

SYNTHESIS AND STRUCTURAL CHARACTERIZATION
OF THREE-LAYER AURIVILLIUS CERAMICS

BY
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Acknowledgements

I'm looking out my office window upon the town where I've spent the past 13 or so years and the feeling I have is bittersweet. It's Autumn, the leaves are changing and the days of wearing shorts are over. On the one hand I am incredibly happy that I just defended and passed, but yet I am leaving this place that I love so much. I originally had so many thoughts in mind for what I'd like to write in this spot, but now that the time has come, I think I'm going to keep it short and sweet. The people who know me know how much I will miss this place so we don't need a dozen pages of gushing praise. I was about to start writing all about the reasons why yesterday (my defense) almost didn't happen, but let's just say that I had a rough time and about three years of my life were lost to the physical, financial, and emotional ravages of a tumor that decided to take residence in my pituitary gland. There are two key people that deserve credit for me being here today. Mike Calabrese took me into his home when no one else would and took care of me when I couldn't. I can never repay him for his kindness. There are a lot of supposed "Christians" out there who could learn a thing or two from Mike. Thanks dude. I need to thank Dan Kim. I met Dan at the tail end of my illness and he brought me out of the pit of depression that I was in and I saw the light again. Dan was my shrink and a damn good one too. Yeah, I just said shrink. You see, tumors don't just damage the body, but also take a chunk out of the soul as well. Thanks Dan.

All right, enough with the serious shit. I met a ton of people here over the 13 years that had a huge impact on my life. I'll try and thank them in chronological order. First of all, I am probably going to forget someone. So if you are that someone, please insert your name here, thank you (insert name here) for your help.

John Buckner was my room mate for something like three years. John was the first one who told me I should get my PhD. John was the guy who stood up in Sophomore Mat.

Sci. class with Dr. Jones and asked her “when did you buy into this electron thing?” He was the guy that helped me dump a container full of rotten beef stew over our balcony at Medusa F. He was a great guy to talk to and a great friend. Thanks Buck! Dr. Amarakoon. I took 309 when I was a junior and I hated it. It was such a hard class and the teacher was a real hard ass. I couldn’t stand it! Why should I have to memorize the Schoedinger wave equation? Here it is just in case you forgot.

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi \quad (1)$$

And the nerve of the guy to actually look at my transcripts to see why I wasn’t doing well in his class! I actually really like Dr. Amarakoon. He was a guy that I could always just walk into his office and talk when I needed to. I eventually learned that the person responsible for not doing well in class was me. So I changed my attitude and came to love Dr. Amarakoon’s classes. Dr. Amarakoon was the first person I spoke to when I decided I wanted to come back to Alfred to finish my degree and he has been one of my strongest advocates. Thanks Doc. I want to thank X-ray group #1 and X-ray group #2. Chan, Sriram, Martin, PJ, you guys were awesome! Myles, Chris, Mick, Steve, Justin, Scott, Viral, you guys were even awesomer! Hoffman! are you out there? Thanks dude! Swavek! you are the man! It is said that Swavek can make a diffractometer with any three tools. Swavek has been known to make a flat head screwdriver out of a phillips, then make it back into a phillips, then into and x-ray tube cleaner. Swavek is old school and an all around great guy. Fran Williams deserves a ton of credit for keeping McMahon functioning. The guy is worth 10 times what they pay him and the faculty would be wise to remember that and keep him happy. Fran is a great guy and I really appreciate his help.

Myles, thanks for all your advice dude. You have been a great friend and your advice has taught me a different way of thinking. You got me to keep the volvo!!! Eventually I’ll get a turbo-diesel Mercedes though.

I want to thank the bike gang. ET, Myles, Mick, Steve, Fletch, Aubree and Kristin, and Goda! Goda and Lynch got me into biking and I went from having one old mountain bