_6$ system is redundant and convolutes the role of the A$_2$O’ and B$_2$O$_6$ networks and therefore will be excluded from the following discussion.

4.3.2 Electronic Structure

The results presented in Section 4.3.1 clearly indicate that S substitution on the A$_2$O’ network is needed to suppress cation displacement. This section will focus on understanding the differences in the electronic structures between the Bi$_2$Ti$_2$S’O$_6$ and Bi$_2$Ti$_2$O’S$_6$ systems and how these systems relate to the Bi$_2$Ti$_2$O’O$_6$ pyrochlore both before and after atomic displacement. The electron localization function (ELF) maps the probable distribution of electrons graphically, where a fully localized or delocalized electron has an ELF value of 1 or 0, respectively (see Section 1.3.4.4 for additional details). The ELF function is used below to identify active lone pair formation on the Bi cations as a function of S substitution on the X (48f) and X’ (8b) sites.

The ELF is plotted in Figure 4-1 for the Bi$_2$Ti$_2$O’O$_6$ pyrochlore after atomic displacement in the (110) plane intersecting the Bi-O and Ti-O bonding environment. After simulated annealing, the Bi cation displaces to the right with an asymmetric lobe of increased electron localization forming to the left of the Bi cation in the vacant space. It is through the development of this asymmetric lone pair that atomic displacement is
favored in the Bi$_2$Ti$_2$O’O$_6$ system. To understand why atomic displacement is not observed in the Bi$_2$Ti$_2$S’O$_6$ system the electronic structure was examined for this system with the same atomic displacement as that seen in the Bi$_2$Ti$_2$O’O$_6$ pyrochlore without allowing atomic relaxation.

![Figure 4-1](image1.jpg)

Figure 4-1. The electron localization of the Bi$_2$Ti$_2$O’O$_6$ with atomic displacement for part of the (110) plane passing through one Bi atom (center) and four O ions (in the corners). The ELF values range from 0.0 (red) to 0.8 (purple) as indicated by the scale.

The ELF for the Bi$_2$Ti$_2$S’O$_6$ pyrochlore with forced displacement is plotted in Figure 4-2 in the same (110) plane. Though the Bi cation in the center of Figure 4-2 is displaced in the same fashion as that in Figure 4-1, the electron localization observed in Figure 4-2 surrounding the Bi cation shows negligible asymmetry character, indicating a $p$-type lone pair does not form in this system. In fact, the ELF for the Bi$_2$Ti$_2$S’O$_6$ system more closely resembles the symmetric localization previously reported for Bi$_2$Ti$_2$O’O$_6$ pyrochlore without atomic displacement on the A$_2$O’ network [14]. In the earlier study the observed symmetric lobes are due to site symmetry with the Bi and O’ in their ideal 16$d$ and 8$b$ crystallographic sites and are termed a s-type lone pair. In the systems, it is interesting to note within the same atomic structure (i.e. displacement pattern) that Bi-O’ interactions lead to atomic displacement and an asymmetric $p$-type electron localization for Bi$_2$Ti$_2$O’O$_6$ (Figure 4-1) while Bi-S’ suppresses $p$-type electron localization for Bi$_2$Ti$_2$S’O$_6$ (Figure 4-2).
Figure 4-2. The electron localization of the Bi$_2$Ti$_2$S’O$_6$ with forced atomic displacement for part of the (110) plane passing through one Bi atom (center) and four O ions (in the corners). The ELF values range from 0.0 (red) to 0.8 (purple) as indicated by the scale.

Figure 4-3 illustrates the ELF plotted in the same (110) plane for the Bi$_2$Ti$_2$O’S$_6$ pyrochlore after simulated annealing. It is clear the atomic displacement in this system does not exactly match that observed in the Bi$_2$Ti$_2$O’O$_6$ pyrochlore but surrounding the Bi cation is an asymmetric lone pair. Therefore the development of a p-type lone pair on the Bi cation is observed in the two pyrochlore with favorable atomic displacement and not observed in the pyrochlore with forced atomic displacement. The effect of S substitution onto the X’ site on the p-type lone pair formation is explored in more detail in the discussion of pDOS below.

Figure 4-3. The electron localization of the Bi$_2$Ti$_2$O’S$_6$ with atomic displacement for part of the (110) plane passing through one Bi atom (center) and four O ions (in the corners). The ELF values range from 0.0 (red) to 0.8 (purple) as indicated by the scale.

To quantify charge transfer in these systems the Bader atomic charges [61] were determined using the code of Henkelman et al. [62]. The Bader charges for the most
favored structure, i.e. either with or without displacement, of each of the pyrochlore systems examined are included in Table 4-3. The importance of covalency can be seen in these systems since all ions deviate from their formal charge values. Wang and co-workers [102] addressed covalent versus ionic bonding in bismuth pyrochlore using differences in the ion electronegativity. Ionic (covalent) bonding would dominate with the larger (smaller) difference in electronegativity between the two bonded atoms. In the earlier study, the Bi-O bonds were identified to be more ionic in nature than the B-O bonds in metallic pyrochlores (B=Ru, Os, Ir, and Pt). Inversely, for Bi₂Ti₂O₇, the Bi-O bonds are more covalent in nature than the Ti-O bonds. These observations suggest that to observe cation displacement and p-type lone pair formation requires either to increase the strength of the Bi-O' interactions or alternatively weaken the B-O interactions. As is shown below, this simple rule is not sufficient to describe the behavior of Bi pyrochlores upon S substitution.

Table 4-3. Bader atomic charges in units of e for the Bi, B, X', and X atoms are shown for the Bi₂Ti₂O'O₆, Bi₂Ti₂S'O₆, Bi₂Ti₂O'S₆, Bi₂Ru₂O'O₆, and Bi₂Ru₂O'S₆ pyrochlore systems. The * indicates systems that prefer atomic displacements.

<table>
<thead>
<tr>
<th>Lattice Parameter (Å)</th>
<th>Bader Charge (e)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi₂Ti₂O'O₆*</td>
<td>10.34</td>
<td>1.88</td>
<td>2.18</td>
<td>-1.22</td>
</tr>
<tr>
<td>Bi₂Ti₂S'O₆</td>
<td>10.65</td>
<td>1.63</td>
<td>2.21</td>
<td>-0.81</td>
</tr>
<tr>
<td>Bi₂Ti₂O'S₆*</td>
<td>12.00</td>
<td>1.47</td>
<td>1.62</td>
<td>-1.14</td>
</tr>
<tr>
<td>Bi₂Ru₂O'O₆</td>
<td>10.205</td>
<td>1.90</td>
<td>1.61</td>
<td>-1.27</td>
</tr>
<tr>
<td>Bi₂Ru₂O'S₆*</td>
<td>11.75</td>
<td>1.37</td>
<td>0.66</td>
<td>-1.13</td>
</tr>
</tbody>
</table>

The Bader charges for both the ideal and S substituted Bi₂Ti₂O₇ pyrochlores are reported in Table 4-3. These Bader values may be interpreted in conjunction with the changes to the electronegativity differences upon sulfur substitution. With increasing
sulfur content, the Bi Bader charge decrease from 1.88 $e$ for $\text{Bi}_2\text{Ti}_2\text{O'O}_6$ to 1.63 $e$ for $\text{Bi}_2\text{Ti}_2\text{S'O}_6$ to 1.47 $e$ for $\text{Bi}_2\text{Ti}_2\text{O'S}_6$, indicating the degree of covalent bonding is increasing with increasing sulfur content. Using Pauling’s [108] electronegativity (EN) for Bi, Ti, and O, in $\text{Bi}_2\text{Ti}_2\text{O'O}_6$ the difference in EN between Bi and O is 1.42 while the difference between Ti and O is 1.9. In $\text{Bi}_2\text{Ti}_2\text{S'O}_6$, the difference in EN between Bi and S is 0.56 significantly lower than the Ti-O; therefore, the Bi-S' bond should be more covalent in comparison to the Ti-O bond. Table 4-3 shows the Bader charges of Bi and S' are significantly less than their respective formal charges and that the Ti and O charges do not change between $\text{Bi}_2\text{Ti}_2\text{O'O}_6$ and $\text{Bi}_2\text{Ti}_2\text{S'O}_6$. With sulfur occupying the X site, the difference in EN between Ti and S is 1.04, between Bi and O' is 1.42 and between Bi and S is 0.56. It can be predicted that the Bi-O' bond should be more ionic than the Bi-S bond which should be more ionic than the Ti-S bond. The calculated Bader charges again agree with this prediction with reduction of the Bi, Ti, O' and S charges. While the Bader charges reflect the changes in covalency expected from using the differences in EN, they fail to predict the systems were cation displacement occurs. For example, the Bi cation becomes more covalent going from $\text{Bi}_2\text{Ti}_2\text{O'O}_6$, $\text{Bi}_2\text{Ti}_2\text{S'O}_6$, and $\text{Bi}_2\text{Ti}_2\text{O'S}_6$ but only the two end systems show atomic displacement. While $\text{Bi}_2\text{Ti}_2\text{S'O}_6$ shows larger charge transfer between the Bi and X' than in the $\text{Bi}_2\text{Ti}_2\text{O'O}_6$ system, it is only the latter that produces a strong $\rho$-type lone pair and atomic displacement. As is discussed below, cation displacement and lone pair formation are dictated by the nature of the Bi-X' cation hybridization, which is distinctly different in the $\text{Bi}_2\text{Ti}_2\text{O'O}_6$ and $\text{Bi}_2\text{Ti}_2\text{S'O}_6$ systems.
Figure 4-4 compares the partial density of states (pDOS) determined for the previously reported Bi$_2$Ti$_2$O’O$_6$ [104] (a-d) before and (e-h) after atomic displacement, with the states separated for each atom type. Figures 4-4a and Figure 4-4e compare the O’2s and 2p states before and after displacement, respectively. At the low energy band corresponding to the Bi 6s states (see Figure 4-4b and 4-4f), there is considerable hybridization between the O’ 2s and 2p states to overlap with the Bi 6s orbital.

Additionally, displacement significantly alters the valence band near the Fermi level with increased hybridization of the Bi 6s and 6p states and improves the overlap with the O’ 2p orbital. The central features of the pDOS responsible for lone pair formation can be identified by examining the partial electron density at specific energy windows. The partial electron density was examined for the low energy band (-11 to -8
eV), the intermediate energy band (-6 to -2 eV) and the top of the valence band (-2 eV to the Fermi level). The energy range at the top of the valence band shows the most clear asymmetric electron density and can be attributed with the lone pair with the Bi 6s and 6p orbitals strongly overlapping with the O' 2p orbital in the Bi$_2$Ti$_2$O'O$_6$ displaced system (see Figure 4-4f).

Figure 4-5 shows the partial electron density for Bi$_2$Ti$_2$O'O$_6$ (Figure 4-5a) with atomic displacement and Bi$_2$Ti$_2$S'O$_6$ (Figure 4-5b) with forced atomic displacement. The planes illustrated in Figure 4-5 correspond to a Bi cation, in the center of the plane, displaced upward and surrounded by its six O anions.

![Figure 4-5](image)

Figure 4-5. The partial electron densities for the (a) Bi$_2$Ti$_2$O'O$_6$ with atomic displacement and (b) Bi$_2$Ti$_2$S'O$_6$ with forced atomic displacement for the states between -2 eV to the Fermi level for part of the (111) plane passing through one Bi atom (center) and six O ions (edges) with the scale indicating the contour levels between 0.0 (blue) and 0.1 eÅ$^3$ (red).

Similar to Figure 4-1, the lone pair on the Bi cation can be observed in the opposite direction of the displacement. In both cases, an asymmetric lobe is formed but the size and magnitude of density are much smaller in Bi$_2$Ti$_2$S'O$_6$ (Figure 4-5b) than in Bi$_2$Ti$_2$O'O$_6$ (Figure 4-5a), agreeing with the observations made from the ELF that lone pair formation is not favored for Bi$_2$Ti$_2$S'O$_6$ (Figure 4-2).
Figure 4-6 shows the pDOS for the Bi₂Ti₂S'O₆ pyrochlore (a-d) at equilibrium and (e-h) with forced atomic displacement. The forced displacement system is the same structure mentioned above with regards to Figure 4-2. Although Bi₂Ti₂S'O₆ is insulating like Bi₂Ti₂O'O₆ (Figure 4-4), the magnitude of the band gap has been reduced from 1.8 eV to 1.5 eV. The pDOS associated with the S' site, shown in Figure 4-6a, shows the 3s and 3p states directly overlap in the low energy band corresponding to the Bi 6s states (see Figure 4-6b) which differs from that observed for O' in Bi₂Ti₂O'O₆ (Figure 4-4a and 4-4e). In the upper valence band, the S' 3p states are considerably lower in energy than equivalent O' states resulting in a peak split of the Bi 6p at the low energy range of this band. This split results in a small energy window where only the Bi 6p orbital interacts with the S' 3p orbital, which is not observed in any other pyrochlore.

After forced displacement (Figure 4-6e-f), this interaction is shifted in energy towards the other interactions within the upper valence band. Additionally, the direct overlap of the S' 3s and 3p states seen in the low energy valence band is reduced and mirrors that observed for Bi₂Ti₂O'O₆ (Figure 4-4a and 4-4e). While there is an increase in hybridization of the Bi 6s and 6p (Figure 4-6f) near the Fermi level after forced displacement its magnitude is much smaller than that seen in Bi₂Ti₂O'O₆ (Figure 4-4f). This corresponds to the previous observation of the symmetric electron localization (Figure 4-2) surrounding the Bi cations within this structure.

Figure 4-7 compares the pDOS for Bi₂Ti₂O'S₆ (a-d) before and (e-h) after atomic displacement. In the Bi₂Ti₂O'S₆ system, the band gap between the conducting and valence band is not observed but the energy gap between the two valence bands is retained.
Figure 4-6. Partial density of states of S' 3s, S' 3p, Bi 6s, Bi 6p, O 2p, and Ti 3d in states per electron volt for the Bi2Ti2S′O6 pyrochlore at 10.65 Å (a-d) before and (e-h) after forced atomic displacement.

The O' 2s and 2p states (Figure 4-7e) in the lower valence band overlap with the Bi 6s states (Figure 4-7f) at the higher and lower energy respectively. This hybridization matches that seen for Bi2Ti2O'O6 (Figure 4-4e-f). In the upper valence band, atomic displacement significantly increases the overlap of the Bi 6s and 6p orbitals near the Fermi level (see Figure 4-7f) with the O' 2p states (see Figure 4-7e), corresponding to the formation of the lone pair observed in Figure 4-3.

The essential interactions between Bi 6s and O' states at the low energy band and subsequent hybridization between the Bi 6p near the Fermi level that mediate the forming of the lone pair in Bi2Ti2O'O6 is similar to the findings of Walsh and co-workers for a range of oxides [94,100,105,106].
4.3.3 Bismuth Ruthenate

This study is concluded by returning to a representative metallic bismuth pyrochlore, Bi$_2$Ru$_2$O$_6$O’, that in the earlier DFT study did not show any cation displacement [104] (see Section 3.3.2.2). Experimental studies of Bi$_2$Ru$_2$O$_6$O’ showed atomic displacement [20], but the samples had significant oxygen deficiency on the A$_2$O’ network. This oxygen deficiency might force the experimentally observed displacement and disagreement with DFT [104], but the study of O vacancies on cation displacement is left for discussion in Chapter 5. Section 3.3.3 on metallic Bi pyrochlores concluded atomic displacement is not favored due to the stronger interactions between Bi and the O atoms on the B$_2$O$_6$ network in these systems. For Bi$_2$Ti$_2$O$_6$O’ the cation displacement is enhanced and the $p$-type lone pair formation more pronounced when S is substituted in the B$_2$O$_6$ network. This result suggests that substituting sulfur in the B$_2$O$_6$ network for
the metallic pyrochlores may induce cation displacement. Below this hypothesis is

tested by examining sulfur substitution on Bi₂Ru₂O₆O'.

The lattice optimization procedure discussed in Section 4.3.1 is repeated for the
Bi₂Ru₂O'S₆ structure to determine the equilibrium lattice parameter and favorability of
atomic displacement. The structural details of the ideal pyrochlore both with and without
sulfur are included in Table 4-1. Following simulated annealing, it is found that atomic
displacement is favored in the Bi₂Ru₂O'S₆ pyrochlore, with the details summarized in
Table 4-2. The Bi cations in the Bi₂Ru₂O'S₆ pyrochlore displace towards one of the two
O' anions thereby creating two long and two short Bi-O' bonds within each A₄O'
tetrahedron (see Figure 2-3b). In other bismuth based pyrochlores, this type of Bi cation
displacement has been discussed as “spin-ice” tetrahedron bonding [14]. The
pyrochlore O’ anions are equated to oxygen within ice with two hydrogen ions covalently
bonded and two hydrogen ions more weakly bound at significantly longer distances.
While the spin-ice arrangement does not affect the average Bi-O’ bond in the
pyrochlore, structurally a single long and short Bi-O’ bond can be seen by looking at the
atoms included in Figure 4-8.

In addition to showing some structural details, Figure 4-8 illustrates the partial
electron density for a portion of the (101) plane, which slices through the S-Bi-O’
bonding network. The energy range of interest, -2 eV to the Fermi energy, is the same
as that examined in the Bi₂Ti₂O₇ pyrochlore (Figure 4-5). A similar asymmetric electron
density to that seen in the Bi₂Ti₂O₇ is observed for the Bi₂Ru₂O’S₆ pyrochlore after
atomic displacement, but the electron density maximum is larger (0.1 e/Å³ versus 0.05
e/Å³) in Bi₂Ti₂O₇.
Figure 4-8. The partial electron densities for Bi$_2$Ru$_2$O’S$_6$ with atomic displacement for the states between -2 eV to the Fermi level for part of the (101) plane passing through one Bi atom (center), two O’ (atoms included) and two S ions with the scale indicating the contour levels between 0.0 (blue) and 0.1 e/Å$^3$ (red).

Figure 4-9 shows the ELF for Bi$_2$Ru$_2$O’S$_6$ with atomic displacement in the (101) plane and illustrates an asymmetric lobe forms along the long Bi-O’ bond direction created behind the Bi cation displacement towards the opposite O’. Though the magnitude of electron localization in Bi$_2$Ru$_2$O’S$_6$ (Figure 4-9) is lower than that seen in Bi$_2$Ti$_2$O’O$_6$ (Figure 4-1), it can seen in Bi$_2$Ru$_2$O’S$_6$ the lone pair formation is favored and triggers the atomic displacement. The Bader charges for the Bi$_2$Ru$_2$O’O$_6$ and Bi$_2$Ru$_2$O’S$_6$ systems are reported at the bottom of Table 4-3. Similar to the bismuth titanate systems, sulfur incorporation increases the degree of covalent bonding in the system, as indicated by the reduction of the Bi, Ru, O’ and O/S site Bader charges.

These results suggest that modifying the B$_2$O$_6$ network to weaken Bi-O interactions is a plausible strategy to increase cation displacement and in turn induce larger dielectric permittivity in these materials. It will be interesting to compare the lone pair formation and role in cation displacement in the more complex Bi pyrochlores such as BZN to the observations of Bi$_2$Ti$_2$O$_7$. 
4.4 Summary

In this chapter, DFT calculations were employed to further clarify the lone pair formation in Bi$_2$Ti$_2$O’O$_6$ through sulfur substitution on the O’ and O sites. Atomic displacement is not favored in the case of S substituted on the O’ site, confirming the primary importance of the Bi-O’ interactions. Analysis of the partial density of states, ELF and partial electron density shows that the S substitution on the O’ site suppresses the formation of the lone pair by modifying the Bi-anion hybridization. The electronic structure was examined for the Bi$_2$Ti$_2$S’O$_6$ pyrochlore fixed with the same displacement pattern as that seen in Bi$_2$Ti$_2$O’O$_6$. In Bi$_2$Ti$_2$S’O$_6$ with forced displacement, the ELF displayed symmetric lobe around the bismuth cations with a significant reduction of the asymmetric electron density in the energy range of -2 eV to the Fermi level. In the case of sulfur on the O site, atomic displacement is significantly favored energetically in Bi$_2$Ti$_2$O’S$_6$ and showed the largest atomic displacement. Specifically, the Ti and O’ atoms displaced considerably more in Bi$_2$Ti$_2$O’S$_6$ than in Bi$_2$Ti$_2$O’O$_6$ which is attributed to weaker Bi-S versus Bi-O interactions that leads to stronger hybridization between the

Figure 4-9. The electron localization function for Bi$_2$Ru$_2$O’S$_6$ with atomic displacement for part of the (101) plane passing through one Bi atom (center), two O’ (atoms included) and two S ions. The ELF values range from 0.0 (red) to 0.8 (purple) as indicated by the scale.
Bi and O’ states that favors the lone pair formation. Finally, it is shown that by substituting S on the B$_2$O$_6$ network of Bi$_2$Ru$_2$O’O$_6$ cation displacement and lone pair formation can be induced in the metallic Bi pyrochlores by disrupting the Bi-O interactions. This result suggests that modifying the B$_2$O$_6$ network to reduce the interactions with the A$_2$O’ network will assist in promoting cation displacement.
CHAPTER 5
ROLE OF VACANCIES ON CATION DISPLACEMENT IN PYROCHLORES

5.1 Introduction

As shown in Chapter 3, even without cation substitutions, various bismuth pyrochlores exhibit atomic displacements [20,23,28,35]. Section 3.3.2 examined cubic bismuth pyrochlores without cation substitutions, with molecular formula Bi$_2$B$_2$O$_6$O' ($B^{4+}$=Ti, Ru, Rh, Ir, Os, and Pt), and directly probed for atomic displacements [104]. It was found that atomic displacement was energetically favorable only in Bi$_2$Ti$_2$O$_7$ and the observed displacement magnitudes and patterns [104] agreed very well with experimental reports [23,28]. These simulations provided critical insight into the main driving force behind the atomic displacement through electronic structure features. In Bi$_2$Ti$_2$O$_7$, it was shown increased overlap between Bi $s$, Bi $p$, and O’ 2$p$ states not observed in any of the other compounds considered and these interactions lead to the formation of an asymmetric $p$-type lone pair on the Bi cations. These interactions were suppressed in the metallic pyrochlores (e.g. Bi$_2$Ru$_2$O$_6$O’) due to strong O-{$B^{4+}$} and O-Bi interactions. In Chapter 4, sulfur was substituted onto the oxygen site in both sub-networks to determine the necessary interactions that lead to lone pair formation. Sulfur substitution on the bismuth ruthenate, in Section 4.3.3, showed lone pair formation could be induced by modifying the O-{$B^{4+}$} and O-Bi interactions.

Bismuth ruthenate pyrochlores have been synthesized with several stoichiometries including oxygen and bismuth vacancies [20,22,109,110] and in general can be considered a non-stoichiometric compound. Further, based on neutron diffraction data atomic displacement occurs on both the bismuth and oxygen sites [20]. As discussed in Section 3.3.2.2, the first principles calculations [104] of stoichiometric bismuth ruthenate
directly disagreed with the experimental reports on the favorability of atomic
displacements [20]. Based on the discussion in Section 4.3.3, the observed atomic
displacement was attributed to the O’ vacancies. However, Goodwin et al. question the
likelihood of the oxygen vacancies in triggering the observed displacements since their
reverse Monte Carlo models of the stoichiometric system showed atomic displacement
and the simulated electron diffraction patterns were qualitatively comparable to
experimental results [98]. Section 4.3.3 for stoichiometric bismuth ruthenate (i.e.
Bi$_2$Ru$_2$O$_7$) showed atomic displacement may be induced by strengthening the Bi-O’
interactions as a secondary effect of weakening the Bi-O interactions by substituting S
onto the Ru$_2$O$_6$ sub-network [111]. In the case of O’ and Bi vacancies the local Bi-O’
bonds should be strengthened due to the under-coordination, and likely trigger atomic
displacements within the deficient bismuth ruthenate.

This chapter used DFT calculations to (1) provide additional confirmation that
oxygen and bismuth vacancies trigger atomic displacements within bismuth ruthenate
pyrochlore and (2) illustrate the displacement patterns and electronic structure differ for
vacancy triggered displacement from the displacement observed in Bi$_2$Ti$_2$O$_7$ attributed
to the formation of a p-type lone pair [104].

5.2 Calculation Details

As discussed in Section 2.2.1, the pyrochlore structure is often viewed as two
interpenetrating networks of Bi$_2$O’ and Ru$_2$O$_6$ [15] (see Figure 2-3). This chapter
focuses on the Bi$_2$O’ network since the vacancies and atomic displacements are
isolated to this sub-network [20]. For completeness, the crystallographic details of the
structure reported in Section 3.3.1 for stoichiometric Bi$_2$Ru$_2$O$_7$ [104] and that determined
based on neutron diffraction data taken at 12 K by Avdeev et al. [20] for Bi$_{1.9}$O’$_{0.9}$Ru$_2$O$_6$
are both reported in Table 5-1. This ideal structure previously determined for Bi$_2$Ru$_2$O$_7$ served as the starting point for all calculations which were performed with Vienna *Ab-initio* Simulation Package (VASP) [44-47] with details matching that reported in Section 3.2 except the force criteria was slightly lowered to 0.005 eV/Å. The Bi$_2$Ti$_2$O$_7$ system before (from Section 3.3.1) and after atomic displacement (from Section 3.3.2.1) was reexamined with the force criteria used here and confirmed the energy of displacement and displacement pattern are equivalent to that previously reported in Section 3.3.2.1.

### 5.3 Vacancy Configurations

The four pyrochlore bismuth ruthenate compositions reported in the literature are Bi$_2$O’$_{0.95}$Ru$_2$O$_6$ [110], Bi$_2$O’$_{0.9}$Ru$_2$O$_6$ [22], Bi$_2$O’$_{0.7}$Ru$_2$O$_6$ [109], and Bi$_{1.9}$O’$_{0.9}$Ru$_2$O$_6$ [20], with the oxygen vacancy attributed to the O’ site. In the ideal pyrochlore there are eight symmetrically equivalent O’ anions within the unit cell. Therefore, the experimental composition (Bi$_2$O’$_{0.9}$Ru$_2$O$_6$) [22] is nearly matched by removing one O’ atom from the unit cell to give Bi$_2$O’$_{0.875}$Ru$_2$O$_6$ as the simulated composition. Since the choice of which O’ anion is removed is irrelevant due to symmetry, one O’ anion in the middle of the ideal unit cell was selected to serve as the O’ vacancy site.

**Figure 5-1** illustrates the Bi$_2$O’ subnetwork with two unit cells connected along the [110] direction of this configuration viewed along the [110] (in Figure 5-1a) and [001] (in Figure 5-1b) direction. The two empty unit cells along the [110] direction are outlined to aid in visualizing the perspective between the two filled cells. This type of structure is termed V$_{0^*}$ with the O’ vacancy site outlined by an empty frame. The experimentally reported composition of Bi$_{1.9}$O’$_{0.9}$Ru$_2$O$_6$ [20] was simulated by removing one of the 16 Bi cations to give a nearly equivalent simulated composition of Bi$_{1.875}$O’$_{0.875}$Ru$_2$O$_6$. 


Figure 5-1. The Bi$_2$O’$_{0.875}$ subnetwork viewed along the (a) [$\overline{1}$10] and (b) [001] direction. For visual aid, the tetrahedra at the O’ vacancy site is distinguished by an empty frame, the unit cell is outlined by a dashed line, and the (empty) unit cell along [100] and [010] are included. (c) The Bi$_{1.875}$O’$_{0.875}$ local structure is isolated with two types of Bi vacancy sites distinguished by half and quarter filled atoms.

Following the selection of the O’ vacancy the symmetry of the structure reduces the number of distinguishable Bi vacancy sites to two types. The first type has the bismuth vacancy within the tetrahedron outlined as the empty frame and one possibility is illustrated as a half filled Bi cation site in Figure 5-1c. This type of structure places the
Bi vacancy as the first nearest neighbor to the O’ vacancy and is referred to as $V_{O'}^\circ - V_{Bi}^\circ$.

The second type of vacancy configuration places the Bi vacancy at the second nearest neighbor site or one tetrahedron away from the oxygen vacancy. This configuration is named $V_{O'}^\circ - Bi_3O' - V_{Bi}^\circ$ and one of the possible Bi sites meeting this symmetry is highlighted in Figure 5-1c as a quarter filled Bi cation.

The crystallographic details for all three deficient structures after simulating annealing are reported for the Bi and O’ atoms in Table 5-1. Figure 5-2a shows the O’-Bi-O’ structure with the three different Bi displacement types $96h$, $96g$, $192i$ from light to dark isolated in Figure 5-2b and the two types of O’ displacements isolated in Figure 5-5c along with the experimentally reported displacement parameters as the gray ellipsoids.

Figure 5-2. A local (a) O’-Bi-O’ bonding network with the three possible Bi (from light to dark $96h$, $96g$, $192i$) and two O’ types of displacements reported in Table 5-1. An alternative view along the [111] direction isolating the (b) Bi and (c) O’ local displacement pattern. The displacement reported by Avdeev et al. [20] is included as the translucent gray ellipsoids.
Table 5-1. Complete crystallographic parameters for B-centered ideal Bi$_2$Ru$_2$O$_7$ from DFT for space group Fd3m with $a = 10.205$ Å compared with refinement for Bi$_{1.9}$O$_{0.9}$Ru$_2$O$_6$ from neutron diffraction data taken at 12 K with $a = 10.270$ Å. Crystallographic parameters for Bi and O' following simulated annealing for Bi$_2$O'$_{0.875}$Ru$_2$O$_6$, and both Bi$_{1.875}$O'$_{0.875}$Ru$_2$O$_6$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>Site</th>
<th>Site</th>
<th>Site</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hinjosa et al. Bi$_2$O'Ru$_2$O$_6$ [104]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td>16d</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>Ru</td>
<td>16c</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>O</td>
<td>48f</td>
<td>0.329</td>
<td>0.125</td>
<td>0.125</td>
<td>1</td>
</tr>
<tr>
<td>O'</td>
<td>8b</td>
<td>0.375</td>
<td>0.375</td>
<td>0.375</td>
<td>1</td>
</tr>
<tr>
<td>Avdeev et al. Bi$<em>{1.9}$O'$</em>{0.9}$Ru$_2$O$_6$ [20]</td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td>96h</td>
<td>0</td>
<td>0.240</td>
<td>0.760</td>
<td>0.157</td>
</tr>
<tr>
<td>Ru</td>
<td>16c</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>O</td>
<td>48f</td>
<td>0.327</td>
<td>0.125</td>
<td>0.125</td>
<td>1</td>
</tr>
<tr>
<td>O'</td>
<td>(model 2)</td>
<td>8b</td>
<td>0.375</td>
<td>0.375</td>
<td>0.375</td>
</tr>
<tr>
<td>O'</td>
<td>(model 3)</td>
<td>32e</td>
<td>0.382</td>
<td>0.382</td>
<td>0.382</td>
</tr>
<tr>
<td>Bi$<em>2$O'$</em>{0.875}$Ru$_2$O$_6$ (configuration V'O')</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td>96h</td>
<td>0</td>
<td>0.240</td>
<td>0.760</td>
<td>0.167</td>
</tr>
<tr>
<td>O'</td>
<td>32e</td>
<td>0.388</td>
<td>0.388</td>
<td>0.388</td>
<td>0.125</td>
</tr>
<tr>
<td>O'</td>
<td>32e</td>
<td>0.380</td>
<td>0.380</td>
<td>0.380</td>
<td>0.094</td>
</tr>
<tr>
<td>Bi$<em>{1.875}$O'$</em>{0.875}$Ru$_2$O$_6$ (configuration V'O' - V'Bi)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td>at V'O'</td>
<td>192i</td>
<td>0.506</td>
<td>0.512</td>
<td>0.520</td>
</tr>
<tr>
<td>Bi</td>
<td>96h</td>
<td>0</td>
<td>0.238</td>
<td>0.762</td>
<td>0.125</td>
</tr>
<tr>
<td>O'</td>
<td>at V'Bi</td>
<td>32e</td>
<td>0.391</td>
<td>0.391</td>
<td>0.391</td>
</tr>
<tr>
<td>O'</td>
<td>32e</td>
<td>0.380</td>
<td>0.380</td>
<td>0.380</td>
<td>0.125</td>
</tr>
<tr>
<td>Bi$<em>{1.875}$O'$</em>{0.875}$Ru$_2$O$_6$ (configuration V'O' - Bi$_3$O' - V'Bi)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td>at V'O'</td>
<td>96h</td>
<td>0</td>
<td>0.238</td>
<td>0.762</td>
</tr>
<tr>
<td>Bi</td>
<td>96g</td>
<td>0.509</td>
<td>0.509</td>
<td>0.487</td>
<td>0.115</td>
</tr>
<tr>
<td>O'</td>
<td>at V'Bi</td>
<td>32e</td>
<td>0.389</td>
<td>0.389</td>
<td>0.389</td>
</tr>
<tr>
<td>O'</td>
<td>32e</td>
<td>0.380</td>
<td>0.380</td>
<td>0.380</td>
<td>0.094</td>
</tr>
</tbody>
</table>
5.4 Results and Discussion

5.4.1 Structural Details

5.4.1.1 Bi$_2$O'$_{0.875}$Ru$_2$O$_6$ composition

Within the V$_{O'}^-$ configuration, the Bi cations directly surrounding the O’ vacancy site experience unbalanced forces when occupying the high symmetry sites; therefore, following minimization, the local Bi cations displace off their ideal site towards the missing O’. Following simulated annealing, the other Bi cations within the structure also displace but the difference in the total system energy is negligible between the two states. The Bi cation displaces to a 96h(0, y, -y) Wyckoff site with y=0.010 Å. As seen in Figure 5-2b, this type of Wyckoff site has six equally occupied positions with a displacement magnitude of 0.14 Å from the ideal high symmetry site. The Bi cations near the vacancy site before and after annealing showed the Bi displaced preferentially towards the open space created by the vacancy. This is further illustrated by the change in bond lengths following displacement, summarized in Table 5-2.

In the ideal structure, the Bi-O’ bond length was 2.21 Å but the Bi-O’ bond length is shortened to 2.11 Å after displacement for the Bi cations located at the O’ vacancy, i.e. the Bi cations illustrated as half filled in Figure 5-1c. For the Bi cations illustrated as quarter filled in Figure 5-1c, the Bi-O’ bond lengths are elongated to 2.28 Å. However, the Bi cations linking two complete (O’Bi$_4$) tetrahedra follow the equal probability occupation of the equivalent Wyckoff positions. The bond lengths for these Bi cations are 2.23 Å and match that seen for the ideal structure. The Bi displacement splits the six Bi-O bonds into three types with bond lengths of 2.41 Å, 2.51 Å, and 2.65 Å, which agrees very well with experimentally determined bond lengths [20,110].
Table 5-2. Average bond lengths (in Å) in the ideal and displaced structure for the various configurations, all standard deviations are less than 0.005. The Bi-O’ bond lengths near and away from the vacancy site are separated and any short/long bonds at the vacancies are distinguished.

<table>
<thead>
<tr>
<th>Bond Lengths</th>
<th>Bi-O’ at vacancy</th>
<th>Bi-O</th>
<th>Ru-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi$_2$Ru$_2$O$_7$</td>
<td>2.21</td>
<td>2.51</td>
<td>1.98</td>
</tr>
<tr>
<td>Bi$<em>2$O’$</em>{0.95}$Ru$_2$O$_6^a$</td>
<td>2.23</td>
<td>2.55</td>
<td>1.98</td>
</tr>
<tr>
<td>Bi$<em>2$O’$</em>{0.9}$Ru$_2$O$_6^b$</td>
<td>2.23</td>
<td>2.55</td>
<td>1.98</td>
</tr>
<tr>
<td>Displaced</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi$<em>2$O’$</em>{0.875}$Ru$_2$O$_6$ (V’$_O$)</td>
<td>2.23</td>
<td>2.11,2.28</td>
<td>2.41,2.51,2.65</td>
</tr>
<tr>
<td>Bi$<em>2$O’$</em>{0.95}$Ru$_2$O$_6^a$</td>
<td>2.23</td>
<td>2.42,2.56,2.69</td>
<td>1.98</td>
</tr>
<tr>
<td>Bi$<em>{1.875}$O’$</em>{0.875}$Ru$_2$O$_6$ (V’$<em>O$’ - V’$</em>{Bi}$)</td>
<td>2.21</td>
<td>2.09,2.31</td>
<td>2.39,2.51,2.69</td>
</tr>
<tr>
<td>Bi$<em>{1.875}$O’$</em>{0.875}$Ru$_2$O$_6$ (V’$_O$’ - Bi$<em>3$O’ - V’$</em>{Bi}$)</td>
<td>2.23</td>
<td>2.09,2.31</td>
<td>2.39,2.51,2.70</td>
</tr>
<tr>
<td>Bi$<em>{1.9}$O’$</em>{0.9}$Ru$_2$O$_6^c$</td>
<td>2.23</td>
<td>2.42,2.55,2.67</td>
<td>1.98</td>
</tr>
</tbody>
</table>

$^a$Ref. [110], $^b$Based on structure in Ref. [22], $^c$Based on structure in Ref. [20]

Additionally, following annealing the O’ anions displace off the high symmetry site to retain appropriate bonding distances to the displaced Bi cations. However, the degree of displacement depended on the proximity to the vacancy site. For the O’ anions that are directly bound to the Bi cations forming the empty frame illustrated in Figure 5-1a or the vacancy site’s nearest neighboring Bi cations, the O’ anions displace into a 32e(x, x, x) type site with an x parameter of 0.388 and 4 equally probable positions 0.23 Å away from the ideal site. The O’ anions away from the first nearest Bi cations displace with a magnitude of 0.09 Å also into a 32e site. The O’ anions bound to the half filled Bi cations in Figure 5-1c displace preferentially towards these three fold coordinated Bi cations and the O’ anions away from the vacancy equally occupy the four equivalent 32e sites. The preferential displacement of the O’ anions towards the half filled in Figure 5-1c leads to the splitting of the Bi-O’ bond lengths detailed above. As will be shown later through bond valance sums, this difference in displacement
magnitude is due to the degree of under-coordination of the Bi at the vacancy site. The resulting displacement pattern for both the Bi and O’ determined here match well to those reported by Avdeev et al. [20] One notable discrepancy is the assignment for the O’ anions, Avdeev et al. also reports a 32e(x, x, x) site however the magnitude of displacement is significantly lower at 0.12 Å. The displacement pattern of both types of O’ reported here are within the ellipsoids predicted by the thermal parameter reported by Avdeev et al. [20], as seen in Figure 5-2c. In Bi$_2$Ti$_2$O$_7$, it was observed that following atomic displacement the cubic lattice expands from 10.23 Å to 10.34 Å to accommodate the Bi and O’ displacements and Bi lone pair formation [104]. A similar expansion is anticipated in bismuth ruthenate, especially since the lattice constant is underestimated by DFT at 10.205 Å versus the experimental values from 10.270 Å [20] to 10.299 Å [109]. Following simulated annealing, lattice expansion was investigated by reevaluating the lattice constant versus total lattice energy profile with the annealed structure. No lattice expansion was found in any of the three configurations. Though this seems to contradict previous observations, when considering the displacement patterns and lone pair formation discussed in Section 5.4.2, the bismuth ruthenate lattice is less perturbed by atomic displacement than the bismuth titanate lattice. The displacements are smaller in magnitude and the atoms tend to displace towards the open space created by the vacancy near the vacancy.

5.4.1.2 Bi$_{1.875}$O’$_{0.875}$Ru$_2$O$_6$ composition

For the V$_{O’}$ - V$_{Bi}$ configuration, the Bi and O’ atoms in the ideal sites immediately displace due to unbalanced forces and the displacement magnitudes depend on the proximity to the vacancy sites, as seen in Table 5-2. Near the O’ vacancy, the Bi cations
displace into a $192i(x, y, z)$ type site with $x=0.006$, $y=0.012$, and $z=0.020$ and a displacement magnitude of 0.24 Å. This displacement pattern would result in 12 equivalent positions, shown in Figure 5-2b, but again the Bi cations preferentially displace towards the vacancy site. Away from the O’ vacancy site, the Bi cations displace into a $96h(0, y, -y)$ type with $y=0.012$ and a displacement magnitude of 0.17 Å. As with the $V^\bullet_O$ configuration, the Bi cations away from the vacancy site occupy the six equivalent positions equally. The O’ anions near the Bi vacancy displace off the high symmetry site by a much larger magnitude of 0.29 Å into a $32e$ site with $x=0.391$. The O’ anions away from the Bi vacancy follow the same pattern as those O’ anions in the $V^\bullet_O$ configuration with a displacement magnitude of 0.09 Å. The larger Bi and O’ displacements shortened the Bi-O’ bond length to 2.09 Å for the half filled Bi cations in Figure 5-1c and slightly elongate the Bi-O’ bond length to 2.31 Å for the quarter filled Bi cations in Figure 5-1c. The Bi-O bonds are slightly altered from the $V^\bullet_O$ configuration, as summarized in Table 5-2.

Similarly, the $V^\bullet_O$ - Bi$_3$O’ - V$^\bullet_{Bi}$ configuration showed the same type of displacement pattern with regards to proximity to the vacancy sites. The Bi cations near and away from the O’ vacancy displace into a $96h$ and $96g$ site with a magnitude of 0.17 and 0.18 Å, respectively. Again all O’ anions displace into a $32e$ site but the 0.09 or 0.24 Å magnitude of the displacement depends on the proximity to the Bi vacancy. Despite the differences in the displacement patterns seen in Figure 5-2, the bond lengths in Table 5-2 for the $V^\bullet_O$ - Bi$_3$O’ - V$^\bullet_{Bi}$ configuration essentially match the $V^\bullet_O$ - V$^\bullet_{Bi}$ configuration.

In both configurations with O’ and Bi vacancies, the atomic displacements are favored by 1.38 eV/unit cell over the ideal high symmetry sites and that annealing does
not significantly affect the final displacement pattern or total energy. In comparison, displacement and lattice expansion was favored on average by 2.3 eV/unit cell in Bi$_2$Ti$_2$O$_7$ [104]. The clustering of the vacancies into one tetrahedron (the V$^{\cdot\cdot}_O$ - V$^{\cdot\cdot}_Bi$) is slightly more favorable by 0.25 eV/unit cell than the V$^{\cdot\cdot}_O$ - Bi$_3$O$^{\cdot\cdot}$ - V$^{\cdot\cdot}_Bi$ configuration. Unlike Goodwin et al. [98], a long range correlation is not found in the displacements of the Bi cations. In Bi$_2$Ti$_2$O$_7$, displacement correlation reduced the local lattice strain due to stereochemical restriction of the bismuth lone pair [104]. However, in the Bi$_{1.875}$O$^{\cdot\cdot}_{0.875}$Ru$_2$O$_6$ system the local network is not strained due to the open space created by the vacancy. Therefore, correlation of the displacement may not be necessary to stabilize the atomic displacement to reduce the local strain. Goodwin et al. [98] used Bi$_2$O$'Ru_2$O$_6$ and upon displacement the corner sharing tetrahedra rotate in a β-cristobalite type displacive disorder with minimal tetrahedron distortion as described by rigid unit modes [73-76]. Though the concentration of oxygen vacancies is low it essentially matches the experimental concentrations. At these concentrations, within a single unit cell with periodic boundary conditions, a single oxygen vacancy disrupts the long range network every third tetrahedron along the <110> direction. This frequent disruption is sufficient to overcome the rigid unit mode type of displacive disorder and leads to tetrahedra distortion and rotation.

Bond valance sums (BVS) is often used to measure the degree of bonding strain at the local bonding level by combining the local bond lengths and geometry to determine if the coordination satisfies each atom’s oxidation state [80,112], see Section 2.2.3 for details. Using the appropriate parameters [80,113], the BVS was determined for the ideal stoichiometric and deficient structures and compared them to that of the
fully relaxed deficient structures, which are summarized in Table 5-3. In the ideal structure, the O' vacancy introduces a significant decrease in the large BVS of the Bi cations neighboring the vacancy site from 3.4 v.u. to 2.7 v.u. With the inclusion of a Bi vacancy, the local O' BVS reduces from 2.9 v.u. to 2.2 v.u. It is clear to see with these significant changes in the local bonding environment that the O' and Bi cations would alter their local bonding networks through displacement to reduce the local strain.

Table 5-3. Average bond valence sums (BVS) in valence units (v.u.) for each atom type in the ideal and displaced structure for the various configurations, all standard deviations are less than 0.05. For the Bi and O' types the BVS near (away from) the vacancy site are distinguished.

<table>
<thead>
<tr>
<th>BVS</th>
<th>Bi</th>
<th>Ru</th>
<th>O'</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi2Ru2O7</td>
<td>3.4</td>
<td>4.1</td>
<td>2.9</td>
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</tr>
<tr>
<td>Bi2O'0.875Ru2O6</td>
<td>2.7 (3.4)</td>
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<td>2.9</td>
<td>2.0</td>
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<tr>
<td>Bi2O'0.9Ru2O6a</td>
<td>3.0</td>
<td>4.0</td>
<td>2.8</td>
<td>1.9</td>
</tr>
<tr>
<td>Bi1.875O'0.875Ru2O6</td>
<td>2.7 (3.4)</td>
<td>4.1</td>
<td>2.2 (2.9)</td>
<td>2.0</td>
</tr>
<tr>
<td>Displaced</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi2Ru2O7b</td>
<td>3.0</td>
<td>4.1</td>
<td>2.2</td>
<td>2.0</td>
</tr>
<tr>
<td>Bi2O'0.875Ru2O6</td>
<td>3.0 (3.3)</td>
<td>4.1</td>
<td>2.8</td>
<td>2.0</td>
</tr>
<tr>
<td>Bi1.875O'0.875Ru2O6</td>
<td>3.1 (3.3)</td>
<td>4.2</td>
<td>2.2 (2.7)</td>
<td>2.0</td>
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<tr>
<td>Bi1.9O'0.9Ru2O6c</td>
<td>3.2</td>
<td>4.0</td>
<td>2.8</td>
<td>1.9</td>
</tr>
</tbody>
</table>

aBased on structure in Ref. [22], bRef. [98], cBased on structure in Ref. [20]

Within (Bi1.5Zn0.5)(Zn0.5Nb1.5)O7 (BZN), Withers et al. [10] showed BVS play a key role in pushing the under-coordinated Bi (2.5 v.u.) cations towards the under-bonded O (1.7 v.u.) within the in B2O6 network to reduce both the Bi and O under-bonding instead of displacing towards the O' anions with a BVS of 2.0 v.u. within the A2O' network.

Within bismuth ruthenate, after displacement it is observed that the BVS (in Table 5-3) of Bi near the O' vacancy is 3.1 v.u. and 3.3 v.u. away from the vacancy, with corresponding Bi-O' bond lengths (in Table 5-2) of 2.09 Å and 2.23 Å, respectively.

Also, the BVS of O' near the Bi vacancy is 2.2 v.u. while away it is 2.7 v.u. This reduction in the total BVS across the Bi2O' network leads to a slight increase in the BVS.
of Ru from 4.1 v.u. in the ideal structure to 4.2 v.u. in the displaced system, with only a slight decrease in the Ru-O bond length from 1.98 Å to 1.97 Å. The average BVS values were determined based on the structures reported for the experimental compounds [20,22] and find good agreement with the DFT values. For Bi$_2$O’$_{0.9}$Ru$_2$O$_6$,[22] within the ideal pyrochlore structure, the BVS values are 3.0 v.u., 4.0 v.u., and 2.8 v.u. for Bi, Ru, and O’, respectively and for Bi$_{1.9}$O’$_{0.9}$Ru$_2$O$_6$[20] the average BVS values only differed for Bi with 3.2 v.u. When the values are averaged, the Bi values agree very well but the experimental based Ru values are slightly lower and the O’ values are slightly higher than what was determined here.

5.4.2 Electronic Structure

To help identify changes in the bonding within the displaced structure, the electron localization function (ELF) was examined for various planes. The ELF provides a real space mapping of the probable distribution of electrons based on the Pauli exclusion principle, where a fully localized (delocalized) electron has an ELF value of 1 (0).[65,66,114] The ELF is plotted in Figure 5-3a for the fully relaxed V’’’$_O$ - Bi$_3$O’ - V$_{Bi}$ configuration in the (111) plane isolating the Bi cations near the O’ vacancy and the O’ anions at the Bi vacancy with the scale shown. Figure 5-3b outlines the equivalent structure plane in a black box. The three Bi cations displaces toward the center of the O’ vacancy site in Figure 5-3a. An asymmetric lobe of increased electron localization forms at each of the Bi cations and each of these lobes point towards the vacant space.

In other bismuth pyrochlore systems that exhibit displacement, the lone pair forms in the opposite direction to the observed displacement; however, here the lone pair and displacement are in the same direction. This difference is due to the open space
created by the vacancies within the structure. In fact, unlike stoichiometric bismuth pyrochlores, within the ideal high symmetry sites, the Bi cations still exhibit an asymmetric lobe pointed into the open space created by the vacancy. Within the other vacancy configurations the Bi cations also illustrated an asymmetric lobe both before and after displacement off the high symmetry site.

Figure 5-3. Part of the (111) plane of the $V_{O'}^+ - Bi_{3}O' - V_{Bi}^{'''}$ configuration showing the (a) electron localization function with scale and the (b) solid black box outlining the equivalent structure plane including the three Bi cations near the O’ vacancy (center of empty tetrahedron frame) and the two O’ anions at the Bi vacancy (quarter filled atom). For visual aid two RuO$_6$ octahedra are included and Bi cations above and below the plane are lighten.

### 5.5 Summary

Through DFT calculations, it is shown that vacancies on the Bi$_2$O’ network trigger atomic displacements of both the Bi and O’ atoms due to alterations of the local Bi-O’ interactions. For the three vacancy configurations considered, it is found that the O’ anions displace off the high symmetry site into a 32e site but the magnitude of
displacement depends both on the type of configuration as well as the proximity to the vacancies present in the structure. In all cases, the O’ displacement predicted by DFT is well within the displacement pattern predicted by neutron diffraction data [20]. The magnitude and type of Bi displacement varied both by system and proximity to vacancies. No correlation of the atomic displacements is found, indicating even a small concentration of O’ vacancy is sufficient to reduce the local stretic strain on the A₂O’ network due to Bi lone pair formation from atomic displacement.

This work suggests the intentional inclusion of oxygen vacancies could be used to induce atomic displacements in bismuth pyrochlores and disrupt long range correlation which should improve the observed dielectric properties. Du et al. [115] examined various compositions of BZN and found the dielectric constant decreased with increasing oxygen vacancy concentration; however, this reduction was partially attributed to the substitution of the less polarizable Zn cation for the Bi cations due to valance compensation for the increasing oxygen vacancy concentration on the O’ site, in addition to the formation of secondary phases. Therefore, it would be interesting to see a similar study of vacancy concentration influence on dielectric properties in a bismuth pyrochlore with only Bi on the A site.

Additionally, it was previously shown that displacement may be triggered by weakening the Bi-O interactions and thereby strengthen the Bi-O’ interactions [104]. This chapter showed altering the bond strain at a local level by the inclusion of Bi and O’ vacancies also induces atomic displacement. Though the role of vacancies is sufficiently important since many synthesized bismuth pyrochlores are slightly deficient in the A₂O’ network, this strain affect should not be limited to the presence of vacancies.
alone. Intentionally doping the system with cation substitutes on the $A_2O'$ or $B_2O_6$
network would create varying local bond strain affects as well as significant alterations
of the Bi-O' and Bi-O interactions and either may trigger atomic displacements.
CHAPTER 6
BISMUTH PYROCHLORES WITH CATION SUBSTITUTES

6.1 Introduction

Chapters 3, 4, and 5 focused on isolating and understanding the triggers behind atomic displacement in bismuth pyrochlores without cation substitution. Section 3.3.3 showed the interactions between Bi-O and Bi-O’ are critical to atomic displacement induced by lone pair formation. Section 5.4 showed atomic displacement may also be induced by altering the local interactions, through the introduction of a vacancy. Though these simple pyrochlores are also important, the majority of work investigating the bismuth pyrochlore family has focused on compounds that include Bi$_{1.5}$ZnNb$_{1.5}$O$_7$ (BZN) [13] Bi$_{1.5}$ZnTa$_{1.5}$O$_7$ (BZT), Bi$_{1.5}$MgNb$_{1.5}$O$_7$ (BMN), Bi$_{1.5}$MgTa$_{1.5}$O$_7$ (BMT), and Bi$_{1.5}$ZnSb$_{1.5}$O$_7$ (BZS) due to their dielectric properties [37,38] in addition to compounds incorporating multiple substitutions such as (Bi$_{1.5}$Zn$_{0.5}$)(Ti$_{1.5}$Nb$_{0.5}$)O$_7$ (BZNT) [39].

These complex bismuth based pyrochlores are often studied due to their combination of ideal characteristics for capacitors and high-frequency filter applications [3]. The phonon modes for BZN, BZT, BMN and BMT have been indentified [38] and the dielectric properties of ten bismuth pyrochlore compounds have been examined [3]. Though each of the compounds detailed above have interesting properties, one system of particular interest is BZN, with Bi$_{1.5}$Zn$_{0.92}$Nb$_{1.5}$O$_{6.92}$ as the molecular formula, has been shown to be both zinc and oxygen deficient and to have disordered displacement on both the A and O’ site [13].

As discussed in Section 5.4.1.2, bond valence sum analysis of BZN has shown the atomic displacement observed is necessary to alleviate the under-coordination of O’ and Bi [10]. Based on the structural analysis in Section 5.4, it is expected in BZN the O’
and Zn deficiencies would also contribute to the atomic displacements locally with the displacements magnitudes decreasing with increasing distance from the vacancy sites.

Experimentally the atomic displacements that have been reported through the neutron and X-ray diffraction data have been linked to the dielectric permittivity [37]. It is proposed that the atomic displacement of Bi cations is due to the formation of an active lone pair. The lone pair formation has been linked to the atomic displacement in Section 3.3.3 and 4.3.2 in addition to 5.4.2. It is therefore expected that the Bi cations within these complex pyrochlores would also exhibit lone pairs.

The active lone pair and local dipole moments should both contribute to the overall dielectric permittivity as discussed in Section 1.1.2. As discussed by Melot et al., the magnitude of the A and O’ atomic displacement is correlated to the dielectric permittivity due to the dipole moments created between these atoms [37]. Due to all of these structural details that affect the dielectric permittivity, the bond lengths and atomic displacement magnitudes will be discussed in Section 6.4.2.

Based on neutron diffraction data of BZN, short range ordering of metal ions and under-coordination of cations induced relaxation has been proposed [10]. As will be discussed in Section 6.2, there are various ways the cation substitutes could be arranged within the ideal pyrochlore structure.

DFT may examine various atomic structure changes in the complex bismuth pyrochlores to identify energy differences between the atomic structures. To help focus the investigation Section 6.4.1 and 6.4.2 will examine the energetics of Zn ordering and predicted structural details including atomic displacements in BZN. Then Section 6.4.3 will compare both the energetics and structures of BZN, BZT, BMN, and BMT.
6.2 Atomic Structure Ordering Predictions in BZN

6.2.1 Bond Valence Analysis of BZN

Using the local chemistry of the pyrochlore structure, Withers et al. [10] predicted favorable configurations and identified four potential rules for the Zn substitution into the $A_2B_2O_7$ compound. Withers et al. completed a bond valence analysis for both the $A_2O'$ and $B_2O_6$ network for Bi, Zn, and Nb cations and O' and O anions to determined the magnitude of atomic displacement needed to satisfy each atom's bond valence (see Section 2.2.3) [10].

Using an assumed stoichiometric system ($Bi_{1.5}ZnNb_{1.5}O_7$), the bond valence sums calculations predicted a $Nb^{5+}$-$O$ bond length of 1.98 Å and a $Zn^{2+}$-$O$ bond length of 2.11 Å for the $(Zn_{0.5}Nb_{1.5})O_6$ network. These bond lengths were compared to the average cation to oxygen bond length on the B site from experiment of 2.01 Å, indicating the Nb would pull O in by about 0.03 Å and the Zn would push O away by about 0.09 Å.

In the $(Bi_{1.5}Zn_{0.5})O'$ network, the predicted $Bi^{3+}$-$O'$ bond length was 2.35 Å and the $Zn^{2+}$-$O'$ bond length was predicted to be 1.96 Å. Based on the structural parameters determined experimentally, the average A-O' bond length is 2.287 Å [11,18]. This would cause the Bi cations to pull the O' in by only 0.06 Å but the Zn will push the O' out by 0.33 Å.

Based on these displacement magnitudes, it can be seen that the four Zn cations that substitute onto the $A_2O'$ network cannot occupy the same tetrahedron, indicating there are favorable arrangements of Zn substitutions in the $A_2O'$ network.

In contrast, the displacement magnitudes predicted in the $B_2O_6$ network indicate this network is more receptive to the Zn substitution and therefore, Withers et al. predicted that the $B_2O_6$ network does not require specific ordering.
6.2.2 Zn Ordering Rules on the A$_2$O’ Network

Second, the A$_2$O’ is quite sensitive to Zn substitution so preferred configurations are identified to alleviate the strain created by Zn substitution. In each tetrahedron formed by four A cations (see Figure 2-3b), only one Zn will be favorably accepted resulting in a three to one ratio of Bi to Zn cations. The structural differences between the [2:2] ratio and the [3:1] ratio can be seen in Figure 6-1a and Figure 6-1b, respectively.

Thirdly, within the A$_2$O’ network there are two directional ordering possible, while maintaining the [3:1] ratio of Bi:Zn, one along $<011>$ and the second along $<211>$. Figure 6-1b shows a [3:1] ratio of Bi:Zn with all the Zn cations ordering along the $<211>$ direction and Figure 6-1c shows the [3:1] ratio with all the Zn cations ordering along the $<011>$ direction. Withers et al. [10] determined the $<211>$ direction, illustrated in Figure 6-1b, will be almost exclusively favored for the Zn substitution. These four rules were confirmed through comparing diffraction patterns from Monte Carlo models with those determined experimentally.

Fourthly, even in with an optimal ordering of the Zn substitutes, the atoms within BZN will exhibit displacement to satisfy their respective bond valence. The first three rules provide a framework to reduce the number of possible configurations that incorporate the Zn substitution to a subset that may be probed using density functional theory.

Section 6.3.1 outlines the various arrangements of Zn substitution on the A$_2$O’ network tested within this chapter and illustrated in Figure 6-1.
6.3 Calculation Details

6.3.1 Configuration Setup

As discussed in Section 2.2, the pyrochlore structure single unit cell contains sixteen A and sixteen B cation sites. In the BZN crystal, the Zn cations equally distribute into both the A and B cation site, resulting in four of the sixteen sites in both networks occupied by Zn cations. Even with the restriction on the relative distribution of the Zn cations between the A\(_2\)O\(^-'\) and B\(_2\)O\(_6\) networks, there exists a wide range of possible short-range and long-range cation ordering configurations. A large system containing multiple unit cells would be required to completely probe the role of short-range ordering of the Zn substitutions but such calculations using DFT are not computationally practical. Instead, a single unit cell was used and the effect of the Zn distribution was sampled by examining 120 different configurations. Using the results of Withers et al. [10] discussed in Section 6.2, ordering of the Zn in the A\(_2\)O\(^-'\) network, termed Zn\(_A\), was applied and a random distribution of Zn in the B\(_2\)O\(_6\) network, termed Zn\(_B\). Based on this observation, all of the configurations examined in this chapter fall into four types distinguished by the Zn\(_A\) cation ordering in the A\(_2\)O\(^-'\) network.

Figure 6-1 illustrates the differences between these four types of configurations. The first, labeled [2:2], has two of the four Zn cations sharing the center tetrahedron, as seen in Figure 6-1a. The remaining three types restrict the Bi to Zn ratio to [3:1] within each tetrahedron. As mentioned in Section 6.2, with the first Zn\(_A\) cation substitution site selected there are two directions to orient the remaining Zn cations in the unit cell [10], either along the \(<211>\) or the \(<011>\) direction. The second and third types strictly follow the \(<211>\) and \(<011>\) directional ordering and can be seen in Figure 6-1b and Figure 6-1c, respectively.
Figure 6-1. The A₂O’ network of oxygen centered tetrahedra with Znₐ (black) substitution in a (a) [2:2] ratio of Bi:Zn within the center tetrahedral and in a [3:1] ratio of Bi:Zn within all tetrahedra strictly ordering (b) along <211> or (c) <011> and (d) combining <211> with 1/3 <011> of the Znₐ substitutes. The arrows provided indicate the <211> (solid) and <011> (dashed) direction between the Znₐ cations.

The last configuration, illustrated in Figure 6-1d, combines the <211> and <011> ordering of the Znₐ-Znₐ, with 2/3 of the Znₐ-Znₐ cations oriented along <211> and 1/3 of the cations along <011>. It should be noted that the [2:2] configurations has 2/3 of the Znₐ-Znₐ oriented along <211> and 1/3 along <011>. For simplicity, these four types of
Zn\textsubscript{A} ordering within the A\textsubscript{2}O’ network will be referred to as [2:2], <211>, <011>, and 1/3 <011> throughout the chapter.

While the A\textsubscript{2}O’ network shows short-range ordering, to date there is no experimental evidence of ordering of the Zn substitutions within the B\textsubscript{2}O\textsubscript{6} network for BZN. The 120 configurations were created by selecting 30 different random distributions of Zn substitutions within the B\textsubscript{2}O\textsubscript{6} network and pairing the B\textsubscript{2}O\textsubscript{6} network with each of the four A\textsubscript{2}O’ networks detailed above. From an analysis of the energy distribution among the configurations, preferred ordering can be identified along with information on the average structure. This approach used here would not identify any long-range or superlattice ordering within BZN, but currently no experimental evidence indicating such long-range ordering in BZN has been reported.

6.3.2 VASP details

First-principles calculations were performed with Vienna Ab-initio Simulation Package (VASP),[44-47] and details match those discussed in Section 3.2. The Bi(5d, 6s, 6p), O(2s, 2p), Nb(4p, 4d, 5s), Ta(5p, 5d, 6s), Zn(4s,3d), and Mg(2p, 3s) orbitals were included as the valence electrons for the projector augmented wave (PAW) pseudopotentials provided in the VASP database [48,49]. The DFT calculations were performed within the local density approximation (LDA) [50] and a plane wave energy cutoff of 400 eV. All calculations were performed for a cubic cell with the lattice constant fixed to the low temperature experimental value of 10.55668 Å [13] for BZN, 10.54075 Å for BZT, 10.5525 Å for BMN, and 10.529 Å for BMT. The force criteria was reduced to 0.03 eV/Å with no significant changes observed between structures optimized to 0.03 eV/Å and those optimized to 0.001 eV/Å. Due to the number of configurations explored, only the Γ-point (1×1×1) was used for the k-mesh. This level of accuracy was confirmed
sufficient to capture the preferences in chemical ordering and atomic displacements by examining a few configurations with a cutoff energy of 500 eV and a $k$-mesh of $3 \times 3 \times 3$ with no difference to the level of accuracy reported within this chapter seen in structures.

6.4 Results and Discussion

6.4.1 Energetics of Zn Ordering in the A$_2$O’ Network in BZN

Figure 6-2 shows the energy after relaxation for all 120 configurations examined. Based on the average energy of each configuration type, the most stable Zn ordering is found in the $<211>$ type A$_2$O’ network, illustrated in Figure 6-1b. The $<211>$ configuration type is more favored by 0.47, 1.63, and 0.49 eV/unit cell than the [2:2], <011>, and 1/3 <011>, respectively. The average total lattice energy of all 30 configurations with the $<211>$ A$_2$O’ network provides the reference zero energy state for all energies values reported. Figure 6-2 shows the scaled energies of all 120 configurations with respect to this reference energy state.

Figure 6-2 also includes the average for each A$_2$O’ type (horizontal lines) and error bars (vertical lines on left and right of the data set) associated with one standard deviation from the average. Most of the individual configurations follow the stability order suggested by the average values but there are some outliers. This suggests that the Zn$_6$ distribution on the B$_2$O$_6$ network can have some influence on the stability of BZN. There is one B$_2$O$_6$ configuration that combines with the $<011>$ A$_2$O’ network to give a structure whose energy is well outside three standard deviations and is therefore removed from Figure 6-2 and the resulting discussion. Nevertheless, the ordering of the Zn$_A$ in the A$_2$O’ network is the dominant factor influencing the stability of the BZN system.
Figure 6-2. The relaxed energy in eV scaled by the average of the most favored $A_2O'$ network type for each of the 120 structures studied. The 30 $B_2O_6$ configurations (numbered 1-30 along the x-axis) are shown for each of the four types of the $A_2O'$ network separated into the [2:2] ratio (open diamond), the [3:1] ratio with only <211> ordering (square – most favored), the [3:1] ratio with only <011> ordering (triangle) and the [3:1] ratio with 1/3 <011> ordering (open circle).

The observed preference of the <211> ordering within the $A_2O'$ network over the other three $A_2O'$ networks agrees with Withers et al. [10]. However, the magnitude of energy by which the <211> type $A_2O'$ network is favored over the [2:2], <011>, and 1/3 <011> type networks indicates the energy cost of a higher local Zn$_A$ concentration is not as great as the energy needed order Zn$_A$ along the <011> direction.

It is important to note there is a configuration where the [2:2] $A_2O'$ network is more favored in the relaxed structure by a degree of about 0.1 eV. Though the 3 to 1 ratio is more often preferred, the $B_2O_6$ configuration of Zn cation substitution sites can mediate the unfavored cation ratio within the $A_2O'$ network by acquiring an appropriate
arrangement. However, since this is observed in only one of 30 B$_2$O$_6$ configurations it suggests that <211> would be preferred within the real crystal but the [2:2] is not forbidden.

Figure 6-2 contains a lot of information but the degree of scatter for some of the configurations can lead to confusion. To help simplify the information, the energies shown in Figure 6-2 are compressed into just the differences between the A$_2$O$'$ network and the B$_2$O$_6$ network is no longer distinguished. The compressed view is shown in Figure 6-3.

![Energy (eV)](image)

Figure 6-3. The relaxed energy in eV scaled by the average of the most favored A$_2$O$'$ network type for each of the 120 structures studied. The 30 B$_2$O$_6$ configurations are shown for each of the four types of the A$_2$O$'$ network separated into the [2:2] ratio, the [3:1] ratio with only <211> ordering (most favored), the [3:1] ratio with only <011> ordering and the [3:1] ratio with 1/3 <011> ordering.
The degree of scatter of these energies is seen by examining the energy difference between the most and least favored configuration for each A$_2$O’ type in Figure 6-3. The energy range for the configurations with the [2:2], <211>, <011>, 1/3 <011> A$_2$O’ networks are 1.25 eV, 1.0 eV, 1.75 eV, and 2.0 eV, respectively. The range for the <211> set is the smallest with the [2:2] set following as the next smallest. This ordering matching the order of favorability based on the average scaled energies. However, the 1/3 <011> average energy is nearly the same as the [2:2] set but the energy range for the 1/3 <011> set is the largest at 2.0 eV.

To understand the effect of atomic displacement with the BZN compound, the energy distribution was examined among the 120 configurations before atomic relaxation occurred. On average for the BZN system the <211> is (0.25±0.59) eV more favorable than a [2:2] in the unrelaxed “ideal” crystal structure. After atomic relaxation, the <211> is more favorable by (0.47 ± 0.28) eV. The total unrelaxed energy scaled to the average of the <211> configurations for each of the 30 configurations with the [2:2] A$_2$O’ network is shown as open diamonds in Figure 6-4.

The [2:2], <211>, <011>, and 1/3 <011> A$_2$O’ networks are shown as open diamonds, filled squares, filled triangles, and open circles, respectively. As with Figure 6-2, the average of each A$_2$O’ configuration is shown in solid (dashed) lines for the filled (open) symbols with error bars for one standard deviation included on the far left and right side of the graph.

It is interesting to note that the <011> and 1/3 <011> set averages are more favorable (lower thermodynamic energy) than the <211> set unlike in the relaxed structures. This indicates the <211> configurations significantly improve the
thermodynamic stability through preferred atomic displacements to reduce forces for all atoms. Additionally, by comparing the averages for each A\textsubscript{2}O\textsuperscript{'} set in both Figure 6-4 and 6-2 the order of the unrelaxed and fully relaxed scaled energies change. Before optimization, the order of thermodynamic stability is the [2:2], <211>, <011>, and 1/3 <011> but after the atomic forces are minimized, the order is <011>, 1/3 <011>, [2:2], and <211>, with the 1/3 <011> and [2:2] average energies being nearly equivalent (as seen in Figure 6-2).

Figure 6-4. The unrelaxed energy in eV scaled by the average of the <211> A\textsubscript{2}O\textsuperscript{'} network type for each of the 120 structures studied. The 30 B\textsubscript{2}O\textsubscript{6} configurations (numbered 1-30 along the x-axis) are shown for each of the four types of the A\textsubscript{2}O\textsuperscript{'} network separated into the [2:2] ratio (open diamond), the [3:1] ratio with only <211> ordering (square – most favored), the [3:1] ratio with only <011> ordering (triangle) and the [3:1] ratio with 1/3 <011> ordering (open circle).

As before in Figure 6-2, the degree of scatter for the scaled energy with each configuration is very large and there is a lot of information included in Figure 6-4 making
it difficult to compare these $A_2O'$ sets. To help visualize the differences between these configurations Figure 6-5 illustrates the same energies but the configurations are only distinguished by the $A_2O'$ network. As seen above for Figure 6-3, the energy range of the $A_2O'$ networks before optimization can be teased out and compared for each type of $Zn_A$ distribution. Before optimization, the energy range for the [2:2], <211>, <011>, 1/3 <011> sets are 2.25 eV, 2.0 eV, 2.0 eV, and 1.75 eV, respectively. In contrast, following atomic displacement the energy ranges are 1.25 eV, 1.0 eV, 1.75 eV, and 2.0 eV. It can be seen reducing the atomic forces significantly improves the spread of the [2:2] and <211> sets and only slightly improves the spread of the <011> set. However, the energy range of the 1/3 <011> set increases following relaxation from 1.75 eV to 2.0 eV.

Figure 6-5. The unrelaxed energy in eV scaled by the average of the <211> $A_2O'$ network type for each of the 120 structures studied. The 30 $B_2O_6$ configurations are shown for each of the four types of the $A_2O'$ network.
6.4.2 Structural Differences between A₂O’ Network Types in BZN

To determine the primary atomic interactions that affect BZN stability, the correlation of the energy to the average bond lengths in the system for the Bi-O’, Bi-O, Znₐ-O’, Znₐ-O, Nb-O, and Znₐ-O bonds were examined. The correlation plot for Znₐ-O’ showed interesting results and is included in Figure 6-6a. There is a much narrower distribution of Znₐ-O’ bond lengths for the configurations associated with the <211> type ordering. The average and standard deviation of the bond lengths for each A₂O’ network type are included in Table 6-1.

Figure 6-6. The relaxed energy in eV scaled by the average of the most favored A₂O’ network type plotted versus (a) the average Znₐ to O’ bond length (Å) and (b) O’ displacement (Å) for each of the 120 BZN configurations studied. Each of the four types of the A₂O’ network are separated into the [2:2] ratio (open diamond), the [3:1] ratio with only <211> ordering (square – most favored), the [3:1] ratio with only <011> ordering (triangle) and the [3:1] ratio with 1/3 <011> ordering (open circle).
Table 6-1. The total lattice energy in eV before and after atomic relaxation, as well as the average bond lengths and atomic displacements (δ) for each of the configurations studied is averaged and separated into the four A₂O’ network types.

<table>
<thead>
<tr>
<th></th>
<th>[2:2]</th>
<th>&lt;211&gt;</th>
<th>&lt;011&gt;</th>
<th>1/3&lt;011&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Unrelaxed</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Energy (eV)</td>
<td>0.25 ± 0.59</td>
<td>0 ± 0.53</td>
<td>-0.17 ± 0.44</td>
<td>-0.22 ± 0.46</td>
</tr>
<tr>
<td><strong>Relaxed</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Energy (eV)</td>
<td>0.47 ± 0.28</td>
<td>0 ± 0.23</td>
<td>1.63 ± 0.39</td>
<td>0.49 ± 0.44</td>
</tr>
<tr>
<td>d(Bi-O’) (Å)</td>
<td>2.341 ± 0.024</td>
<td>2.340 ± 0.020</td>
<td>2.326 ± 0.023</td>
<td>2.352 ± 0.025</td>
</tr>
<tr>
<td>d(Bi-O) (Å)</td>
<td>2.347 ± 0.011</td>
<td>2.343 ± 0.016</td>
<td>2.356 ± 0.036</td>
<td>2.323 ± 0.022</td>
</tr>
<tr>
<td>d(Znₐ-O’) (Å)</td>
<td>1.946 ± 0.030</td>
<td>1.933 ± 0.021</td>
<td>1.963 ± 0.036</td>
<td>1.937 ± 0.027</td>
</tr>
<tr>
<td>d(Znₐ-O) (Å)</td>
<td>2.129 ± 0.046</td>
<td>2.138 ± 0.051</td>
<td>2.137 ± 0.052</td>
<td>2.175 ± 0.050</td>
</tr>
<tr>
<td>d(Nb-O) (Å)</td>
<td>2.001 ± 0.002</td>
<td>2.000 ± 0.002</td>
<td>2.002 ± 0.002</td>
<td>2.001 ± 0.003</td>
</tr>
<tr>
<td>d(Znₐ-O) (Å)</td>
<td>2.089 ± 0.008</td>
<td>2.090 ± 0.007</td>
<td>2.094 ± 0.012</td>
<td>2.088 ± 0.008</td>
</tr>
<tr>
<td>δBi (Å)</td>
<td>0.433 ± 0.099</td>
<td>0.435 ± 0.080</td>
<td>0.399 ± 0.110</td>
<td>0.432 ± 0.086</td>
</tr>
<tr>
<td>δNb (Å)</td>
<td>0.154 ± 0.068</td>
<td>0.155 ± 0.065</td>
<td>0.140 ± 0.063</td>
<td>0.142 ± 0.056</td>
</tr>
<tr>
<td>δZnₐ (Å)</td>
<td>0.685 ± 0.086</td>
<td>0.673 ± 0.070</td>
<td>0.683 ± 0.104</td>
<td>0.630 ± 0.064</td>
</tr>
<tr>
<td>δZnₐ (Å)</td>
<td>0.116 ± 0.048</td>
<td>0.125 ± 0.052</td>
<td>0.107 ± 0.052</td>
<td>0.088 ± 0.033</td>
</tr>
<tr>
<td>δO’ (Å)</td>
<td>0.496 ± 0.020</td>
<td>0.516 ± 0.024</td>
<td>0.452 ± 0.049</td>
<td>0.493 ± 0.020</td>
</tr>
</tbody>
</table>

Correlation of the energy to the average of each atom type’s displacement magnitude (δ) was examined in the relaxed crystal. The results for the correlation plot for δO’ is shown in Figure 6-6b. Since a connection between the lattice energy and the Znₐ-O’ bond length was observed, a link between the energy and the atomic displacement of either the Znₐ or the O’ atoms is not unexpected. The observation of the O’ atomic displacement correlating to the overall lattice energy is attributed to the type of displacement Znₐ atoms undergo. Within the configuration with the <211>
ordering, the displacement pattern of every ZnA site was determined and 95 percent of
the time the ZnA cation would not displace towards the O’ anions. Therefore, any
variation in the ZnA-O’ bond length must be attributed to the movement of the O’ anion.

This information helps explain why the energy costs are so high for the <011>
ordering with respect to the [2:2] network. If each O’ anion displaces towards the ZnA
cation within its tetrahedron, the <011> type ordering could lead to a splitting of the unit
cell. The network illustrated in Figure 6-1c can provide further explanation. In this
configuration, the O’ anion located at the top and bottom of the unit cell would displace
upwards along the z-axis, while the O’ anion in the center of the cell would displace
downwards. This could results in a spatial separation of the previously evenly
distributed corner sharing tetrahedra. Additionally, this type of displacement would lead
to a reduction of bonding with the two Bi cations forming the top of the center
tetrahedron. In the case of the [2:2] type ordering, most of the ZnA cations are ordered
along the <211> direction with only one set having the <011> directional ordering. As
seen in Figure 6-1a, the O’ anions can displace towards the ZnA cations evenly in all
directions. Also, the O’ anion in the center tetrahedron has multiple displacement
pathways towards either one of the two ZnA cations within the tetrahedron or towards
both ZnA cations simultaneously.

6.4.3 Energetics and Structure in other Complex Pyrochlores

As seen in Section 6.4.1, the <211> A₂O’ set is the most favored for BZN. For the
other complex bismuth pyrochlores examined (BZT, BMN, and BMT), it was of interest
to compare the <211> A₂O’ set with the [2:2] and <011> A₂O’ sets. Instead of showing
the energy associated with each configuration, as shown for BZN in Figure 6-2, the
difference in energy between the <211> A₂O’ and either the [2:2] or the <011> A₂O’ type
for each $B_2O_6$ configuration was determined. The average and standard deviation for the difference between the [2:2] and <211> $A_2O'$ sets are shown in Figure 6-7 for the four complex compounds. Figure 6-8 shows a similar plot for the difference between the A site substitutes (either $Zn_A$ or $Mg_A$) ordering along the <211> versus the <011> directions. The positive values indicate the <211> $A_2O'$ type is more thermodynamically favorable. Since the total lattice energies varied considerably between the four different pyrochlores, the energies reported are scaled by A site cations, or 16, in order to make comparisons between the different pyrochlores.

![Figure 6-7. Energy difference (eV/A site) between [2:2] and <211> $A_2O'$ configuration sets for BZN, BZT, BMN, and BMT.](image)

As seen in Figure 6-7, the [3:1] ratio is preferred in the BZN, BZT, BMN, and BMT compounds. Upon inspection of the energy difference between the [2:2] and <211> for the individual configurations for BZT, BMN, and BMT, it was observed that some structures show the [2:2] $A_2O'$ type to be favored over the <211> $A_2O'$ type, as was
seen for one structure in the BZN compound. One configuration was found in the BZT and BMT compound where the [2:2] \(A_2O'\) set is more favorable than the [3:1] with \(<211>\) ordering. The \(\text{Zn}_B/\text{Mg}_B\) distribution in these two configurations did not match each other or the previously discussed BZN configuration with favorable [2:2] \(\text{Zn}_A\) distribution. For the BMN compound, three structures were found where the [2:2] \(A_2O'\) is more favorable than the [3:1] with \(<211>\) ordering. Of these three structures, one of the \(\text{Mg}_B\) distributions matched the \(\text{Zn}_B\) distribution from the BZN compound with favorable [2:2] \(A_2O'\) type.

![Figure 6-8](image)

**Figure 6-8.** Energy difference (eV/A site) between \(<211>\) and \(<011>\) \(A_2O'\) configuration sets for BZN, BZT, BMN, and BMT.

When comparing the \(<211>\) and \(<011>\) \(A_2O'\) sets, seen in Figure 6-8, the \(<211>\) configuration is favored by a larger degree over the \(<011>\) set than the \(<211>\) \(A_2O'\) was favored over the [2:2] set for all four compounds. Unlike for the [2:2] \(A_2O'\) set, there are
no Zn$_B$/Mg$_B$ distributions in any of the four compounds where the $<011>$ A$_2$O' Zn$_A$/Mg$_A$ is more thermodynamically favorable over the $<211>$ A$_2$O' Zn$_A$/Mg$_A$ distribution. There are a few Zn$_B$/Mg$_B$ distributions with energy differences between the $<211>$ and $<011>$ A$_2$O' types above 0.2 eV/A site, resulting in larger standard deviations for the BZN, BZT, and BMN compounds. The BMT does not show this effect and therefore the standard deviation is only about 0.01 eV/A site versus 0.03 eV/A site for the other four compounds.

Based on the differences in energies, the $<211>$ directional ordering of Zn$_A$/Mg$_A$ cations is predicted to be preferred in the BZN, BZT, BMN, and BMT complex pyrochlores. While the [3:1] ratio of Zn$_A$/Mg$_A$ to Bi cations within each tetrahedron is preferred with the majority of Zn$_B$/Mg$_B$ distributions tested, the [2:2] ratio is not forbidden.

In addition to examining the energetics of Zn/Mg distributions, the average bond lengths and displacement magnitudes were also identified in each of the complex pyrochlores, which are summarized in Table 6-2. All four compounds show similar Bi-O' and Bi-O bond lengths between 2.32 – 2.34 Å and 2.34 – 2.35 Å, respectively. The Zn$_A$-O’ bond lengths for BZN and BZT between 1.94-1.95 Å are slightly lower than the Mg$_A$-O’ bond lengths in BMN and BMT between 2.0-2.03 Å. In all four systems the Zn$_A$/Mg$_A$-O bond lengths are between 2.13 – 2.16 Å.

On the B$_2$O$_6$ network, the Nb-O bond lengths in BZN and BMN at about 2.0 Å are only slightly longer than the Ta-O bond lengths in BZT and BMT at about 1.98 Å. However, there are larger standard deviations of the B-O bond lengths in the BZT,
BMN, and BMT systems than that observed in BZN. The ZnB/MgB-O bond lengths in all four compounds are between 2.09 – 2.10 Å.

Table 6-2. The average bond lengths and atomic displacements (δ) for BZN, BZT, BMN, and BMT compounds.

<table>
<thead>
<tr>
<th></th>
<th>BZN</th>
<th>BZT</th>
<th>BMN</th>
<th>BMT</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(Bi-O') (Å)</td>
<td>2.340 ± 0.023</td>
<td>2.341 ± 0.170</td>
<td>2.321 ± 0.171</td>
<td>2.331 ± 0.161</td>
</tr>
<tr>
<td>d(Bi-O) (Å)</td>
<td>2.342 ± 0.021</td>
<td>2.345 ± 0.167</td>
<td>2.353 ± 0.164</td>
<td>2.350 ± 0.162</td>
</tr>
<tr>
<td>d(ZnA/MgA-O') (Å)</td>
<td>1.945 ± 0.029</td>
<td>1.942 ± 0.029</td>
<td>2.030 ± 0.024</td>
<td>2.001 ± 0.020</td>
</tr>
<tr>
<td>d(ZnA/MgA-O) (Å)</td>
<td>2.145 ± 0.050</td>
<td>2.129 ± 0.156</td>
<td>2.159 ± 0.142</td>
<td>2.155 ± 0.171</td>
</tr>
<tr>
<td>d(Nb/Ta-O) (Å)</td>
<td>2.001 ± 0.002</td>
<td>1.984 ± 0.065</td>
<td>2.001 ± 0.080</td>
<td>1.983 ± 0.057</td>
</tr>
<tr>
<td>d(ZnB/MgB-O) (Å)</td>
<td>2.090 ± 0.009</td>
<td>2.100 ± 0.060</td>
<td>2.088 ± 0.043</td>
<td>2.091 ± 0.042</td>
</tr>
<tr>
<td>δBi (Å)</td>
<td>0.425 ± 0.094</td>
<td>0.414 ± 0.087</td>
<td>0.422 ± 0.106</td>
<td>0.492 ± 0.059</td>
</tr>
<tr>
<td>δNb/Ta (Å)</td>
<td>0.148 ± 0.063</td>
<td>0.123 ± 0.053</td>
<td>0.163 ± 0.084</td>
<td>0.089 ± 0.037</td>
</tr>
<tr>
<td>δZnA/MgA (Å)</td>
<td>0.668 ± 0.081</td>
<td>0.686 ± 0.118</td>
<td>0.654 ± 0.088</td>
<td>0.574 ± 0.058</td>
</tr>
<tr>
<td>δZnB/MgB (Å)</td>
<td>0.109 ± 0.046</td>
<td>0.110 ± 0.045</td>
<td>0.145 ± 0.033</td>
<td>0.069 ± 0.028</td>
</tr>
<tr>
<td>δO' (Å)</td>
<td>0.489 ± 0.028</td>
<td>0.476 ± 0.097</td>
<td>0.433 ± 0.125</td>
<td>0.453 ± 0.092</td>
</tr>
</tbody>
</table>

The average atomic displacement magnitudes for each atom type are also included in Table 6-2. On average, the Bi cations displace by a larger degree in the BMT at 0.49 Å than in the BZN, BZT, and BMN compounds. In contrast, the Ta cations in BMT and BZT displace by smaller about of 0.09 Å and 0.12 Å, respectively, versus the Nb cations in BZN and BMN with displacement magnitudes between 0.15 – 0.16 Å. The substitute cations on the B site displace by nearly the same magnitude as the Nb/Ta cation for the BZT and BMN compounds. For the BZN and BMT compounds, the ZnB/MgB displacements are only slightly smaller than the Nb/Ta. However, on the A site, the substitute cations displaced by a larger degree in all four compounds. For the
compounds with Zn on the A site, the displacement magnitudes are between 0.67 – 0.69 Å versus the 0.41 – 0.43 Å for the Bi cations. However, the Mg at the A site displaces by a much larger degree in BMN at 0.65 Å versus 0.57 Å in BMT. For the O’ anions, the displacement magnitude is larger in the zinc substituted compounds between 0.48 -0.49 Å versus in the magnesium substituted compounds between 0.43 – 0.45 Å.

Recently, Melot et al. [37] has shown a connection between the average A site displacement magnitudes and the experimentally determined dielectric constant in zinc substituted bismuth pyrochlores. The average A site and O’ site atomic displacement magnitudes from DFT are plotted in Figure 6-9 with the experimentally determined relative dielectric permittivity. For BZN, BMN, BZT, and BZS the relative permittivity is reported at 1 MHz. However, there is no data in the literature for BMT at 1 MHz therefore, the value shown in Figure 6-9 corresponds to BMT at 900 GHz. The correlation observed between these structures should not be affected by using the different frequency result for BMT, since the ordering of the BZN, BMN, BZT, and BMN are the same for 900 GHz as that seen at 1 MHz.

Since the displacement magnitudes and dielectric constants on BZN, BZT, BMN, and BMT were so similar, Bi1.5ZnSb1.5O7 (BZS) was also examined, where a much lower of average A site (~ 0.32 Å) and O’ site (~0.38 Å) displacement magnitude is reported from neutron powder diffraction data [37]. The details of the structure determined by DFT for the BZS systems will not be detailed but both the A site (0.36 Å) and O’ site (0.42 Å) average displacement magnitudes in Figure 6-9. It can be seen from Figure 6-9 that the correlation between the average A site displacement
magnitudes and the dielectric constants is seen for the DFT predicted atomic
displacements in BZS, BMT, BZT, BMN, and BZN. The O’ site average displacement
magnitudes correlate for the zinc substituted systems but are lower for the magnesium
substituted compounds. Also, in Figure 6-9, it can be seen that the large jumps in
dielectric permittivity occur with changing the occupation on the B site, with BZN and
BMN being grouped with the highest $\varepsilon_r'$, then BZT and BMT, and then BZS. As was
seen with the energetics of the various configurations, this observation indicates the
importance of the $\text{B}_2\text{O}_6$ network in these systems which should be examined further.

![Figure 6-9. The average displacement for the A and O' site in the BZN, BMN, BZT,
BMT, and BZS compounds in order of increasing experimental dielectric
constant.]

6.5 Summary

DFT calculations were performed on a range of cation substituted Bi pyrochlores,
$\text{Bi}_{1.5}\text{M}^{2+}\text{B}^{5+}_{1.5}\text{O}_7$ (with $\text{M}^{2+}\text{=Zn or Mg and B}=\text{Nb or Ta}$). The distribution of the cation
substitutes was varied with specific rules on the $A_2O'$ network and a random arrangement on the $B_2O_6$ network. By combining 4 ordered $A_2O'$ distributions with 30 random $B_2O_6$ distributions, 120 configurations were tested to probe the affects of cation ordering on the $A_2O'$ network. The cation distributions on the $A_2O'$ varied the local concentration (difference between [2:2] and [3:1] bismuth to substitute ratio) and the substitute to substitute directional ordering (either along the $<211>$ or the $<011>$ directions). In all four complex pyrochlores, on average a more distributed [3:1] ratio was observed for each tetrahedron, for some $B_2O_6$ configurations the [2:2] $A_2O'$ configuration was favored. The ordering of both Zn and Mg cations along the $<211>$ direction was found in all four compounds confirming the predictions from Monte Carlo models previously reported [10]. Though previous reports have suggested the importance of the $A_2O'$ network over the $B_2O_6$ network, large deviations in the energies of the configurations with randomly distributed cation substitutes on the $B_2O_6$ network indicate some ordering on the $B_2O_6$ network may be preferred. A relationship between DFT determined A site cation displacement magnitudes and the experimentally reported dielectric constants.
CHAPTER 7
ION HOPPING IN BISMUTH PYROCHLORES

7.1 Introduction

The dielectric properties of pyrochlores are often attributed to ion hopping of A and O’ atoms [13,52] and a better atomic-level understanding of the hopping mechanisms and energetics will be invaluable in tailoring substitutions. A general feature observed in all the Bi pyrochlores that show high dielectric permittivity is large ion displacement from the ideal Fd3m sites of the cubic pyrochlore structure. This atomic displacement results in multiple energetically equivalent sites, as discussed in Section 3.3.2.1, which facilitate cation hopping. Nevertheless, open questions remain on the relative influence of substitutional disorder [63] on the A2O’ versus B2O6 network (Figure 2-3b,c) on the ion hopping in these systems [10].

Within Bi1.5Zn0.92Nb1.5O6.92 (BZN) [13], the infrared (IR) active phonon modes were indentified and the contribution of each mode to the dielectric permittivity was assigned [63]. Later, Nino et al. explored how the IR modes that contributed the most to the dielectric permittivity may affect the dielectric relaxation observed in BZN [64]. Nearly 80% of the ionic dielectric permittivity is accounted for by the phonon modes associated with O’-A-O’ and O-A-O bend modes [63]. In contrast, in Bi1.5ZnTa1.5O7 (BZT) and Bi1.5MgTa1.5O7 (BMT) these modes are associated with 66 % and 56 % of the permittivity, respectively [38]. While in Bi1.5MgNb1.5O7 (BMN), these modes also account for 81 % of the ionic dielectric permittivity [38]. Based on the IR results Nino and co-workers proposed that the relaxation observed in BZN is due to ion hopping mechanisms associated with the A and O’ atoms between equivalent positions [11,64].
Investigating this proposed mechanism would be difficult experimentally due to the rapid movement of the atoms within a crystal even at low temperatures. Sensitive structure techniques such as neutron or X-ray diffraction used to examine changes at the atomic scale average over the entire bulk structure and require a finite measuring time. The identification of pair distribution function to examine the interatomic distances between atom types can be used to approximate changes in the local bonding environment [116]. Extended X-ray absorption fine structure (EXAFS) has been used in BZN to refine displacement patterns of both Bi and Zn\textsubscript{A} based on the local bonding environment of the nearest O atoms [117]. However, these measurements are taken over the course of some measurement time and if applied instantaneously following the application of an electric field to examine hopping mechanisms the collected information would contain a larger component of final state structure information that may dilute any transitional state structure. Additionally, the frequency of these hopping mechanisms events may be faster than the measurement time hindering the capture of intermediate structures within the atom hopping mechanisms. This limitation may be overcome through simulations using density functional theory (DFT). The DFT calculations discussed up to this point in the dissertation have been restricted to identification of local minima. While this information provides insight on cation hopping behavior, for instance the identification of multiple local minima for Bi cations displaced from the ideal Fd\textbar\textbar m site, they do not directly probe the cation hopping process. One approach to probe cation hopping would be to directly simulate the pyrochlore system at relevant temperatures over the time scale of the cation hopping using molecular dynamics (MD). While \textit{ab initio} MD can be performed on the pyrochlore system the appropriate time
scales to observe cation hopping are computationally expensive. Performing MD simulations using classical potentials would allow cation hopping to be observed on experimentally time and length scales, but sufficient accurate potentials for the Bi pyrochlores are not yet available.

Instead of MD simulations, DFT was used in combination with nudged elastic band (NEB) method [55-57] to identify transition states between the displaced local minima. NEB calculations have been used to identify transition states in proton transfer [58], surface diffusion [59], and surface chemistry, such as in the water gas shift reaction on copper [60]. The background of how NEB calculations are implemented into DFT is detailed in Section 1.3.4.2.

In this work, NEB calculations are applied on various bismuth pyrochlores to identify pathways to cation hopping and the associated energy barriers. While there is no guarantee that the lowest energy pathway has been identified since the NEB method depends on providing two relevant connected minima, several different possible pathways were examined to determine the relevant hopping mechanisms. The various minima that serve as input to the NEB calculations are associated with the specific spatial location of the cations with respect to the ideal position. As mentioned before, the characterization of these spatial positions is done by using Wyckoff positions which have been explained in Section 2.2 and Section 3.3.2.1.

7.2 Calculation Details

First-principles calculations were performed with Vienna Ab-initio Simulation Package (VASP) [44-47], with details matching those reported in Section 3.2. The Bi(5d, 6s, 6p), Ti(3s, 3p, 3d, 4s), O(2s, 2p), Nb(4p, 5s, 4d), Zn(4s, 3d), Ca(3s, 3p, 4s) orbitals were included as the valence electrons. The DFT calculations were performed within
the local density approximation (LDA) [50]. All calculations were performed at fixed volume and shape, while the atoms were relaxed until the forces were less than 0.03 eV/Å. The cubic lattice constants for the BZN and Ca$_{1.5}$Ti$_{1.5}$Nb$_{1.0}$O$_{7}$ (CTN) systems are fixed to their experimentally determined values of 10.55668 Å [13] and 10.2301 Å [52]. Though all atoms are free to relax in these optimized structures the crystal lattice is fixed to the cubic pyrochlore structure. A plane wave cutoff energy of 400 eV was used along with a 3×3×3 Monkhorst-Pack [54] mesh, resulting in 14 irreducible $k$-points for the Bi$_2$Ti$_2$O$_7$ system and only the $\Gamma$-point for the BZN and CTN systems.

To probe for equivalent minima associated with displaced cations, one bismuth cation was selected and moved it into an equivalent site within the same Wyckoff position where it was held fixed. Simulated annealing calculations were then performed under fixed crystal shape and volume using \textit{ab initio} molecular dynamics (MD) [44-47]. The MD simulations were conducted with only the $\Gamma$ point within the NVT ensemble starting at 1000 K and cooling to 300 K over 500 MD steps with a time step of 0.5 femtoseconds. After MD simulation, the system was minimized using the same approach as outlined above. Following all of these steps, the fixed cation was released and the forces were relaxed.

The climbing-image nudged elastic band (cNEB) method was used to identify the minimum energy paths between equivalent minima [55-57]. The process was completed in two steps. The first step used one image, or intermediate structure along the pathway, to confirm the presence of an energy barrier between two minima and the second step provided more detail to the resulting pathway by adding two additional images resulting in a total of three intermediate structures. The calculation details of the
compound’s minima were repeated within the NEB calculations, e.g. cutoff energy, k-mesh, etc. For the NEB calculations a force criteria of 0.05 eV/Å was used and confirmed the equivalency of both the energy profile and structure intermediates are well within the values reported. Though the force criteria is lowered for the intermediate structures, test calculations were performed to confirm the energy barriers determined are accurate to within 0.02 eV.

As shown in Chapter 6, the distribution of cation substitute in BZN and CTN may vary significantly. For this work, the distribution was limited to a single configuration for the BZN and CTN systems. One other distribution was tested for each system to confirm the energy barriers determined were not dependent on the distribution.

7.3 Results and Discussion

7.3.1 Bismuth Titanate

7.3.1.1 Identification of equivalent minima

The first step in studying the hopping mechanism within Bi$_2$Ti$_2$O$_7$ is to identify possible linked minima. Within bismuth titanate, a stable minimum was attempted for each of the six equivalent Wyckoff positions for two different bismuth cations in the unit cell. The two bismuth cations were selected based on the occupancies of the 96$g$ and 96$h$ positions and their positions with respect to the correlation observed in bismuth titanate (see Section 3.3.2.1 for details on the Bi$_2$O’ correlation). Though two cations were forcibly pushed into each of the five equivalent Wyckoff positions, these minima were created independently by moving one cation for each minimum thereby creating ten different structures. For one of the bismuth cation in the 96$h$ site, following the simulated annealing and releasing the cation to reduce its forces (see Section 7.2 for fully details of procedure), the cation shifted out of two of the equivalent positions back
into one of the other four positions. This indicates that though the six equivalent positions could be stabilized when starting from the ideal pyrochlore structure, once the displacements are initiated the probability of each position being occupied is not equal. However, for the second bismuth cation that was pushed, each of the equivalent 96g positions could be stabilized. Since six equivalent positions were stabilized with this Bi cation, these structures will be focused on for the ion hopping pathways discussed below.

Figure 7-1 plots the total energies for each of the six minima at the 96g sites scaled by the lowest energy structure (s2). For visual aid, the energy of the sixth position, or s6, is shown to the left of s1 and to the right of s5. This is to help reflect the spatial arrangement of these points and visualize the difference in energy between s1 and s6.

Additionally, the pushed bismuth cation’s final position for each of the structures is also shown in the inset of Figure 7-1. Though there is some shift in the cations, the characteristic ring of the 96g Wyckoff site is maintained including the displacement component along the O’-Bi-O’ bonding axis, which is perpendicular to the view shown.

The difference in the total lattice energy between the structures is about 0.2 eV/88 atoms, which is about 0.002 % of the total energy. In comparison to the energy difference observed following atomic displacement and volume expansion from the ideal pyrochlore structure[104], discussed in Section 3.3.2.1, the total energy difference between these structures is 0.0125 eV/Bi cation which is only 8% of that reported for atomic displacement and volume expansion. This degree of difference is minimal and should be expected among the various structures.
7.3.1.2 Ion hopping mechanisms in bismuth titanate

Once these six minima are established, possible hopping mechanisms may be examined between the minima. Three different types of mechanisms were considered: single site, double site, or triple site hop mechanism. Figure 7-2 illustrates the difference between the initial structure, shown in red, and the final structure for the single site hop, in orange, and the double site hop mechanism, in yellow. Note in Figure 7-2, the numbers centered in the schematic to the right of the tetrahedra network correspond to the hopping mechanism and not the site assignment, as was used in Figure 7-1.

From Figure 7-2, it can be seen that though a single bismuth cation is pushed into equivalent positions, multiple bismuth respond to this perturbation. Based on previous work in pyrochlores and other materials with connected tetrahedra, the concerted motion is not unexpected and this type of response has been termed rigid unit modes [73-76] and discussed in Section 2.2.3.
Figure 7-2. The $\text{A}_2\text{O}^-$ tetrahedra network for three energetically equivalent 96g sites. A single site hop and double site hop is represented by the red to orange and red to yellow tetrahedra network, respectively.

Several attempts to examine a three site hop mechanism yielded only large barrier mechanism ($E_b$ of 1.4 eV). Upon inspection of the electronic localization function (ELF), it is found that along the triple site hop mechanism, the transition state places multiple lone pair towards each other, reducing the lone pair to lone pair spacing, producing large sterical strain, and the resulting high energy barrier. The triple site hop mechanism will be discussed further in Section 7.3.1.4.

The single site hop mechanism was examined for transition between each of the sites in Figure 7-1. The energy pathways are illustrated in Figure 7-3 with respect to the spatial pathway of the pushed bismuth cation. The pathways are broken down by color and symbol for each of the transitions between each position. In addition to the pathways, the scaled energy for each minimum was included in the Figure 7-3 as the black stars.

Upon inspection of the pathways, the barriers between the minima fall into two categories, no barrier or a barrier between 0.11 and 0.16 eV. Note, the accuracy of
these calculations was tested and the total energy is accurate to within 0.02 eV, therefore the range of this barrier is $0.11 \pm 0.02$ eV to $0.16 \pm 0.02$ eV.

Figure 7-3. Energy profile for the single site hop mechanisms for Bi$_2$Ti$_2$O$_7$. Each original minimum is included as the black star with each component of the pathway shown as a separate series.

There is no barrier from s1 to s2, from s1 to s6, or between s3 and s4, in either direction. This indicates that s1 is not a true minimum since there is no barrier between s1 and either of its single site hop neighbors. Given this observation, the phonon modes for each minimum should be examined using the finite differences method within VASP. This would determine all real and imaginary phonon modes for the bismuth titanate in each minimum. In addition to providing the frequency for each mode, the structure movement at that frequency would be reported by VASP. The occurrence of any imaginary phonon modes within any structure would indicate there is some instability within the structure. In that case, the atoms involved in the unstable mode would need
to be “pushed” in the direction identified. Following relaxation, the structure could result in reproducing one of the other Wyckoff positions or even an entirely different configuration. These calculations are currently underway to confirm this hypothesis.

As mentioned above, there are two different reasonable hopping mechanisms within bismuth titanate, a single site hopping and double site hopping mechanisms. The double site hop mechanisms was also examined and showed energy barriers between 0.20 and 0.32 eV. For double site hop mechanisms that started or ended with the s1 minimum, the barrier out of the s1 site was 0.03 eV or less and the barrier into the s1 site was 0.25 eV or higher. For two hop site pathway from s6 to s2, the s1 structure nearly matches the intermediate structure along the pathway. These observations regarding the barriers around the s1 minimum further support that the structure determined for the s1 site is not a stable minimum.

7.3.1.3 Ion hopping pathways in bismuth titanate

In addition to examining the energy profile along the various single site hop pathways, the local structure of the “pushed” Bi cation provides some insight into these hopping mechanisms. Figure 7-4 shows the two Bi₄O’ tetrahedra connected by the “pushed” Bi cation for each of the end points and the intermediate structures along the s2 to s3 pathway. The darkness of the atoms illustrated is increased along the pathway from light (s2) to dark (s3) for both the Bi (purple) and the O’ (red).

The outline for the tetrahedra of only the stable minima is included for visual aid. Though it may be difficult to view, the O’-Bi-O’ bond angle for the Bi cation that was pushed (center atom) is relatively unchanged along the pathway. This may be easier to see by looking at the front corner of the upper tetrahedron, since the push of one Bi cation results in the subsequent transition of additional bismuth cations to maintain
appropriate bonding with the O’ anions. The front corner Bi cation in the upper tetrahedron illustrates from light to dark the pathway from the s2 to s3 structures involves movement of the bismuth cation away from the ideal high symmetry site. This type of bismuth displacement was observed for each of the single site and double site hop mechanisms examined. The detailed variation of the O’-Bi-O’ bond angle of the “pushed” bismuth cation (center cation in Figure 7-4) along the s2 to s3 single site hop mechanism is shown in Figure 7-6 and will be discussed below in Section 7.3.2.

![Figure 7-4](image)

Figure 7-4. Local structure, including intermediate structures, for the s2-s3 single site hop mechanism. The atom colors (purple for Bi and red for O’) are graded from light (s2) to dark (s3) along the pathway.

The double site hop mechanism structure intermediates were also examined and the show similar structures along the pathway as the single site hop mechanism. The intermediate structures have the bismuth cation following a pathway away from the high symmetry site and the transition is not isolated to the “pushed” cations. The tetrahedra within the intermediate structures do not exhibit any distortions or significant changes to the Bi-O’ bond lengths.
7.3.1.4 Role of displacement correlation in bismuth titanate

As mentioned above, the triple site hop mechanism was examined and the large energy barrier of 1.4 eV indicates this is not a reasonable pathway to ion hopping in bismuth titanate. Upon inspection of the determined structural intermediates, it is found in the three hop mechanism the bismuth cations transition near the high symmetry center site. The previously observed correlation of Bi and O’ atoms in stable bismuth titanate minima [104] may provide further understanding of the intermediate structures observed in the triple site hop mechanism.

The schematic of the β-cristobalite type displacive disorder discussed in Section 2.2.3 is repeated in Figure 7-5 to show the concerted displacement along the [110] direction and corner sharing tetrahedra in bismuth titanate. It is expected the atomic correlation in bismuth titanate will affect the cation hopping mechanisms. Ion hopping was probed for two different bismuth cations located at different places within the pyrochlore structure. These two cations experience different types of displacement based on the correlation observed. One cation shows downward displacement along the [110] direction while one exhibits the rotation illustrated in Figure 7-5. The hopping mechanisms associated with these two cations were examined and both showed the same energy barriers and equivalent structure intermediates. Upon examination of each intermediate structure for any single site or double site hop mechanism and at any point along the pathway, the β-cristobalite type displacive disorder is maintained.

With regards to the triple site hop mechanism, the two stable minima exhibit completely opposite correlation. To further explain, the bismuth cation that displaces downward along the [110] direction in Figure 7-5 for one minimum will displace upwards in the other minimum. The NEB calculations try to map out a reasonable pathway
connecting these two minima and the initial intermediate structures placed the bismuth cation transitioning through the high symmetry sites. This type of transition would result in the loss of the correlation. Following relaxation, the bismuth cations shift out of the high symmetry site as was seen in the single site and double site hop mechanisms but the ELF plots for the intermediate structure show a reduction in the lone pair-lone pair spacing. The reduced lone pair spacing results in the loss of the correlation within the intermediate structures. It is predicted that the correlation is needed to stabilize the bismuth displacement within the bismuth titanate compound and therefore destabilizes the triple site hop mechanism. This observation will be further discussed in Section 7.3.2 where the hopping mechanisms in BZN are examined, since correlation of the atomic displacement was not observed in BZN.

![Figure 7-5. Local structure illustrating the β-cristobalite type displacive disorder in bismuth titanate. The Bi (purple) and O’ (red) atoms are in their ideal position with the black arrows indicating direction of displacement.](image)

7.3.2 Bismuth Zinc Niobate

As discussed in Section 7.1, the dielectric properties of BZN have been linked to O’-A-O’ and O-A-O bending phonon modes [63]. Additionally, the dielectric relaxation observed in BZN is proposed to be due to the A and O’ atoms hopping between
equivalent positions [11,64]. The same minimum finding procedure was used for the BZN compound as discussed for the Bi$_2$Ti$_2$O$_7$ compound. Similar to the bismuth titanate system, it was found that each of the six equivalent Wyckoff positions for the “pushed” Bi cation are not equally favorable after atomic displacement has occurred. Four of the six minima were stabilized for two different Bi cations. The single site hop and double site hop mechanisms were examined between these stable minima. It was found for the single site hop mechanism the energy barriers are between 0.12 and 0.20 eV. For the double site hop mechanism, similar energy barriers are observed with nearly the same energy range of 0.12 to 0.31 eV. Unlike in bismuth titanate, a triple site hop mechanism was stabilized in BZN with energy barriers within a range of 0.12 to 0.35 eV. It is proposed that the triple site hop mechanism may occur in BZN, since there is no correlation of atomic displacement in the A$_2$O’ network. Based on these energy barriers, the bismuth cation in various positions may respond to an applied electric field through all three mechanisms.

Minima associated with pushing a Zn cation at the A site were also indentified. The energy barriers associated with both the single and double site hop mechanism range from 0.12 to 0.32 eV. Smooth energy profiles were observed along the hopping pathways for both the single site and double site hop transitions. Though a triple site hop mechanism was not examined for the Zn cation, based on the observation for the Bi cation the triple site hop mechanism should be possible for the Zn cation as well.

Experimental reports have shown dielectric relaxation in BZN and with changing applied electric field frequency the maximum permittivity occurs at shifting temperature (T$_m$). An Arrhenius function may fitted to the frequency versus T$_m$ and yields an
activation energy of ~0.14 eV for the BZN system [3,16,64]. Since the relaxation observed in BZN is attributed to these ion hopping events, the activation energy determined experimentally is predicted to be for the jump mechanism of ions sampling multiple equivalent minima. While there is no guarantee that DFT is capturing the same activated hopping mechanisms, the activation energy determined by experiment of 0.14 eV compares well to the DFT predicted energy range of 0.12 to 0.35 eV.

Figure 7-6. The O'-Bi-O' local bond angle of the “pushed” Bi cation is shown for a single site hop mechanism in Bi₂Ti₂O₇ (s2-s3 circles) and BZN (s1-s2 squares). Each original minimum is included as the black star.

Further, examination of the intermediate structure for all three hopping mechanisms showed the Bi cations transition nearly through the ideal high symmetry site in contrast to the bismuth titanate system. Therefore, this type of transition of Bi cations within BZN may lead to the similarity among the energy barriers associated with
all three hopping mechanisms. The DFT predicted bismuth cation pathway in BZN agrees well with experimental predictions since there are significant variations in the local O’-Bi-O’ bond angle along the pathway but minimal Bi-O’ bond length variations. Figure 7-6 details the variation of the O’-Bi-O’ bond angle of the “pushed” bismuth cation along the s1 to s2 single site hop mechanism for the BZN system and the s2 to s3 single site hop mechanism for the bismuth titanate system. Within BZN, the bond angle varies significantly between the s1 (166.3º) and s2 (177.5º) minima. In comparison, the local O’-Bi-O’ bond angle in bismuth titanate varied only by couple degrees between the s2 (158.2º) and the s3 (156.2º) minima. Along the pathway, for both systems, the bond angles vary within the range created by their respectively minima with the exception of one intermediate structure in bismuth titanate with a bond angle of 155.7º.

7.3.3 Calcium Titanium Niobate

It has been thought that bismuth pyrochlores exhibit interesting dielectric properties such as high permittivity and dielectric relaxation, due to the highly polarizable Bi cation occupancy of the A site. However, recently a pyrochlore compound within the CaO:TiO2:Nb2O5 (CTN) system has been synthesized and it shows high permittivity and dielectric relaxation without the incorporation bismuth cations [52]. Though the dielectric constant is lower for the CTN pyrochlore versus the BZN system, the Arrhenius function fitted to the dielectric relaxation data yields a much larger activation energy of 0.32 eV [52] versus the 0.14 eV reported for the BZN system [3,16,64]. This activation energy is higher than any values previously reported for the pyrochlore systems but it is reasonable when the compared with other fluorite related structures such as the weberite Gd2(Gd,Nb)2O7 where an activation energy of ~0.45 are
reported [118]. The CTN forms a pyrochlore solid solution with compositions ranging from \( \text{Ca}_{1.48} \text{Ti}_{1.48} \text{Nb}_{1.02} \text{O}_7 \) to \( \text{Ca}_{1.41} \text{Ti}_{1.37} \text{Nb}_{1.14} \text{O}_7 \) [52].

In order to examine ion hopping mechanisms in CTN, the CTN system was simulated based on the \( \text{Ca}_{1.48} \text{Ti}_{1.48} \text{Nb}_{1.02} \text{O}_7 \) and the composition was approximated to \( \text{Ca}_{1.5} \text{Ti}_{1.5} \text{Nb}_{1.0} \text{O}_7 \). Unlike the complex pyrochlores discussed so far, the A site and the B site have a stoichiometry of \( (\text{Ca}_{1.5} \text{Ti}_{0.5}) \) and \( (\text{Nb}_{1.0} \text{Ti}_{1.0}) \), respectively. For the purpose of these simulations, the stoichiometry means there will be 12 A sites occupied by Ca, 4 A sites occupied by Ti\(_A\), 8 B sites occupied by Nb, and 8 B sites occupied by Ti\(_B\).

The CTN configuration was simulated assuming the \( A_2O' \) network would prefer a \([3:1]\) ratio of Ca to Ti\(_A\) cations within each tetrahedron and that the Ti\(_A\) cations would order along the \(<211>\) direction. Variations of the \( A_2O' \) network have been discussed for other complex pyrochlores in Chapter 6 and in all complex pyrochlores previously discussed this \( A_2O' \) configuration was favored. These assumptions were made in order to examine ion hopping mechanisms more rapidly in the CTN system. As a follow up additional \( A_2O' \) configurations should be tested to confirm the preference of the \([3:1]\) ratio and \(<211>\) ordering.

The dielectric permittivity and relaxation observed in the CTN system are due to the atomic displacement from the ideal high symmetry sites therefore accurately capturing these displacements is important. Based on the X-ray diffraction refinement, the Ca, Ti\(_B\) and Nb ions are located at their respective high symmetry sites [52]. The Ti\(_A\) ion displace by 0.7 Å into the 96g position and the O’ ions displace by 0.48 Å into the 32e position [52].
Structural minima for the CTN were identified following the procedure discussed in Section 7.2. Following atomic relaxation, the atomic displacements observed are reported in Table 7-1. The experimental values included in Table 7-1 are for the Ca$_{1.46}$Ti$_{1.38}$Nb$_{1.11}$O$_7$ pyrochlore using X-ray diffraction at room temperature [52]. Though the experimental composition of this pyrochlore does not match the simulated composition, the authors indicate the displacement parameters are the same for the Ca$_{1.48}$Ti$_{1.48}$Nb$_{1.02}$O$_7$ compound. Though DFT determines additional displacement of Ca, Nb, and Ti$_b$ cations, the magnitude of the Ti$_a$ and O’ atomic displacement agree very well with the experimentally reported values. Additionally, the displacement patterns agree between DFT and experiment determining the Ti$_a$ and O’ atoms displacing to a 96g and 32e Wyckoff position, respectively.

Table 7-1. The displacement magnitude for each atom type within the CTN compound.

<table>
<thead>
<tr>
<th>Atomic Displacement</th>
<th>DFT</th>
<th>Experiment$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta$Ca (A – site)</td>
<td>0.23 Å</td>
<td>0.00 Å</td>
</tr>
<tr>
<td>$\delta$Ti (A – site)</td>
<td>0.75 Å</td>
<td>0.70 Å</td>
</tr>
<tr>
<td>$\delta$O’ (A – site)</td>
<td>0.50 Å</td>
<td>0.48 Å</td>
</tr>
<tr>
<td>$\delta$Nb (B – site)</td>
<td>0.16 Å</td>
<td>0.00 Å</td>
</tr>
<tr>
<td>$\delta$Ti (B – site)</td>
<td>0.16 Å</td>
<td>0.00 Å</td>
</tr>
<tr>
<td>x O (B – site)</td>
<td>0.3234</td>
<td>0.3237</td>
</tr>
</tbody>
</table>

$^a$From Ref. [52]

Following the determination of a stable minimum that compares well with the experimental reports, focused was placed on identifying additional minima with the Ti$_a$ and Ca cations occupying equivalent Wyckoff positions, using the procedure discussed in Section 7.2. Both A site cations were examined to discern if it is the Ti$_a$ cation that is participating in “activated” cation hopping mechanisms. Similar to both bismuth titanate and BZN systems, it was found that all six equivalent Wyckoff positions are not equally
probably when starting with a previously displaced structure. Starting with the ideal high
symmetry Wyckoff site both the Ti$_A$ and Ca cations it was confirmed that each cation will
equally occupy the equivalent positions. Four different minima were stabilized for both
the Ti$_A$ and Ca cations and the single site and double site hop mechanisms were
examined among these minima. For the Ca cations, energy barriers of 0.05 eV or less
were identified indicating these hopping mechanisms are not those being observed
experimentally. The Ti$_A$ cations hopping between equivalent minima exhibit energy
barriers between 0.18 to 0.42 eV for both single site hop and double site hop
mechanisms. The Ti$_A$ cations in the intermediate structures transition away from the
high symmetry site similar to the Bi cations in the bismuth titanate system. In contrast to
the transition in BZN, the minimum changes to the O’-Ti$_A$-O’ bond angle would indicate
if IR phonon mode information were available for CTN the O’-A-O’ phonon mode would
contribute to the dielectric permittivity to a lower degree than that observed in BZN.

Often for the double site hop mechanisms, when three images are used, the
middle structure along the pathway matches the stable minimum between the two
minima. For example, the hopping mechanism from s1 to s3 for the Ti$_A$ cation within the
CTN system transitions through the s2 site combining the two single site hop
mechanisms on either side. The energy barriers and transition state structures match
for both pathway components (the s1 to s2 and s2 to s3 mechanisms). When the Ti$_A$
cations are forced through the high symmetry site the energy barrier increases to ~1 eV.
As with BZN, there is no guarantee that DFT is capturing the exact hopping
mechanisms that are approximated experimentally. The larger energy barriers present
in CTN versus those observed in both bismuth titanate and BZN indicates DFT is able to capture differences among the hopping mechanism between these three systems.

7.4 Summary

Using DFT, three different ion hopping mechanisms (single, double or triple site) were examined in bismuth titanate, bismuth zinc niobate, and calcium titanium niobate. In bismuth titanate, the energy barriers ranged from 0.11-0.16 eV, 0.20-0.32 eV, and ~1.4 eV for the single, double, and triple site hop mechanisms, respectively. The large energy barrier associated with the triple site hop mechanism is attributed to the breaking of the correlation of atomic displacement observed in the A<sub>2</sub>O’ network. In BZN, the energy barriers for the single, double, and triple site hop mechanisms ranged from 0.12-0.20 eV, 0.12-0.31 eV, and 0.12-0.35 eV, respectively, and agree well with the experimentally predicted activation energy of ~0.14 eV [3,16,64]. In CTN, Ca ions hopping between equivalent minima has an energy barrier of 0.05 eV or less indicating these mechanisms are not being captured in the experimental study. However, DFT predicts energy barriers associated with both single and double site hop mechanisms of Ti<sub>A</sub> between 0.18 and 0.42 eV. Experimentally, an activation energy of 0.32 eV is approximated from the dielectric measurements [52].

The transition state structures were examined in all mechanism and for the bismuth titanate and CTN system the A cation transitions away from the high symmetry site, while in BZN both the Bi and Zn cations transition through the high symmetry site. This transition pathway leads to variations of the O’-A-O’ bond angle by up to 10 degrees in BZN. This predicted pathway agrees well with experimental IR phonon mode assignment which show ~80% of the dielectric permittivity in BZN is attributed to O’-A-O’ and O-A-O bending modes [63].
7.5 Future Efforts

The minima determined by moving cations from one Wyckoff site to an equivalent Wyckoff site, within the same Wyckoff position must be thoroughly tested for each site. It was observed that some positions, though ideally equally likely in nature, may not be obtained by forcible moving select cations.

For CTN, Section 7.3.3 showed the number of images used to capture the ion hopping pathways is important since, as seen with the s1 to s3 pathway, the double site hop mechanism often resulted in the combination of two single site hop mechanisms (s1 to s2 and s2 to s3) with the center image structure matching the middle minima structure (s2). Therefore, the number of images should be increased for all mechanism (single, double, and triple) for each system studied.

The calculations reported in this chapter were using a single substitutional configuration for the BZN and CTN systems. Though a few single and double site hop mechanisms were tested to confirm the energy barriers and transition pathways did not significantly vary, an exhaustive investigation was not completed. Additional single, double, and triple site hop mechanisms should be investigated and both the A_2O’ and B_2O_6 configurations should be varied to confirm these results.
8.1 Motivation

8.1.1 Project Overview

Surface chemistry is a broad term to define a large component of the chemical engineering industry with focus in chemical separation [119] and improved catalytic properties leading to efficient chemical reactions. In addition to environmental considerations, there is increasing interest in improving the efficiency of various chemical reactions in order to fully utilize the current resources. The chapter will focus on part of a larger effort at the University of Florida to design methods to deliver metal clusters to specific sites on oxide surfaces through the use of organometallic ligands with hydroxyl and/or amine terminal groups.

8.1.2 Background

Transition metal surfaces have provided a rich source of reactivity in a variety of areas, but with a large price tag. Attempts have been made to merge the reactivity of expensive transition metals with inexpensive substrates, such as metal oxides. Often these heterogeneous catalytic surfaces are created through simple techniques, such as co-precipitation or wet-impregnation, which results in non-uniform metal particle distributions. In fact, the poor control of where and how the metal particles will arrange leads to a large portion of the expensive metal particles occupying inactive surface sites.

By exploiting the selective binding nature of specific functional groups to low coordination surface sites, this work hopes to accomplish atomic level control of the metal particle layer on the metal oxide support. This would be accomplished by
depositing the metal particle in two steps. In the first step, the metal particle is delivered to the surface as a part of an organometallic complex with NH$_2$ and OH functional groups. The second step involves the selective removal of the organic ligands using oxygen or hydrogen plasmas as low temperatures, as to not affect the metal adsorption sites. While this ultimate goal will require multiple levels of investigation, DFT may provide reactivity and adsorbate configuration information for various small molecules that would replicate the functional groups.

8.1.3 DFT Component

The initial investigation is focused on examining if NH$_3$ and H$_2$O selectively bind to specific sites on various SrTiO$_3$ (STO) surfaces. These probe molecules are used to gauge how the organometallic will bind to the oxide surface. The STO surfaces that are of interest include the low Miller index surfaces, (100), (110), and (111) in addition to higher Miller index surfaces. The (621) surface is selected as the initial high Miller index surface based on its steps, kinks, and terrace size. The DFT results will complement experimental work being conducted in the Jason Weaver research group. They will perform various surface science techniques under ultra high vacuum (UHV) on the order of 1x10$^{-10}$ torr. Temperature programmed desorption (TPD) will utilized to determine the desorption temperatures and masses of adsorbates from the surface. TPD is a technique that can be used to approximate adsorption energy [120]. Conversely, desorption temperatures can be approximated from the calculated binding energies to compare effectively. Additionally, if there are multiple peaks present in the TPD spectra, indicating the possibility of multiple adsorbate phases, DFT can predict the adsorbate configurations corresponding to each TPD peak to provide further insight. The ability of the experimentalists to probe the desorbed molecule’s mass allows for the
use of isotopes to investigate the occurrence of dissociation or even atom exchange with the surface. Additional comparisons may be made between experimental work in UHV and DFT calculations, such as determination of the vibrational modes. As part of this work, a manuscript was completed regarding the adsorption of water of STO(100) included in Section 8.2. Within this section, the details of these results are discussed and comparisons are made to available experimental data.

**8.2 A First-Principles Study of H₂O Adsorption and Dissociation on the SrTiO₃(100) Surface**


**8.2.1 Introduction**

The adsorption and reactivity of water on low-Miller index oxide surfaces serves as a model system to understand the structure-reactivity relationship of oxide surfaces. Water-oxide interfaces are also important in a range of applications in catalysis, environmental remediation, and biomineralization. Even under ultrahigh vacuum (UHV) conditions it is often difficult to avoid contamination of low coverages of water, which can affect the reactive properties of the surface. An important first step in understanding the reactive behavior of H₂O/oxide interfaces is to resolve if water adsorbs associatively or dissociatively on the oxide surface. While one may expect that the characterization of the structure of water on low-Miller index oxide surfaces under UHV conditions should be readily resolved with a combination of experimental and theoretical studies, the literature, for example on H₂O on rutile TiO₂(110) [121-123] and MgO(100) [121,124-126], shows that conflicting models can exist and are non-trivial to resolve. This challenge in resolving the structure of water on the oxide is due in part to a
combination of the difficulty of controlling oxide surface reconstructions, contaminants in UHV, coverage effects, the potential presence of complex water clusters, and approximations that must often be made in first-principles studies (e.g. size of system, accuracy of exchange-correlation functionals).

Water adsorption on SrTiO$_3$(100), including the role of defects such as oxygen vacancies and step edges, has been the focus of several experimental studies [127-133]. Like many oxides, SrTiO$_3$ can have multiple terminations for a given surface plane and SrTiO$_3$(100) can be terminated by a SrO or a TiO$_2$ plane (see illustration in Figure 8-1). The presence of the TiO$_2$-termination of SrTiO$_3$(100) has motivated some of the studies of H$_2$O on this surface, since it offers an opportunity to compare with the extensive studies of TiO$_2$ surfaces to shed light on the role of structure on the chemistry of the oxide [127]. SrTiO$_3$ also garners interest for potential use as a catalyst in photoelectric splitting of water [134,135].

![Bulk unit cell of SrTiO$_3$](image)

**Figure 8-1.** The bulk unit cell of SrTiO$_3$ highlighting the SrO termination (top) and TiO$_2$ termination (middle) of the SrTiO$_3$(100) surface.

Ultraviolet and X-ray photoemission spectroscopy (UPS, XPS) studies of water on SrTiO$_3$(100) under UHV conditions suggests that water adsorbs molecularly on the
pristine surface, but upon the inducement of oxygen vacancies via ion bombardment [130-133] or step edges by vacuum fracturing [128,129] the presence of dissociated water is detected. High resolution electron energy loss spectroscopy (HREELS) has also been used to probe the phonon modes of H₂O and D₂O on stoichiometric and reduced SrTiO₃(100) [130-132]. While the identification of phonons attributed to the adsorbate is complicated by the overlap with surface phonons of the oxide, the HREELS study suggests that water adsorbs dissociatively on SrTiO₃(100) only in the presence of oxygen vacancies [130,131]. Lopez et al. report in another HREELS study that the presence of Na on the SrTiO₃(100) surface can also result in dissociative adsorption of water [136]. Wang and co-workers have performed to date the only temperature programmed desorption (TPD) experiments in UHV of water adsorption on SrTiO₃(100) [127]. They found that water adsorbs on the pristine SrTiO₃(100) with a maximum peak desorption temperature of 260 K which shifts to lower temperatures with increasing water coverage. The TPD study also concludes non-dissociative adsorption on the SrTiO₃(100) surface with the primary evidence that the observed peak temperature in the TPD is too low to be assigned to dissociated H₂O. They approximate the surface to consist of ~80% TiO₂-termination and have confirmed via low energy electron diffraction (LEED) that the bare surface is initially the (1×1) unreconstructed SrTiO₃(100) surface. After sputtering the surface the TPD spectra shows a long tail starting at ~ 300 K and decaying at around 480 K. This tail in the TPD spectra is assigned to dissociated water on O vacancies and matches the general conclusions from earlier XPS and UPS studies of reduced SrTiO₃(100) surfaces. Wang et al. suggest that the lack of bridging O atoms on the pristine TiO₂-terminated SrTiO₃(100)
surface prevents strong H-bonding with the surface O atoms that would make it favorable to strip the H atoms from the water molecule [127]. In comparison, water binds dissociatively (associatively) on the defect-free TiO$_2$(100) (TiO$_2$(110)) surfaces [137-139]. DFT calculations suggest that on the TiO$_2$(100) the adsorbed water molecule has access to low-coordinated bridging O atoms, but on TiO$_2$(110) the distance between the H-atoms on the water molecule and the bridging O atoms is longer and prevents strong formation of H-bonds with the oxide surface O atoms [127,140]. In summary, the experimental results to date point to a model of associative adsorption of H$_2$O on pristine SrTiO$_3$(100) surface, with dissociation only observed at defects such as O vacancies and step edges.

This chapter reports on DFT calculations of H$_2$O adsorption and dissociation on both terminations of SrTiO$_3$(100). There has been a recent hybrid HF-DFT study examining water on both terminations of SrTiO$_3$(100) and they find that molecular water is favored over dissociated water on both terminations with this difference more pronounced on the TiO$_2$-termination [141]. This earlier DFT study examined coverages down to 1/2 monolayer (ML) on a 1×1 surface cell (see Section 8.2.2 for definition of 1 ML for this system). More dilute coverages are explored down to 1/8 ML using a 2×2 surface cell and it is found that both the adsorption energy and structure of water is sensitive to coverage. At coverages below 1/2 ML, DFT predicts dissociated H$_2$O is favored on both terminations of SrTiO$_3$(100). Possible sources of the differences between the DFT results and the existing experimental studies are discussed.

8.2.2 Calculation Details

All the DFT calculations in this chapter were performed with the Vienna ab initio simulation package (VASP) [45-47,142] using the projector augmented wave (PAW)
pseudopotentials provided in the VASP database. The Sr (4s, 4p, 5s), Ti (3s, 3p, 3d, 4s) and O (2s, 2p) orbitals were included as valence states and a plane wave cutoff energy of 400 eV was used. Calculations have been done using the generalized gradient approximation Perdew-Burke-Emzerhof (GGA-PBE) exchange correlation functional [51]. The effects of the functional on the accuracy of the DFT calculations will be discussed in Section 8.2.3.4.1. Electronic relaxation was performed with a block Davidson iteration method accelerated using Fermi-level smearing with a Gaussian width of 0.1 eV [53]. All calculations used a 6-layer slab with the bottom two layers fixed. The system is relaxed until all the forces are less than 0.03 eV/Å. An 8-layer and 10-layer slab was tested to confirm the binding energy and adsorbate structure match that found on the 6-layer slab. The water adsorbates were examined in increments of 1/2 and 1/8 ML for the 1×1 or 2×2 surface unit cells, respectively. A monolayer (ML) is defined as 2 water molecules per surface cation, which matches the definition used by the earlier HF-DFT study [141]. A vacuum region of about 24 Å is included to prevent the slab from interacting with its periodic image in the surface-normal direction. All calculations were completed using dipole corrections in the surface-normal direction [143]. The effects of spin polarization corrections were checked and found not to affect the adsorption energy for any of the high symmetry sites. An 8×8×1 and 4×4×1 Monkhorst-Pack mesh [54] was used for the 1×1 and 2×2 surface unit cells, respectively. A bulk lattice constant of 3.95 Å for SrTiO₃ was found, which matches fairly well to that previously reported from experiment (3.90 Å) [67] and DFT (3.94 Å) [68]. Minimum energy pathways and the barrier to water dissociation are calculated using the nudged elastic band (NEB) method [55-57].
8.2.3 Results and Discussion

8.2.3.1 Half-monolayer water on SrTiO$_3$(100)

On the (1×1)-SrTiO$_3$(100) surface four high symmetry adsorption sites were examined for both the SrO- and TiO$_2$-terminated surfaces, with each shown in Figure 8-2. Figure 8-2a, 8-2b, 8-2c, and 8-2d highlight the fourfold hollow site, the bridge site between the surface O and Sr, on top the Sr and O atoms, respectively, for the SrO-terminated surface. Figure 8-2e, 8-2f, 8-2g, and 8-2h illustrates the surface sites for on top O, the bridge site between surface Ti and O, on top surface Ti, and the fourfold hollow site, respectively, for the TiO$_2$-terminated surface. For simplicity these sites will be referred to as fourfold, bridge, Sr, Ti, and O.

![Figure 8-2](image)

Figure 8-2. The top layer of the (a)-(d) SrO-terminated and (e)-(h) TiO$_2$-terminated SrTiO$_3$(100) surface showing the 1×1 (2×2) surface cell outlined by dashed (solid) lines. The high symmetry adsorption sites examined are identified on the SrO-termination as (a) fourfold, (b) bridge, (c) Sr, (d) O and on the TiO$_2$-termination as (e) O, (f) bridge, (g) Ti, and (h) fourfold.

The adsorption of one water molecule on a single high symmetry site for this surface unit cell corresponds to a surface coverage of 1/2 ML, with ML defined in Section 8.2.2. Initially molecular water was placed with the oxygen atom in each of the high symmetry surface sites with various orientations for the hydrogen atoms ranging from pointing away from, perpendicular to, and downward towards the surface atoms.
After relaxation, the final adsorbate configurations depend only on the surface adsorption site (i.e., the initial oxygen position) and not on the initial hydrogen orientation.

Table 8-1. Adsorption energy \( (E_{ads}) \) of water at 1/8 and 1/2 ML on various high symmetry sites, defined in Figure 8-2, on the SrO- and TiO\(_2\)-terminated SrTiO\(_3\)(100). The values in parenthesis correspond to a dissociative state.

<table>
<thead>
<tr>
<th>Adsorption Site</th>
<th>( E_{ads} ) (eV/H(_2)O)</th>
<th>SrO termination</th>
<th>TiO(_2) termination</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1/8 ML on 2×2</td>
<td>1/2 ML on 1×1</td>
<td>1/8 ML on 2×2</td>
</tr>
<tr>
<td>Fourfold</td>
<td>0.90 (1.31)</td>
<td>0.58 (0.85)</td>
<td>0.23</td>
</tr>
<tr>
<td>Bridge</td>
<td>unstable (1.14)</td>
<td>0.84 (unstable)</td>
<td>0.89 (1.11)</td>
</tr>
<tr>
<td>Sr / Ti</td>
<td>converges to fourfold</td>
<td>converges to fourfold</td>
<td>0.76</td>
</tr>
<tr>
<td>O</td>
<td>0.11</td>
<td>0.06</td>
<td>0.72</td>
</tr>
</tbody>
</table>

Table 8-1 reports the adsorption energy for each of the surface adsorption sites at both 1/2 and 1/8 ML coverage. The adsorption energy \( (E_{ads}) \) is defined in Equation 8-1 where \( E_{slab} \) is the total energy of the relaxed SrTiO\(_3\) slab in the absence of any adsorbed H\(_2\)O, \( E_{H_2O, gas} \) is the energy of an isolated water molecule, \( E_{H_2O, slab} \) is the total energy of the H\(_2\)O/SrTiO\(_3\) slab, and \( n \) is the total number of water molecules in the H\(_2\)O/SrTiO\(_3\) slab.

\[
E_{ads} = \frac{\left( E_{slab} + n*E_{H_2O, gas} \right) - E_{H_2O, slab}}{n},
\] (8-1)

Figure 8-3a to 8-3d illustrate the most favored associative and dissociative H\(_2\)O configuration on the SrO- and TiO\(_2\)-terminations of SrTiO\(_3\)(100) at 1/2 ML. Table 8-2 presents all the relevant bond lengths associated with the structures illustrated in Figure 8-3a to 8-3d, along with similar values at the 1/8 ML configuration. This section focuses on the results at 1/2 ML and low coverage results are detailed in Section 8.2.3.2. To distinguish between hydroxyl groups consisting of O atom coming from the water versus the oxides surface the O atom from water (oxide surface) will be denoted by \( O_w \) (\( O_x \)).
Figure 8-3. Most favored half monolayer molecular [(a) and (b)] and dissociative [(c) and (d)] water configuration on 1×1-SrO [(a) and (c)] and 1×1-TiO₂ [(b) and (d)] termination as viewed along the [001] direction (above) and the [100] direction (below). The 1×1 surface unit cell is outlined by the dashed box.

Table 8-2. Bond lengths for the most stable water adsorbate configurations at 1/8 and 1/2 ML coverage on the SrO- and TiO₂-terminatated SrTiO₃(100) surface.

<table>
<thead>
<tr>
<th>Bond Length</th>
<th>SrO termination</th>
<th>TiO₂ termination</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1/8 ML (2×2)</td>
<td>1/2 ML (1×1)</td>
</tr>
<tr>
<td></td>
<td>1/8 ML (2×2)</td>
<td>1/2 ML (1×1)</td>
</tr>
<tr>
<td>H₂O</td>
<td>H-OH</td>
<td>H₂O</td>
</tr>
<tr>
<td>O₇-H₁</td>
<td>1.03</td>
<td>0.97</td>
</tr>
<tr>
<td>O₇-H₂</td>
<td>1.03</td>
<td>1.59</td>
</tr>
<tr>
<td>(Sr,Ti)-O₇</td>
<td>2.71</td>
<td>2.59</td>
</tr>
<tr>
<td>Oₓ-H₁</td>
<td>1.62</td>
<td>3.39</td>
</tr>
<tr>
<td>Oₓ-H₂</td>
<td>1.62</td>
<td>1.01</td>
</tr>
</tbody>
</table>

Note: Molecular and dissociative states are identified as H₂O and H-OH, respectively.

The most favored state for molecular H₂O is the bridge site for both terminations.

On the SrO-termination the bridge site is more stable by 0.26 eV over the fourfold site and similarly on the TiO₂-termination the bridge site is favored over water adsorption on the Ti atom by 0.18 eV. A previous investigation using hybrid HF-DFT with a linear combinations of atomic orbitals (LCAO) calculations studied water on SrTiO₃(100) and found both stable molecular and dissociative states on both terminations [141]. To test
the favorability of dissociative binding one hydrogen was separated from the converged molecular H$_2$O/SrTiO$_3$(100) and placed near the neighboring surface oxygen. On both terminations, it was found that after minimization that the dissociated H atom recombines with the hydroxyl group to form molecular water. Evarestov et al. also reported difficulties stabilizing a dissociative state at 1/2 ML coverage on the 1×1 surface cell of SrTiO$_3$(100) [141]. To overcome these difficulties, they used the stabilized dissociated water on SrZrO$_3$(100) surfaces and scaled the resulting configuration to the SrTiO$_3$(100) surface. Upon relaxation of this structure they were able to obtain a stable dissociated configuration on the SrTiO$_3$(100) surfaces. A dissociative state was finally stabilized by using an initial configuration based on the structure reported by Evarestov et al. [141]. The primary feature of the dissociated structure of Evarestov et al. is the distance between the hydroxyl group and the surface cation. If this distance is appropriate in the initial dissociated structure, a local minimum of the dissociative H$_2$O can be stabilized on both terminations. However, the dissociative state on TiO$_2$ is found to be less stable by 0.2 eV/H$_2$O and there is a negligible difference between associative and dissociative H$_2$O (0.01 eV/H$_2$O) on the SrO termination (see Table 8-1). These DFT values for the relative stability of associative versus dissociative H$_2$O on both terminations are very similar to the earlier HF-DFT study where they report molecular H$_2$O is favored by 0.1 eV/H$_2$O on the TiO$_2$-termination and 0.003 eV/H$_2$O difference on the SrO-termination [141]. As can be seen in Figure 8-3c, water rotates out of the bridge site and into a fourfold site on SrO following dissociation. The values for the bond lengths of the minima structures determined in this study also agree well with those reported by Evarestov et al. with
slight under estimation of the Ow-Sr at 2.55 Å vs. 2.61 Å [141] and over estimation of the Ow-Ti at 1.90 Å vs. 1.88 Å [141].

The primary conclusion from the earlier DFT study and this work at 1/2 ML is that H₂O should be expected to adsorb associatively on the defect-free SrTiO₃(100) surface. This conclusion agrees with the general findings of various experimental studies [127-133], especially if the expectation of predominance of TiO₂-termination in these experiments is taken into consideration [127]. While adsorption energies were not extracted in the TPD study of H₂O adsorption on SrTiO₃(100) [127], these values may be approximated from the peak temperature (Tₚ) associated with dilute coverages (~260 K) and assuming first-order desorption with no adsorbate interaction and a prefactor (νₒ) of 1×10¹³. With these assumptions and a heating rate of 1 K/s [127] a value for the adsorption energy of 0.92 eV can be extracted for Tₚ = 260 K. This adsorption energy is larger than the DFT value of 0.79 eV and 0.84 eV on the TiO₂- and SrO-termination respectively, which is not unexpected since the 260 K peak temperature is associated with dilute coverages but suggests that the adsorption energies from DFT are qualitatively similar to that derived from experiment.

Ignoring the adsorbate-adsorbate interactions a value of 0.63 eV for the adsorption energy (Tₚ ~ 180 K) at high coverages can be obtained from the TPD spectra. While these values are not very accurate due to the assumptions, they do illustrate a strong coverage dependence on the adsorption energy that can also be observed from the strong shift in the TPD spectra with coverage [127].
8.2.3.2 Dilute coverage of water on SrTiO_3(100)

To probe coverage affects on the adsorption energy and structure of water on the SrTiO_3(100) surface a 2×2 surface unit cell was used, which reduces the possible coverage increment to 1/8 ML. Water was examined in the same adsorption sites as above and the E_{ads} for each site is summarized in Table 8-1. Figure 8-4 shows the most stable minima for associative and dissociative H_2O found on both terminations at 1/8 ML.

For both terminations there is a general increase in adsorption energy for both the dissociated and molecular water states, but more importantly a crossover to a preference for the dissociative state occurs when the coverage is decreased from 1/2 to 1/8 ML. For the SrO-termination, a stable dissociated state was observed at the fourfold site with an adsorption energy of 1.31 eV/H_2O and shown in Figure 8-4c. As discussed in Section 8.2.3.1 dissociated water on the bridge site could not be stabilized in the 1×1 surface cell, and the dissociative state could only be stabilized by shifting to a fourfold site (see Figure 8-3c). The lower coverage further stabilizes the dissociative state as evident by the more substantial separation of the O\textsubscript{w}-H and free H as seen in Figure 8-4c versus Figure 8-3c.

At a coverage of 1/8 ML, the bridge site does have a stable state associated with dissociated water (not shown), but this site is less favorable over the fourfold by 0.17 eV/H_2O. For molecular H_2O the effect of lower coverage acts in an inverse way and destabilizes the water molecule at the bridge site. At 1/2 ML on the 1×1 SrO-termination the molecular water is prevented from dissociating due to repulsive neighbor interactions with an adjacent hydroxyl group in the [100] direction due to periodic
boundary conditions, but at lower coverages this obstacle is removed and the water molecule dissociates as it would prefer in the absence of this repulsive interaction.

Figure 8-4. Most favored 1/8 monolayer molecular [(a) and (b)] and dissociative [(c) and (d)] water configuration on 2×2 SrO [(a) and (c)] and 2×2 TiO₂ [(b) and (d)] terminations as viewed along the [001] direction (above) and the [100] direction (below). The 2×2 surface unit cell is outlined by the solid box for visual aid of the top view along the [001] direction.
The most stable molecular water state at 1/8 ML is then found on the fourfold site (see Figure 8-4a), and while this state gains 0.32 eV in stability due to the decrease in coverage, the adsorption energy of 0.90 eV/H$_2$O is weaker by 0.41 eV/H$_2$O than the dissociated state. Therefore, these DFT results suggest that at lower coverages dissociated water should be favored on the SrO-termination.

On the TiO$_2$ termination of the 2×2 surface cell, an increase in molecular water stability was found at each site with respect to the 1/2 ML coverage on the 1×1 TiO$_2$ terminated surface. The dissociated water structure at the bridge site on the TiO$_2$ termination shown in Figure 8-4d has an adsorption energy of 1.11 eV/H$_2$O, which is 0.22 eV/H$_2$O more stable than the most stable molecularly bound water shown in Figure 8-4b. Therefore, similar to the SrO-termination there is a crossover to the dissociated state at lower coverages on the TiO$_2$-termination. Evarestov et al. describe the dissociated water configuration on the 1×1 TiO$_2$ termination as having two hydroxyls groups in a trans-position to each other (see Figure 8-3d). On the 2×2 TiO$_2$ termination, a cis-type configuration of the two hydroxyl groups was identified, as illustrated in Figure 8-4d. The stability of a trans-type configuration of the two hydroxyl groups was tested at the coverage of 1/8 ML and a nearly energy equivalent state was found with an $E_{\text{ads}}$ of 1.13 eV/H$_2$O.

The structural information for the most stable water configurations at 1/8 ML are reported in Table 8-2 and can be compared with the values at 1/2 ML. As noted above for the SrO-termination there is a shift in the site of the preferred molecular water, therefore some of the changes in the structural parameters is due to this change. For dissociated H$_2$O on the SrO-termination, the primary change is a decrease in the O$_x$-H
distance from 1.13 to 1.01 Å when the coverage decreases to 1/8 ML. The distance of 1.01 Å is very close to the value of the hydroxyl group from the water molecule (0.97 Å), which implies that the hydroxyl group associated with Oₓ increases in strength upon the decrease in coverage.

On the TiO₂-termination there are less dramatic changes in the structure of water (associated or dissociated) with coverage, but instead the changes occur in the non-interacting bond distances. For molecular water there is a decrease of 0.24 Å in the bond distance between one of the H atoms on H₂O and the adjacent Oₓ atom (Oₓ-H₁) and the Oₓ-Ti bond distance shrinks by 0.06 Å. These changes again reflect the increase in the strength of the water-surface interactions for the molecular configuration with decreasing coverage.

For the dissociated water on TiO₂-termination there is a similar decrease in the Oₓ-Ti bond. But the more important effect of the lower coverage is made clear by comparing Figure 8-4d and Figure 8-3d, which represent the dissociated minima at 1/8 and 1/2 ML, respectively. At 1/2 ML coverage the two hydroxyl groups (Oₓ-H and Oₓ-H) are restricted in the ability to relax to optimize the interaction due to the presence of hydroxyl groups on both sides. This restriction is lifted at 1/8 ML and as can be seen in Figure 8-4d the two hydroxyl groups relax and rotate away from each other. The net effect of this additional relaxation is an increase in the stability of the dissociated H₂O molecule at the lower coverage.

To probe the observed crossover in the preferred structure of water 1/8, 1/4, 3/8, and 1/2 ML coverages were examined on the 2×2 surface cell. The use of the 2×2 surface cell also allows for the study of any size effects due to periodic boundary
conditions at 1/2 ML. Figure 8-5 plots the adsorption energy of the most favored configuration identified as a function of coverage (ML) on the 2×2 TiO₂-termination along with the earlier values at 1/2 ML found on the 1×1 TiO₂-termination.

**Figure 8-5.** $E_{\text{ads}}$ of the most favored molecular (triangle) and dissociative (circle) water configuration at varying coverage on the 2×2-TiO₂ termination. The adsorption energy for the molecular and dissociated H₂O on the 1×1-TiO₂ termination are included as open symbols at 1/2 ML.

Figure 8-6a to 8-6c illustrates the relaxed dissociative water at 1/4 ML coverage (2 water molecules/2×2 surface unit cell) in three different possible adsorbate configurations. The configurations vary in the distance between water molecules (Figure 8-6a versus Figure 8-6b and Figure 8-6c) or the relative orientation (Figure 8-6b versus Figure 8-6c). Water binding molecularly was also examined for each of these three configurations. For molecular binding the adsorbed water interacts similarly for all of the configurations with $E_{\text{ads}}$ of 0.82, 0.88, and 0.88 eV/H₂O, for molecular equivalents of the
dissociative configurations in Figure 8-6a, 8-6b, and 8-6c, respectively. However, for
dissociative binding there are significant variations in the adsorption energy with surface
configuration with an $E_{\text{ads}}$ of 1.02, 1.06, and 0.56 eV/H$_2$O for Figure 8-6a, 8-6b, and 8-
6c, respectively. The reason for this significant reduction in $E_{\text{ads}}$ for the configuration
shown in Figure 8-6c is due to repulsive interactions between the O$_x$-H and the O$_v$-H
groups.

![Figure 8-6. The three possible configurations of dissociatively adsorbed water at 1/4 ML coverage on the 2×2 TiO$_2$ termination viewed along the [001] and [100] directions with $E_{\text{ads}}$ values of (a) 1.02, (b) 1.06, and (c) 0.56 eV/H$_2$O. The 2×2 surface unit cell is outlined by the solid box for visual aid of the top view along the [001] direction.](image)

The unfavorable configuration associated with Figure 8-6c is similar to the
configuration found for 1/2 ML on the 1×1 surface cell (see Figure 8-3c). At a coverage
of 1/4 ML the water adsorbates can avoid this unfavorable interaction by taking on
configurations as shown in Figure 8-6a and 8-6b, which allow for rotations of the two
adjacent hydroxyl groups. However, the addition of one more water to the surface in any
surface site will create this unfavorable row of hydroxyl groups that are restricted by
having 2 neighbors on either side. Therefore, at 3/8 ML coverage the molecular water

200
state is favored over dissociative adsorption, as illustrated by the $E_{\text{ads}}$ in Figure 8-5 the crossover to favorability of dissociative water occurs at coverages below 3/8 ML.

Using the 2×2 surface unit cell, the favored configurations found on 1×1-TiO$_2$ termination were revisited. For the dissociative state at 1/2 ML on the 2×2-TiO$_2$, the cis-type hydroxyl group configuration binds with slightly higher adsorption energy of 0.63 eV/H$_2$O than the trans-type hydroxyl group configuration found on the 1×1-TiO$_2$ termination with an adsorption energy of 0.59 eV/H$_2$O (see Figure 8-5 at 1/2 ML). The adsorbate configuration on the 2×2 TiO$_2$ termination is mediated by surface TiO$_6$ octahedra rotation. Periodic boundary conditions restrict this tilting in the 1×1-TiO$_2$ system thus reflecting the lower adsorption energy. Figure 8-7 isolates the top layer of TiO$_6$ octahedra in order to aid in visualization of this tilting.

![Figure 8-7. Top layer of TiO$_6$ octahedra for the 2×2 surface unit cell of TiO$_2$-terminated with 1/2 ML of dissociated water on the Ti site viewed along the [001] (top) and [100] (bottom). The 2×2 surface unit cell is outlined by the solid box for visual aid of the top view along the [001] direction.](image-url)
This tilting occurs because at this coverage oxygen within each hydroxyl group
binds to a surface Ti atom and thereby completes the octahedral coordination. The
hydrogen freed from each water then binds to the neighboring surface oxygen and
triggers a buckling up or down of the surface oxygen and results in each octahedron
rotation. Specifically, the Ti atom buckles up by about 0.2 Å, while the oxygen atoms
buckle up by 0.31 or down by 0.23 Å. In addition to the buckling normal to the surface,
in the top view shown in Figure 8-7 there is movement of the oxygen perpendicular to
the surface normal direction. The role of the surface response was tested by fixing the
surface atoms to the ideal (optimized bare surface) position and both molecular and
dissociated water at 1/8 ML coverage were examined on the 2×2 TiO₂ surface. The
dissociated water recombines to the molecular state. With the molecularly bound water,
the E_{ads} on the fixed surface is reduced by 0.30 eV/H₂O with respect to the 1/8 ML
molecular state.

Similar to the 2×2 TiO₂-termination, different configurations at 1/4 ML were
examined on the 2×2 SrO-terminated surface. The configurations for dissociated water
following relaxation are shown in Figure 8-8a, 8-8b, and 8-8c with an adsorption
energies of 1.01, 1.22, and 1.20 eV/H₂O, respectively. Molecular water in similar
configurations shown in Figure 8-8a, 8-8b, and 8-8c binds with adsorption energies of
0.85, 0.70, and 0.76 eV/H₂O and therefore, as at 1/8 ML, the dissociated water
configurations will be favored at 1/4 ML on the SrO-termination.

Unlike on TiO₂, the adsorption energy for dissociated H₂O only slightly decreases
(0.1 to 0.3 eV/H₂O) with respect to the favored dissociated configuration at 1/8 ML (E_{ads}
= 1.31 eV/H₂O). Additionally, the configuration that was found to be least stable on the
TiO$_2$-termination (Figure 8-6c) is found to be the most stable on the SrO-termination (Figure 8-8c). Figure 8-8c shows the dissociated hydroxyl groups cluster instead of lining up in a row along the surface cations as was seen in Figure 8-6c. This clustering is due to the favored adsorption site of the hydroxyl group at 1/4 ML on the SrO termination, namely a transition from a bridge to a fourfold type site as illustrated in Figure 8-2a. Within the primitive 1×1 unit cell of the SrO termination there are two equivalent fourfold sites. The close proximity of the second fourfold site allows one of the dissociated water groups to rotate the hydroxyl portion to the neighboring fourfold site and away from the initial fourfold site, which was aligned along the [010] direction.

![Figure 8-8](image)

Figure 8-8. The three possible configurations of dissociatively adsorbed water at 1/4 ML coverage on the 2×2 SrO termination viewed along the [001] and [100] directions with $E_{\text{ads}}$ values of (a) 1.01, (b) 1.22, and (c) 1.20 eV/H$_2$O. The 2×2 surface unit cell is outlined by the solid box for visual aid of the top view along the [001] direction.

At 3/8 ML, an adsorption energy of 1.12 eV/H$_2$O was found for the dissociated water, which is less stable by 0.19 eV to that determined at 1/8 ML. The molecular water configuration has an adsorption energy of 0.71 eV/H$_2$O and therefore at 3/8 ML as at 1/4 and 1/8 ML the dissociated water configuration is favored on the SrO-
termination. Finally at 1/2 ML coverage some repulsive interactions are seen between the adsorbates with an adsorption energy of 0.97 eV/H₂O and one of the water molecules recombines resulting in a mixed adsorption configuration. A pure molecular configuration was identified with the H₂O molecules sitting on the fourfold sites. This configuration had an adsorption energy of 0.64 eV/H₂O, compared to a value of 0.58 eV/H₂O on the 1×1 surface cell. This slight increase can be attributed to the ability of the water molecules to take on alternative up and down orientation (not shown), which slightly stabilizes the molecular water layer. Nevertheless, by comparing the adsorption energy of the mixed adsorption configuration (0.97 eV/H₂O) with molecular water on the bridge site of the 1×1 SrO (0.84 eV/H₂O) or at the fourfold sites of the 2×2 SrO (0.64 eV/H₂O), it is found that the mixed configuration is favored. The mixed adsorbate configuration on the 2×2 SrO surface, the inability to stabilize water molecules on the bridge sites on the 2×2 SrO surface, and the observed octahedra tilting of the TiO₆ octahedra of the 2×2 TiO₂ surface indicate that for even high coverages a minimum 2×2 surface unit cell is needed to fully probe the structure of water due to these subtle adsorbate-adsorbate interactions. If the DFT-predicted configurations at 1/2 ML are accurate they suggest that LEED probing the water layers on SrTiO₃(100) should show doubling of the unit cell.

Utilizing the code of Henkelman et al. [62,144], the Bader charges were determined based on the Bader criteria for decomposing the electron density [61]. Table 8-3 summarizes the Bader charges for the 1×1 and 2×2 surface unit cell of both the SrO and TiO₂ termination. In each case, the hydrogen atom is assigned zero electrons according to the Bader criteria due to the lack of zero-flux surfaces in the electron
density gradient between the hydrogen and oxygen atoms. Though not shown, the
electron charge density was examined to confirm the lack of a gradient between
hydrogen and oxygen. Therefore, the hydrogen atom’s electron is assigned to the
bonding oxygen. This is evident by the significant change in charge associated with the
terminal oxygen before and after dissociation. After dissociation, the water oxygen
losses 0.44 (0.31) electrons on the TiO$_2$ (SrO) termination and the surface oxygen
bound to the free hydrogen gains 0.43 (0.54) electrons.

Table 8-3. The average Bader atomic charges in units of e for Sr, Ti, H, and O within
the oxide and water, are shown for molecular and dissociative water on both
TiO$_2$ and SrO terminations.

<table>
<thead>
<tr>
<th>TiO$_2$ termination</th>
<th>Molecular (1/8, 1/4, 1/2)</th>
<th>Dissociative (1/8, 1/4, 1/2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr</td>
<td>1.58</td>
<td>1.58</td>
</tr>
<tr>
<td>Ti</td>
<td>2.14</td>
<td>2.14</td>
</tr>
<tr>
<td>O$_{surf}$</td>
<td>-1.24</td>
<td>-1.24 (-1.67)</td>
</tr>
<tr>
<td>O$_{water}$</td>
<td>-1.97</td>
<td>-1.53</td>
</tr>
<tr>
<td>H</td>
<td>1.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SrO termination</th>
<th>Molecular (1/8, 1/4, 1/2)</th>
<th>Dissociative (1/8, 1/4, 1/2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr</td>
<td>1.60</td>
<td>1.60</td>
</tr>
<tr>
<td>Ti</td>
<td>2.16</td>
<td>2.14</td>
</tr>
<tr>
<td>O$_{surf}$</td>
<td>-1.24</td>
<td>-1.23 (-1.77)</td>
</tr>
<tr>
<td>O$_{water}$</td>
<td>-2.09</td>
<td>-1.78</td>
</tr>
<tr>
<td>H</td>
<td>1.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Note: For the dissociative adsorption, the surface oxygen bound to the free hydrogen is
distinguished in parenthesis.

Though the Bader charges determined in this study underestimate the ionic
classification of both the Sr and Ti atoms with respect to that determined by Evarestov et al.
[141] the general features agree well. Similar to Evarestov et al., it was determined that
the Sr, Ti, and O (not bound to the free hydrogen) charges are unaffected by the
dissociation of water [141]. On both terminations, the charges are unaffected by
changes in coverage or surface unit cell, e.g. 1/2 ML molecular water on 1×1 TiO$_2$ has
the same charges as 1/2 ML and 1/8 ML molecular water on 2×2 TiO₂. This observation suggests that the observed changes in stability of coverage is not linked with changes in bonding, but instead are dependent on electrostatic interactions. Calculations with larger unit cells (4×4) would also be useful in determining the role of long-range substrate-mediated versus electrostatic interactions, but such analysis are left to future studies.

The larger charge transfer on the SrO termination can help examine the clustering affect observed on the 2×2 SrO surface with 1/4 ML coverage, illustrated in Figure 8-8c. The initial configuration, with the two dissociated water groups aligning along the surface Sr cations, places each hydroxyl group between two surface oxygen bound to two free hydrogen atoms. Since each of these surface oxygen atoms gain 0.54 electrons following adsorption of free hydrogen atoms, each of the two surface oxygen atoms would have a charge of -1.7 e. The two hydroxyl groups from the two adsorbed water would also have a charge of -1.7 e. The close proximity of these charges would lead to significant repulsion between the surface based and water based hydroxyl groups. This repulsion in combination with the close proximity of another free favorable surface adsorption site on the 2×2 surface leads to the rotation previously mentioned.

### 8.2.3.3 Vibrational modes of water on SrTiO₃(100)

A useful experimental probe in attempting to resolve between molecular versus dissociated water is HREELS or other vibrational spectroscopy tools [137,138]. Lopez et al. reported vibrational spectra of water on both clean and sodium modified SrTiO₃(100) at room temperature [136]. The absence of the OH band at 3600 cm⁻¹ indicated water did not adsorb on clean SrTiO₃ but this is likely due to the experiments being performed at room temperature. Wang and co-workers in their TPD study have demonstrated
lower temperatures are needed to have uptake of H$_2$O on pristine SrTiO$_3$(100) [127]. However, after sodium atoms are coadsorbed with water on the SrTiO$_3$(100) a feature was observed at 3660 cm$^{-1}$, attributed to the OH band [136]. This feature was independent of the water exposure indicating surface saturation at low water exposure. Though not discussed, the absence of a feature near 1595 cm$^{-1}$ would indicate that water was adsorbed dissociatively, as this feature is attributed to H-O-H bond angle scissoring. Cox. et al. completed an HREELS study of water adsorption on SrTiO$_3$(100) at 100 K and found two main peaks associated with the a moderate dosage (4 Langmuir) of water [131], a sharp peak at 3662 cm$^{-1}$ and another peak at 1686 cm$^{-1}$. Cox et al. attributed the high frequency mode to symmetric stretching of the OH bond and the low frequency mode with the bond angle bending mode, thereby concluding water binds molecularly on pristine SrTiO$_3$. However, due to a poor noise to signal ratio, the asymmetric OH stretching mode was not resolved. Overall, while there have been vibrational studies of H$_2$O/SrTiO$_3$(100) the coverage in these studies is not known and full mode assignment, including resolving shifts of frequencies upon adsorption, has not been made.

DFT was used to determine the vibrational modes of the most stable dissociative and molecular water structure at 1/8 ML on the SrO- and TiO$_2$-termination. To allow for a computationally tractable but accurate evaluation of the vibrational modes associated with the water adsorbate and its interaction with the surface, the oxide atoms not participating directly in the water adsorption were fixed. A finite central difference method with a displacement of 0.05 Å is used to calculate the Hessian matrix. Neglecting the surface modes the zero point corrections (ZPC) to the adsorption energy
are 0.056 and 0.092 eV/H$_2$O molecule for the 0.125 ML coverage dissociative and molecular state on the TiO$_2$ termination, respectively. These corrections are not sufficient to change the favorability of the dissociative state over the molecular state and therefore do not affect the primary conclusions and ZPC adsorption energies are not reported in this chapter. The frequencies and mode assignments are summarized in Table 8-4.

The mode associated with stretching of the H-O bond is split for molecular water on the TiO$_2$ termination. The hydrogen oriented away from the surface oxide (i.e. H$_1$ in Table 8-2 and 8-4) has the characteristic frequency of 3609 cm$^{-1}$ (3666 cm$^{-1}$), while the hydrogen oriented towards the oxide (i.e., H$_2$) is assigned a frequency nearly 300 cm$^{-1}$ lower at 3337 cm$^{-1}$ (3254 cm$^{-1}$) at 1/8 ML (1/2 ML) coverage. The bond angle scissoring mode has a frequency of 1585 and 1571 cm$^{-1}$, for the 1/8 and 1/2 ML coverage, respectively, are very near the expected 1595 cm$^{-1}$. The dissociatively bound water at 1/8 ML, has vibrational modes of 3762 cm$^{-1}$ and 3644 cm$^{-1}$ associated with O-H stretching of the water hydroxyl group and surface oxide, respectively. The same modes for the 1/2 ML coverage are slightly down shifted at 3734 cm$^{-1}$ and 3513 cm$^{-1}$. At either coverage, the low frequency mode near 1595 cm$^{-1}$ was not observed due to the loss of the H-O-H bond angle scissoring.

Onal et al. computationally investigated water adsorption on small clusters representative of (101) and (100) surfaces of anatase TiO$_2$ structure [145]. Vibrational frequencies determined compare well to available experimental data. Similar to the DFT findings reported here, there were marked differences between the frequencies associated with molecular and dissociative adsorption.
Table 8-4. DFT-derived vibrational frequencies in cm\(^{-1}\) of isolated water, molecular and dissociative water at the favored site on the 2×2 and 1×1 SrO- and TiO\(_2\)-termination and the corresponding mode assignment. For isolated H\(_2\)O the experimental values [130] are given in parentheses.

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Mode Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Isolated H(_2)O</strong></td>
<td></td>
</tr>
<tr>
<td>H-O(_w)</td>
<td>3838 (3756) cm(^{-1}) Asymmetric stretching</td>
</tr>
<tr>
<td>H-O(_w)</td>
<td>3723 (3657) cm(^{-1}) Symmetric stretching</td>
</tr>
<tr>
<td>H-O(_w)-H</td>
<td>1560 (1595) cm(^{-1}) Bending (scissoring)</td>
</tr>
<tr>
<td><strong>1/8 ML H(_2)O on 2×2 TiO(_2)</strong></td>
<td></td>
</tr>
<tr>
<td>H(_1)-O(_w)</td>
<td>3609 cm(^{-1}) Asymmetric stretching</td>
</tr>
<tr>
<td>H(_2)-O(_w)</td>
<td>3337 cm(^{-1}) Asymmetric stretching</td>
</tr>
<tr>
<td>H(_1)-O(_w)-H (_2)</td>
<td>1585 cm(^{-1}) Bending (scissoring)</td>
</tr>
<tr>
<td><strong>1/8 ML H-(\text{OH}) on 2×2 TiO(_2)</strong></td>
<td></td>
</tr>
<tr>
<td>H(_1)-O(_w)</td>
<td>3762 cm(^{-1}) Stretching</td>
</tr>
<tr>
<td>H(_2)-O(_x)</td>
<td>3644 cm(^{-1}) Stretching</td>
</tr>
<tr>
<td><strong>1/2 ML H(_2)O on 1×1 TiO(_2)</strong></td>
<td></td>
</tr>
<tr>
<td>H(_1)-O(_w)</td>
<td>3666 cm(^{-1}) Asymmetric stretching</td>
</tr>
<tr>
<td>H(_2)-O(_w)</td>
<td>3254 cm(^{-1}) Asymmetric stretching</td>
</tr>
<tr>
<td>H(_1)-O(_w)-H (_2)</td>
<td>1571 cm(^{-1}) Bending (scissoring)</td>
</tr>
<tr>
<td><strong>1/2 ML H-(\text{OH}) on 1×1 TiO(_2)</strong></td>
<td></td>
</tr>
<tr>
<td>H(_1)-O(_w)</td>
<td>3734 cm(^{-1}) Stretching</td>
</tr>
<tr>
<td>H(_2)-O(_x)</td>
<td>3513 cm(^{-1}) Stretching</td>
</tr>
<tr>
<td><strong>1/8 ML H(_2)O on 2×2 SrO</strong></td>
<td></td>
</tr>
<tr>
<td>H(_1)-O(_w)-H (_2)</td>
<td>2593 cm(^{-1}) Symmetric stretching</td>
</tr>
<tr>
<td>H(_1)-O(_w)-H (_2)</td>
<td>2542 cm(^{-1}) Asymmetric stretching</td>
</tr>
<tr>
<td>H(_1)-O(_w)-H (_2)</td>
<td>1546 cm(^{-1}) Bending (scissoring)</td>
</tr>
<tr>
<td>H(_1)-O(_w)-H (_2)</td>
<td>1248 cm(^{-1}) Pseudo bending (scissoring)</td>
</tr>
<tr>
<td><strong>1/8 ML H-(\text{OH}) on 2×2 SrO</strong></td>
<td></td>
</tr>
<tr>
<td>H(_1)-O(_w)</td>
<td>3788 cm(^{-1}) Stretching</td>
</tr>
<tr>
<td>H(_2)-O(_x)</td>
<td>2864 cm(^{-1}) Stretching</td>
</tr>
<tr>
<td>H(_1)-O(_w)-H (_2)</td>
<td>1111 cm(^{-1}) Pseudo bending (scissoring)</td>
</tr>
<tr>
<td>H(_1)-O(_w)-H (_2)</td>
<td>1047 cm(^{-1}) Pseudo bending (scissoring)</td>
</tr>
<tr>
<td><strong>1/2 ML H(_2)O on 1×1 SrO</strong></td>
<td></td>
</tr>
<tr>
<td>H(_1)-O(_w)</td>
<td>3780 cm(^{-1}) Asymmetric stretching</td>
</tr>
<tr>
<td>H(_2)-O(_w)</td>
<td>2118 cm(^{-1}) Asymmetric stretching</td>
</tr>
<tr>
<td>H(_1)-O(_w)-H (_2)</td>
<td>1579 cm(^{-1}) Bending (scissoring)</td>
</tr>
<tr>
<td>H(_1)-O(_w)-H (_2)</td>
<td>1113 cm(^{-1}) Pseudo bending (scissoring)</td>
</tr>
<tr>
<td><strong>1/2 ML H-(\text{OH}) on 1×1 SrO</strong></td>
<td></td>
</tr>
<tr>
<td>H(_1)-O(_w)</td>
<td>3785 cm(^{-1}) Stretching</td>
</tr>
<tr>
<td>H(_1)-O(_w)-H (_2)</td>
<td>1543 cm(^{-1}) Pseudo bending (scissoring)</td>
</tr>
<tr>
<td>H(_1)-O(_w)-H (_2)</td>
<td>1345 cm(^{-1}) Pseudo bending (scissoring)</td>
</tr>
<tr>
<td>H(_1)-O(_w)-H (_2)</td>
<td>1251 cm(^{-1}) Pseudo bending (scissoring)</td>
</tr>
</tbody>
</table>
On (101) TiO₂, molecular adsorption exhibited three features at 3005, 3661, and 1605 cm⁻¹ and dissociative adsorption only two at 3666 and 3713 cm⁻¹. The dissociated water on TiO₂(101) frequencies are within 50 cm⁻¹ to those determined on the TiO₂-terminated SrTiO₃(100) surface. For the molecular state on TiO₂(101), there is also a downward shift in the frequency of the O-H stretching mode by 600 cm⁻¹ similar to that observed on SrTiO₃(100) but with larger magnitude.

The vibrational modes of molecular and dissociative water at 1/8 ML on the 2×2-SrO and 1/2 ML on the 1×1-SrO surface are included in Table 8-4. For dissociative water at 1/8 ML, the hydrogen oxygen stretching within the dissociated hydroxyl group has an upward shift in frequency to 3788 cm⁻¹ versus the same mode on the 2×2-TiO₂ surface at a frequency of 3762 cm⁻¹. The dissociated hydrogen to surface oxygen stretching is significantly altered on the 2×2-SrO surface (2864 cm⁻¹) versus 2×2-TiO₂ surface (3644 cm⁻¹). The change in this mode between the two surfaces is related to the adsorbate structures, and adsorption sites.

On the TiO₂ termination, the dissociated hydrogen stretches into the free space above the surface. In the fourfold adsorption site on the SrO termination, the dissociated hydrogen stretches between the surface oxide and the oxygen from the dissociated water. Additional modes not observed on the TiO₂ termination are identified on both the 1×1- and 2×2-SrO surface due to the open nature of the SrO surface plane. The dissociated hydrogen stretches into the open fourfold high symmetry site [see Figure 8-2a]. This stretching results in a pseudo bond angle bending mode with two frequencies of 1111 cm⁻¹ and 1047 cm⁻¹ at 1/8 ML on 2×2-SrO and three frequencies of 1543 cm⁻¹, 1345 cm⁻¹, and 1251 cm⁻¹ at 1/2 ML on 1×1-SrO. These low frequency pseudo bending
modes are also observed for the molecular states on both 1×1- and 2×2-SrO. For 1/2 ML, the expected \( O\text{\textsubscript{w}}-H \) stretching has a frequency of 3780 cm\(^{-1} \) and 2118 cm\(^{-1} \), the bond angle bending mode at 1579 cm\(^{-1} \) and one pseudo bond angle bending modes at 1113 cm\(^{-1} \). At 1/8 ML, the molecular water adsorbed in the fourfold site leads to a downshift in the frequencies. Symmetric stretching of the water hydrogen atoms has a frequency of 2593 cm\(^{-1} \) versus the isolated water mode at 3838 cm\(^{-1} \). The asymmetric stretching of the hydrogen atoms is 2542 cm\(^{-1} \), nearly 1200 cm\(^{-1} \) shift in the mode.

The bond angle bending mode has frequency of 1546 cm\(^{-1} \) similar to the isolated molecule at 1560 cm\(^{-1} \). The pseudo bond angle bending occurs at 1/8 ML as well but at a frequency of 1248 cm\(^{-1} \) versus 1113 cm\(^{-1} \). Despite this pseudo bond angle bending, the \( \sim 400 \text{~cm}^{-1} \) downward shift in the frequency should be sufficiently large to distinguish between a dissociatively or molecularly bond water at a given coverage on the SrO-termination of SrTiO\(_3\)(100). However, care must be taken in identifying the coverage of water on the surface since the pseudo bending mode at 1/8 ML molecular water on SrO (1248 cm\(^{-1} \)) is nearly the same as that of 1/2 ML dissociative water on SrO (1251 cm\(^{-1} \)).

As mentioned in the introduction, water adsorption on MgO (100) has been extensively studied with varying results. Chizallet \textit{et al.} examined IR features of OH groups on MgO using both cluster and periodic DFT calculations [146]. The vibrational modes determined were compared to experimental spectra showing a broad low frequency feature between 3200 and 3650 cm\(^{-1} \) and a sharp high frequency feature between 3650 and 3800 cm\(^{-1} \). The theoretical investigation identified various features based on the water adsorbate configuration providing some insight into the broad low frequency feature. Lower frequency modes around 1800 cm\(^{-1} \) are associated with H-O-
8.2.3.4 Discussion on potential sources of DFT-experiment disagreement

The introduction (Section 8.2.1) discussed the experimental studies that conclude the presence of only molecular water on pristine SrTiO$_3$(100). The only study of water at low coverages is the TPD study of Wang and co-workers [127], and while they see peak temperatures close to 260 K, which is associated with molecular H$_2$O, there is no direct evidence, for example from HREELS vibrational spectra or STM images of the state of H$_2$O at low coverages versus at high coverages. As noted earlier conflicting models between DFT and experiment in the resolution of structure of water on oxide surfaces is not new, as in both TiO$_2$(110) and MgO(100) there have been initial disagreement. Below some possible sources of the difference between the DFT results and experimental studies are addressed.

8.2.3.4.1 Evaluation of the exchange-correlation functional. One often raised concern with DFT studies is the impact of the functional on the accuracy of the calculations. Could the favorability of dissociated H$_2$O found in these calculations be due to error associated with the PBE functional? There are numerous DFT studies of water adsorption on various oxide surfaces [125,145,147,148], including the discussed HF-DFT study of H$_2$O/SrTiO$_3$(100) [141], which suggest in general GGA-type functional will more accurately describe H$_2$O adsorption than the LDA functional. Nevertheless, within GGA there are several different implementations and hybrid functionals, such as PBE0 [149,150] and HSE06 [151,152], are expected to be more accurate than PBE. At least one drawback to the hybrid functionals is the additional computational expense in their current implementation in plane-wave codes such as VASP [153,154].
Table 8-5. Bulk lattice parameter (Å) of SrTiO₃ and the adsorption energy (eV/H₂O) for molecular and dissociative H₂O at 1/8 ML on the TiO₂ terminated SrTiO₃(100) surface for various exchange-correlation functionals.

<table>
<thead>
<tr>
<th>Functional</th>
<th>Lattice parameter</th>
<th>E_{ads} (molecular)</th>
<th>E_{ads} (dissociated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE</td>
<td>3.95</td>
<td>0.89</td>
<td>1.11</td>
</tr>
<tr>
<td>RPBE</td>
<td>3.98</td>
<td>0.84</td>
<td>1.13</td>
</tr>
<tr>
<td>PBEsol</td>
<td>3.90</td>
<td>2.67</td>
<td>2.83</td>
</tr>
<tr>
<td>PBE0</td>
<td>3.90</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HSE06</td>
<td>3.90</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>experiment</td>
<td>3.90</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

To characterize the error in the GGA-PBE calculations reported in this chapter, select calculations with other GGA functional are repeated. Table 8-5 shows the bulk SrTiO₃ lattice parameter and the adsorption energy at a coverage of 1/8 ML on the TiO₂-terminated SrTiO₃(100) surface for both associated and dissociated H₂O.

The testing of the functional was focused on TiO₂-termination since the experimental SrTiO₃(100) surface is expected to be dominated by this termination [127]. PBEsol and the two hybrid functionals reproduce the experimental lattice parameter value of 3.90 Å precisely, while the PBE and RPBE functionals are less accurate with values of 3.95 and 3.98 Å, respectively. These results match earlier studies that have shown that PBEsol is very effective in capturing the bulk structure without the expense of the hybrid functionals [68,154]. Unfortunately, applying the PBEsol to calculate the adsorption energy gives values that are nearly double the PBE results, a trend that matches earlier tests of this functional [154], but even within PBEsol the dissociated structure is favored. The RPBE functional gives very similar results as PBE and most importantly confirms the preference for dissociated water at low coverages.

Unfortunately, similar tests of the adsorption energies using the hybrid functional were not possible due to the computational expense. Future testing with a more computationally tractable system (i.e. Γ-point and thinner slabs) will help to clarify any
quantitative changes to the adsorption energy, but a reversal of the favorability of the water structure is not expected using the hybrid functionals due to the large energy difference (~0.20 eV) between the two structures in the PBE-DFT calculations.

**8.2.3.4.2 Clustering effects – favored dimer configurations.** Clustering of water molecules could dramatically affect the stable structures on the surface. For example, co-adsorbed HO-H₂O complexes have been identified on PdO(101) [148], TiO₂(011) [155], TiO₂(110) [156], MgO(001) [124,157]. While a thorough study of cluster effects on the structure and stability of water on SrTiO₃(100) is beyond the scope of this chapter, stable dimer configurations on the 2×2 TiO₂ termination have been attempted. The goal is to probe on 2×2 surface unit cell if any dimer complexes (H₂O-H₂O, OH-OH, or HO-H₂O) are more favored over the isolated dissociated water structure identified at 1/4 and 1/8 ML. The stabilized molecular and dissociative water structure at 1/8 ML from Section 8.2.3.2 were used with molecular water added to neighboring high symmetry sites from Figure 8-2. It was found when molecular water is added near the dissociated water either the dissociative water recombines or the molecular water shifts over to the next bridge site, thereby increasing the interatomic distance. For most of the configurations with two molecular water adsorbates, the two molecules separate in order to increase the interatomic distance between molecules to a state similar to the molecular equivalent of configuration in Figure 8-6c. In one case the second water adsorbs to the neighboring fourfold site, see Figure 8-2h, and orients itself perpendicular to the original state with one hydrogen pointed towards the surface and one pointed away. For each of these configurations, the total adsorption energy is found to be between 0.11 and 0.16 eV/H₂O less favored than the molecular equivalent shown
in Figure 8-6c. Therefore, these configurations do not stabilize dissociative adsorption and on the 2×2 TiO₂ termination the isolated dissociated H₂O remains the most favored configuration identified. However, the cluster configuration of molecular water adsorbed to the bridge and fourfold site provides some insight into how the TiO₂ termination may favorably accommodate surface saturation at high coverages of 1 ML. While this initial study of dimer configurations has not found any favored clustering on the TiO₂-termination, future studies using larger surface unit cells and probing more configurations for stable clusters of water molecules would assist in more firmly resolving the role of intermolecular interactions of water on the SrTiO₃(100) surface.

8.2.3.4.3 Kinetic barrier to dissociation. One potential scenario that would resolve the difference between DFT and experiment is the presence of an energy barrier to dissociation of H₂O on the surface that is larger than the desorption energy. Under these conditions the molecular state would be kinetically trapped. The NEB method was first used to identify the barrier on the 1×1 SrO- and TiO₂-termination. For the 1×1 SrO surface, the energy difference between the molecular and dissociative state was 0.01 eV (see Table 8-1). Both the barrier to dissociation and association on the 1×1 SrO-termination are negligible at 0.00 and 0.05 eV respectively. On the 1×1 TiO₂ termination surface, where the molecular water is favored, the dissociation (association) barrier is 0.29 (0.13) eV. Both these barriers are relatively small in comparison to the adsorption energies and would suggest that kinetic barriers will not play a large role in the observed species on the surface. Nevertheless, the crossover to dissociated water occurs at lower coverages and therefore the energy barrier on the 2×2 TiO₂ was evaluated at a coverage of 1/8 ML to examine both the role of system
size and adsorbate coverage. The cis-type dissociative structure was used in order to compare with the results for the 1×1 TiO₂ system. Additionally, to reduce the computational expense the force criterion was slightly reduced for the NEB calculations from 0.03 to 0.05 eV/Å. The resulting dissociation barrier is 0.08 eV, while recombination has a barrier of 0.34 eV. Therefore, the dissociation barrier in fact becomes smaller and is negligible at lower coverages. While not explicitly calculated for the 2×2 SrO-termination similar results are expected for the dissociation barrier. These calculated energy barriers suggest the discrepancy between DFT and experimental observations cannot be resolved by invoking large kinetic barriers to dissociations.

8.2.4 Summary

The stability of molecular versus dissociated water as a function of coverage on both terminations of SrTiO₃(100) was studied using DFT. At a coverage of 1/2 ML the general results of an earlier hybrid HF-DFT study [141] were reproduce, which predicts that associative H₂O will be the favored structure on TiO₂-termination and negligible differences in stability between associative and dissociative H₂O on the SrO-termination. Artificial size effects at coverages of 1/2 ML due to periodic boundary conditions were identified by comparison of 1×1 and 2×2 surface unit cells. As the coverage is decreased below 3/8 ML a crossover to dissociative water on the TiO₂-termination was found. On the 2×2 SrO-termination a mixed adsorbate structure can be stabilized at 1/2 ML and further decrease in coverage stabilizes pure dissociative H₂O. The DFT results reported in this chapter at lower coverages conflicts with the general conclusions of experiments examining H₂O/SrTiO₃(100), but these experiments have not yet presented a fully detailed picture of water on SrTiO₃(100). It remains an open question of the source of the differences between these DFT results and the
experimental studies. Possible stabilization mechanisms for molecular water were probed, but clustering or kinetic barriers to dissociation were not found to stabilize molecular over dissociated water. A possibility that would dramatically affect the comparison between experiment and DFT would be adsorbate induced surface reconstructions. As noted in the introduction the experimental studies note a unreconstructed 1×1 SrTiO₃ surface, but several studies have shown that there are numerous reconstructions for SrTiO₃(100) and the surface structure is sensitive to both the environment and preparation [158,159]. The TPD study of H₂O on SrTiO₃(100) does report LEED patterns before the water exposure indicate a 1×1 unreconstructed surface [127], but they did not probe the surface structure during and after exposure to H₂O. The SrTiO₃ surface could reconstruct upon adsorption which would lead to different surface-adsorbate interactions and under that scenario this DFT study would not be examining the relevant configurations. To probe possible reconstructions upon H₂O adsorption would be non-trivial using DFT without any input from experiment. Future experimental studies that probe the surface structure during water exposure, for example with STM, would be critical to resolve the role of clustering and/or ordering of water and any possible adsorbate induced reconstructions. DFT studies to elucidate the role of O vacancies and step edges on water structure, in particular vibrational modes specific to these defects, would assist in the interpretation of experimental data. Such combined DFT-STM studies have been critical for example to resolve the water structure on TiO₂(011) [155] and it is expected that the results reported in this chapter will motivate similar studies on SrTiO₃(100).
9.1 Summary of Dissertation

To rationally design oxide materials for specific applications requires understanding the structure-property relationship which ideally would allow one to link structure on an atomic-level up to macroscopic properties such as dielectric constants or catalytic activity. In this dissertation, modeling work based on density functional theory (DFT), an \textit{ab initio} quantum based method, was presented for two different oxide families with the goal of understanding the structure-property relationships. The majority of the dissertation focused on isolating and understanding the role of atomic displacements, oxygen vacancies, and cation substitutions on the dielectric properties of bismuth based pyrochlores. DFT results for the adsorption and dissociation of H$_2$O on SrTiO$_3$(100) was also presented. These calculations provide a portion of a collaborate effort at the University of Florida on SrTiO$_3$ surfaces to design methods of delivering metal clusters to specific sites on oxide surfaces.

In Chapter 3, DFT was used to explore a range of cubic Bi$_2$B$_2$O$_6$O' (B = Ti, Ru, Rh, Ir, Os, Pt) pyrochlores with no cation substitutions and found significant cation displacement in only Bi$_2$Ti$_2$O$_7$. The atomic displacement stabilizes this structure with an energy change of similar magnitude to that of other bismuth-based pyrochlores. In Bi$_2$Ti$_2$O$_7$, an average displacement of 0.38 Å for the Bi cation, 0.07 Å for the Ti cation, 0.11 Å for the O' anion, and an energy change of \textasciitilde0.15 eV/Bi atom is found. The Bi cation and O' displacements appear to follow a $\beta$-cristobalite type displacive disorder as seen in other more complex bismuth pyrochlores.
The electronic structure shows the main difference between Bi$_2$Ti$_2$O$_7$ and the metallic bismuth pyrochlores is the extent of Bi-O’ interactions. In Bi$_2$Ti$_2$O$_7$ there is more overlap of Bi $s$ and $p$ states with O $2p$ states similar to the reported electronic structure of Bi$_2$Sn$_2$O$_7$, PbO and SnO [94,99], which leads to the asymmetric electronic structure around the Bi cation and the displacement of cations in Bi$_2$Ti$_2$O$_7$. These DFT results match the general understanding from experimental studies, but underestimate the displacement in Bi$_2$Ru$_2$O$_7$ compared with experimental results of defective Bi$_2$Ru$_2$O$_{7-δ}$ [20].

The lone pair formation in Bi$_2$Ti$_2$O’O$_6$ is further examined in Chapter 4 through sulfur substitution on the O’ and O sites in an effort to isolate the Bi-O’ and Bi-O interactions. The primary importance of the Bi-O’ interactions was confirmed since atomic displacement is not favored in the case of S substituted on the O’ site. The electronic structure analysis, including the partial density of states, electron localization function and partial electron density, showed that the S substitution on the O’ site suppresses the formation of the lone pair by modifying the Bi-anion hybridization. The electronic structure of the Bi$_2$Ti$_2$S’O$_6$ pyrochlore fixed with the same displacement pattern as that seen in Bi$_2$Ti$_2$O’O$_6$ was also examined. In Bi$_2$Ti$_2$S’O$_6$ with forced displacement the ELF displayed a symmetric lobe around the bismuth cations with a significant reduction of the asymmetric electron density in the energy range of -2 eV to the Fermi level. Alternatively, atomic displacement is significantly favored energetically in Bi$_2$Ti$_2$O’S$_6$. The Ti and O’ atoms displaced considerably more in Bi$_2$Ti$_2$O’S$_6$ than in Bi$_2$Ti$_2$O’O$_6$ which was attribute to stronger hybridization between the Bi and O’ states that favors the lone pair formation due to weaker Bi-S versus Bi-O interactions.
Substituting S on the B₂O₆ network of Bi₂Ru₂O’O₆ resulting in favorable cation displacement and induced lone pair formation in the metallic Bi pyrochlores by disrupting the Bi-O interactions. This result suggests that modifying the B₂O₆ network to reduce the interactions with the A₂O’ network will assist in promoting cation displacement.

Since vacancies on the A₂O’ network could alter the local interactions of Bi, the bismuth ruthenate compound was examined in Chapter 5 with multiple stoichiometries. As expected, the inclusion of vacancies on the Bi₂O’ network triggered spontaneous atomic displacements of both the Bi and O’ atoms due to alterations of the local Bi-O’ interactions. This finding resolves a discrepancy between experimental results using oxygen-deficient and the earlier DFT results of ideal non-defective bismuth ruthenate. The O’ anions displace off the high symmetry site into a 32e site but the magnitude of displacement depends on the proximity to the vacancies present in the structure. The O’ displacement predicted by DFT is well within the displacement pattern predicted by neutron diffraction data [20]. The magnitude and type of Bi displacement varied both by stoichiometry and proximity to vacancies. Unlike Bi₂Ti₂O₇, there is no correlation of the atomic displacements in Bi₂Ru₂O₇₋ₓ indicating even a small concentration of O’ vacancy is sufficient to reduce the steric strain on the A₂O’ network due to Bi lone pair formation from atomic displacement.

In Chapter 6, a range of cation substituted Bi pyrochlores, Bi₁.₅M²⁺B⁶⁺₁.₅O₇ (with M²⁺=Zn or Mg and B=Nb or Ta) was examined. Preferred substitute ordering was found on the A₂O’ sub-network and the occurrence of locally higher substitute concentrations was found for some B₂O₆ configurations. The ordering of both Zn and Mg cation along
the <211> direction was found in all four compounds confirming the predictions from Monte Carlo models previously reported [10]. Though previous reports have suggested the importance of the A2O’ network over the B2O6 network, large deviations in the energies of the configurations with randomly distributed cation substitutes on the B2O6 network indicates some ordering on the B2O6 network may be preferred. Additionally, a relationship between DFT determined A site cation displacement magnitudes and the experimentally reported dielectric constants was identified.

Finally, while cation displacement seems to be correlated to higher dielectric constants in Bi pyrochlores, the dielectric properties have been linked to the ease of cations in hopping between energetically degenerate positions within the pyrochlore structure. To explore this hopping process, a preliminary study was discussed in Chapter 7 to identify transition states to cation hopping and associated energy barriers for \(\text{Bi}_2\text{Ti}_2\text{O}_7\), \(\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7\), and \(\text{Ca}_{1.5}\text{Ti}_{1.5}\text{NbO}_7\). This study shows that the hopping process can be quite distinct within the pyrochlore family and future studies will explore these differences in more detail.

For the SrTiO\(_3\) oxide, Chapter 8 detailed the stability of molecular versus dissociated water as a function of coverage on both terminations of SrTiO\(_3\)(100). At higher coverages of 1/2 ML DFT predicted molecular H\(_2\)O will be the favored structure on TiO\(_2\)-termination and negligible differences in stability between molecular and dissociative H\(_2\)O on the SrO-termination which confirmed with the general results of an earlier hybrid HF-DFT study [141]. Comparison of 1\times1 and 2\times2 surface unit cells identified artificial size effects at coverages of 1/2 ML due to periodic boundary conditions. At coverages below 3/8 ML a crossover between dissociative and molecular
water was found on the TiO\textsubscript{2}-termination. On the 2\times2 SrO-termination a mixed adsorbate structure was stabilized at 1/2 ML and pure dissociative H\textsubscript{2}O was stabilized lower coverage. The DFT results reported at lower coverages conflicted with the general conclusions of experiments examining H\textsubscript{2}O/SrTiO\textsubscript{3}(100). The source of the differences between the DFT results and the experimental studies remains an open question. Future experimental studies that probe the surface structure during water exposure would be critical to resolve the role of clustering and/or ordering of water and any possible adsorbate induced reconstructions. DFT studies to elucidate the role of O vacancies and step edges on water structure, in particular vibrational modes specific to these defects, would assist in the interpretation of experimental data. Such combined DFT-STM studies have been critical for example to resolve the water structure on TiO\textsubscript{2}(011) [155].

9.2 Outlook of Projects

Both the bismuth pyrochlores and surface chemistry on SrTiO\textsubscript{3} surfaces will require additional examination to aid in the optimal design of future applications using these materials. For the SrTiO\textsubscript{3} project, part of the preliminary effort of DFT calculations have been completed to examine small molecule adsorption. However, only the water adsorption on SrTiO\textsubscript{3}(100) has been examined. Since it is expected that step edges and surface polarity will play a role in the adsorption of water, the examination should be extended to other low Miller index surfaces such as the (110) and the (111) in addition to high Miller indices surfaces that exhibit under-coordinated kink sites along step edges. Further, the study should be expanded to NH\textsubscript{3} on similar surfaces on SrTiO\textsubscript{3} in an effort to identify favorable adsorption and dissociation sites to aid in the oxide support design.
There are several potential pathways to extend the investigation of bismuth pyrochlores. One area of interest would be to examine the role of the small system sizes on the atomic displacements observed. In Section 3.3.2.1, a correlation between the cation and anion displacements was observed on the A₂O’ network. Within DFT, it has been confirmed that a 2x2x2 super-cell structure cannot be successfully modeled due to the large number of atoms. It would be interesting to examine a 2x2x1 super-cell to determine if periodic boundary conditions affect the observed displacement patterns.

As was seen in Chapter 6, ordering is likely to occur with the inclusion of cation substitutes on bismuth pyrochlores. The B₂O₆ sub-network’s influence was identified on the overall stability of the substitutional ordering on the A₂O’ network but it would be of interest to re-examine the BZN compound to determine if any rules exist for substitutional ordering on the B₂O₆ network.

As discussed in Section 7.5, the preliminary work examining ion hopping in pyrochlores needs to be expanded and further analyzed. Specifically, the phonon modes should be determined for the minima created by moving cations from one Wyckoff site to an equivalent Wyckoff site to confirm structure stability. The number of images along each path should be increased to at least three or more depending on the intermediate structures. Additional cation substitution configurations should be tested for the BZN and CTN systems. The hopping mechanisms in bismuth ruthenate, where vacancies triggered atomic displacement, should be examined to determine if vacancies significantly affect hopping pathways or energy barriers.

The initial aim of this work was to perform DFT calculations as part of a multi-scale modeling approach to understand the structure-property relationships in bismuth.
pyrochlores. The DFT calculations would serve as the fitting data to develop core-shell
interatomic potentials. Fitting interatomic potentials was attempted without success
using the fitting potential algorithm within the Generalized Utility Lattice Program
(GULP) [160]. The bismuth titanate system was the focus of the fitting efforts with the
interatomic potential for the Aurivillius phase Bi\textsubscript{4}Ti\textsubscript{3}O\textsubscript{12} as the starting point [161]. Future
attempts to adjust this potential for the pyrochlore phase should implement the
“restrained fitting” option within GULP, where the fitted parameters are bound between
the user-defined range of values.
The atomic displacement observed in bismuth titanate was attributed to the lone pair formation in Section 3.3.3. Both lone pair formation and a $p$-type lone pair (seen in Section 3.3.3) versus a $s$-type lone pair (discussed in Section 4.3.2) are detailed here for further understanding. To simplify the structure, here the PbO and PbS systems will be focused on with details from Walsh et al. [94,100,105,106] used. It had been thought that the lone pair on the Pb atom in PbO was due to hybridization of the 6s and 6p orbitals of Pb but Walsh et al. showed it is actually the cation-anion hybridization that leads to an asymmetric electron density indicative of a lone pair [94,100,105,106]. Walsh et al. further showed it is due to the asymmetric nature of this active lone pair that the layered litharge structure is favored for PbO over the cubic rocksalt structure in direct contradiction to the PbS system. For PbS the lone pair does not display as strong a hybridization between Pb the 6s and 6p state with the S 3p states, resulting in a $s$-type lone pair. This was confirmed by partial density of states, partial electron density plots, and an analysis of the crystal orbital overlap populations (COOP).

This $p$-type of lone pair was observed for Bi$_2$Ti$_2$O$_7$ following atomic displacement, as discussed in Section 3.3.3. The lone pairs observed in Bi$_2$Ti$_2$O$_7$ with atomic displacement are termed $p$-type since they result from the hybridization of the 6s and 6p states of the Bi cations with the O\textquotesingle anions. The hybridization results in asymmetric nature of these lone pairs as seen in Figure 4-1. Alternatively, when the energy states of the Bi 6s and 6p orbitals do not constructively interact with the O\textquotesingle site, as was seen in Section 4.3.2 for the Bi$_2$Ti$_2$S\textquotesingle O$_6$ material, when sulfur replaced oxygen on the O\textquotesingle or X\textquotesingle (as it was termed in Chapter 4 to avoid confusion), a $p$-type lone pair is not observed.
Instead the electron density surrounding the Bi cation remains relatively symmetric as seen in Figure 4-2, even though the bismuth cation was forcibly pushed out of its high symmetry site. This symmetric lobe had been observed previously for bismuth titanate without atomic displacement and is termed a s-type lone pair [14]. These lone pairs, both s-type and p-type, visually look similar to the orbitals they are named after. For the s-type lone pair, the electron density is spherical and symmetrical, similar to the s orbital. For the p-type lone pair, the electron density appears asymmetrical similar to the orbitals which combine the shapes of the spherical s and dumb-bell p orbitals following sp hybridization. These p-type lone pairs show increased electron density in the opposite direction of cation displacement which corresponds to the direction with reduced cation and anion bonding, as was seen in PbO [94,100,105,106].
APPENDIX B
SUPPLEMENTAL MATERIAL FOR PYROCHLORES

Additional details regarding the bismuth pyrochlores that were not included in the body of the dissertation are presented here. For the simple pyrochlores, focus will be placed on the Bi₂Ti₂O₇ and Bi₂Ru₂O₇ systems since these are the only simple pyrochlores that showed atomic displacement. Additionally, the electron localization function is examined for the Bi₁.₅ZnNb₁.₅O₇ system.

B.1 Dipole Moments

As discussed in Section 1.1.2, the dielectric permittivity is expected to depend on the dipole moments created within the material. In addition to the local dipole moments contributing to the total permittivity, the summation of all the dipole moments over the structure can result in a net polarization in a specific direction, which will affect the dielectric permittivity.

The total polarization was calculated for the ideal Bi₂Ti₂O₇ system as well as all ten configurations with atomic displacement to determine if a net dipole moment occurs in this system. These polarization calculations assumed a formal charge for each of the atoms. The polarization vectors, in μC/cm², for these 11 systems are detailed in Table B-1. The Pₓ, Pᵧ, and Pz components correspond to the polarization along the x-, y-, and z-axis, respectively. The total polarization (P) is also included in Table B-1, in addition to the vector components.

As expected, the cubic system with the cations in their ideal positions shows no net dipole in any direction as indicated by the zero values for each component of the polarization vector. However, after atomic displacement and volume expansion, all ten systems show some non-zero polarization. The total polarization was found to be
between 6.44 and 11.76 µC/cm² and three different groupings were observed, ~6.5, ~8.5, ~11.0 µC/cm².

Table B-1. The polarization vectors and total polarization in µC/cm² summarized for the ideal bismuth titanate as well as the ten configurations with atomic displacement discussed in Section 3.3.2.1.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Pₓ</th>
<th>Pᵧ</th>
<th>Pz</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Displaced 1</td>
<td>-2.00</td>
<td>-8.11</td>
<td>-0.31</td>
<td>8.36</td>
</tr>
<tr>
<td>Displaced 2</td>
<td>0.26</td>
<td>-9.85</td>
<td>-4.27</td>
<td>10.74</td>
</tr>
<tr>
<td>Displaced 3</td>
<td>-6.24</td>
<td>-0.60</td>
<td>1.49</td>
<td>6.44</td>
</tr>
<tr>
<td>Displaced 4</td>
<td>-6.65</td>
<td>-0.71</td>
<td>1.50</td>
<td>6.85</td>
</tr>
<tr>
<td>Displaced 5</td>
<td>-6.56</td>
<td>-0.60</td>
<td>1.09</td>
<td>6.67</td>
</tr>
<tr>
<td>Displaced 6</td>
<td>6.69</td>
<td>9.65</td>
<td>-0.56</td>
<td>11.76</td>
</tr>
<tr>
<td>Displaced 7</td>
<td>9.57</td>
<td>5.45</td>
<td>-0.88</td>
<td>11.05</td>
</tr>
<tr>
<td>Displaced 8</td>
<td>3.61</td>
<td>-1.44</td>
<td>10.32</td>
<td>11.03</td>
</tr>
<tr>
<td>Displaced 9</td>
<td>-1.86</td>
<td>2.86</td>
<td>-7.90</td>
<td>8.60</td>
</tr>
<tr>
<td>Displaced 10</td>
<td>-3.60</td>
<td>-10.55</td>
<td>1.05</td>
<td>11.20</td>
</tr>
</tbody>
</table>

Fannin et al. [162] examined bismuth titanate using density functional theory and identified a soft phonon mode that lead to a crystal system transition from the cubic (Fd₃m) to a monoclinic (Cm) structure. This monoclinic structure exhibited a net polarization of 20 µC/cm² along the [110] direction. As can be seen from Table B-1, the polarization vector and magnitude determined here is lower than that found by Fannin et al. [162].

**B.2 Structure Optimization**

The occurrence of a non-zero polarization vector indicates the cubic structure is not stable for the bismuth titanate system with atomic displacement. Since the DFT
calculations are performed at fixed volume and shape, the stability of the cubic structure was initially tested for the ideal structure and was discussed in Section 3.2. However, this test was not repeated following atomic displacement. Therefore, after the polarization results, the ideal Fd̅3m (number 227) space group was again tested for the bismuth titanate with atomic displacement. It was found that the cubic structure is not the lowest energy structure for bismuth titanate with atomic displacement. A monoclinic structure was determined with lattice constants of a=10.35 Å, b=10.30 Å, c=10.38 Å, α=90.0°, β=89.4°, and γ=90.0°. Though Fannin et al. [162] do report a monoclinic structure is the most energetically favorable, no structural details are reported for comparison. Fannin et al. [162] state that the monoclinic structure is relatively more stable than the ideal Fd̅3m structure by 240 meV or 0.24 eV. In fairly good agreement, the monoclinic structure determined here is found to be more energetically favorable than the cubic structure by 0.18 eV. The difference between these relative energies may be attributed to differences between the parameters used in both studies.

B.3 Charge Density Maps

In Section 4.3.2, the electronic structure was examined for Bi\textsubscript{2}Ti\textsubscript{2}O’O\textsubscript{6} and bismuth titanate with sulfur substitutions on the O’ or the O sites. Figure 4-5 examined the partial electron density for both the displaced Bi\textsubscript{2}Ti\textsubscript{2}O’O\textsubscript{6} and the Bi\textsubscript{2}Ti\textsubscript{2}S’O\textsubscript{6} with forced atomic displacement. It was shown that an asymmetric lobe of increased electron density occurs in the wake of the bismuth cation displacement path for both compounds. However, the degree of asymmetry for the Bi\textsubscript{2}Ti\textsubscript{2}S’O\textsubscript{6} system was considerably smaller than that of the Bi\textsubscript{2}Ti\textsubscript{2}O’O\textsubscript{6} system. This electron density profile included only the energy states between -2 eV and the Fermi level. Figure B-1a shows the total charge density
for all energy states for part of the (101) plane. It can be seen that the total charge
density does not show any asymmetry after atomic displacement. To compare, the
electron localization function (ELF) is plotted for the equivalent plane in Figure B-1b and
the signature asymmetric lobe in observed, corresponding to the lone pair.

![Figure B-1](image)

Figure B-1. The (a) total charge density of the displaced Bi$_2$Ti$_2$O$_7$ and the (b) electron
localization function for part of the (101) plane with Bi in the center with the
Bi, and O' ions shown in (a). The contour lines are incremented by 0.1 eV/Å$^3$
and the ELF values range from 0 (light red) to 1 (dark purple), as shown by
the scale.

**B.4 Electron Localization Function Plots**

**B.4.1 Bi$_2$Ru$_2$O$_7$**

As discussed in Section 3.3.2.2 atomic displacement was examined in Bi$_2$Ru$_2$O$_7$.

Atomic displacement could not be stabilized by either simulated annealing or by using
the experimentally reported displaced atomic positions. Since the electronic structure of
Bi$_2$Ti$_2$O$_7$ was key to understanding why atomic displacement occurs (Section 3.3.3), it
was desired to examine the electronic structure of Bi$_2$Ru$_2$O$_7$ in similar detail. To
examine the electronic structure of the Bi$_2$Ru$_2$O$_7$ system both with and without atomic
displacement, a structure was created with the same atomic displacement pattern as
one of the Bi$_2$Ti$_2$O$_7$ configurations. The density of states was discussed in Section 3.3.3
for the Bi$_2$Ru$_2$O$_7$ system with forced atomic displacement but the electron localization function (ELF) was not included in Chapter 3.

Figure B-2 shows the ELF for the (101) plane for the (a) Bi$_2$Ti$_2$O$_7$ and the (b) Bi$_2$Ru$_2$O$_7$ with the same displacement pattern. As indicated by the included key, there is an increase in electron localization behind the Bi cation displacement in the Bi$_2$Ti$_2$O$_7$ system creating an asymmetric lobe surrounding the bismuth cation. However, in Figure B-2b the electron density surrounding the bismuth cation is more symmetric in nature and in fact this symmetry makes the Bi cation seem visually less displaced than in the Bi$_2$Ti$_2$O$_7$ system.

![Figure B-2](image)

**Figure B-2.** The electron localization of the displaced (a) Bi$_2$Ti$_2$O$_7$ and (b) Bi$_2$Ru$_2$O$_7$ for the (101) plane with Bi in the center with the Bi, Ti/Ru, and O$_{48f}$ ions indicated. The ELF values range from 0 (light red) to 1 (dark purple), as shown by the scale.

### B.4.2 Bi$_{1.5}$ZnNb$_{1.5}$O$_7$

Figure 3-11 compared the ELF plots for the (111) plane and the (111) plane for the Bi$_2$Ti$_2$O$_7$ pyrochlore following atomic displacement. An atomic level correlation was found for this system and discussed in Section 2.2.3, as well as in Chapter 3, 4, 5, 6, and 7. In Section 3.3.3, it was proposed that the lone pair on the displaced Bi cations in Bi$_2$Ti$_2$O$_7$ leads to the correlation as a method of reducing the stereochemical strain of
incorporating large lone pairs in a relatively small space. It was stated that the β-
cristobalite type displacive disorder was not found in \( \text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7 \) (BZN) due to the
presence of \( \text{Zn}_A \) cations along the \( \text{O'}-\text{A}-\text{O'} \) bonding network.

Figure B-3 shows the ELF plots for one of the BZN structures examined for the (a)
(111) plane with Bi in the center and the (b) (\( \bar{1}11 \)) plane with the Bi, \( \text{Zn}_A \), Nb, \( \text{Zn}_B \), \( \text{O'} \),
and \( \text{O}_{48f} \) ions indicated. Figure B-3a looks nearly identical to Figure 3-11a with the
exception of the delocalized electron profile near the \( \text{Zn}_B \) cations. The increased
localization of electrons just below the center Bi cation shows the lone pair also forms in
the BZN configuration, as was seen in Figure 3-11a for the \( \text{Bi}_2\text{Ti}_2\text{O}_7 \) case.

(a)  

(b)

Figure B-3. The electron localization of the displaced BZN at 10.34 Å for the (a) (111)
plane with Bi in the center and the (b) (\( \bar{1}11 \)) plane with the Bi, \( \text{Zn}_A \), Nb, \( \text{Zn}_B \),
\( \text{O'} \), and \( \text{O}_{48f} \) ions indicated. The ELF values range from 0 (light red) to 1
(dark purple), as shown by the scale.

Figure B-3b shows the electron density for both the \( \text{Zn}_A \) and \( \text{Zn}_B \) sites are very
similar, with only a slight increase in electron density around the \( \text{Zn}_A \) cations. Though it
may be difficult to see, the Zn\textsubscript{A} cations shown in Figure B-3b all displace towards the O\textsubscript{48f} anions surrounding the Zn\textsubscript{B} cation. Due to the layout of Zn\textsubscript{A} sites, if all the Bi cations displaced away from these O anions then the \(\beta\)-cristobalite type displacive disorder observed in Bi\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} could still be maintained. Instead, two of the Bi cations displace towards the same O\textsubscript{48f} anions surrounding the Zn\textsubscript{B} cation resulting in five of the six surrounding A cations displaced towards this BO\textsubscript{6} octahedra. Therefore, the correlation observed for Bi\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} was not observed in BZN and the ELF plot shows the Bi lone pairs are not orienting themselves to reduce the interactions with the BO\textsubscript{6} octahedra.
LIST OF REFERENCES


BIOGRAPHICAL SKETCH

Beverly L. Brooks was born in Houston, Texas, to William L. Brooks and Karen E. Brooks. She graduated from Spring High School in May 2000 where she focused on math, science, and photography. She continued her education at the University of Houston. In May 2005, she received her Bachelor's of Science in chemical engineering. During part of her undergraduate studies, she worked at the Freeport site for the chemical company BASF Corporation through an internship program. Beverly and Jose Hinojosa were married in July 2005 before joining the chemical engineering department at the University of Florida. In January 2006, she began working for Prof. Aravind Asthagiri, performing computational based research on bulk metal oxides. In May 2008, she began examining small molecule interactions with mixed metal oxide surfaces.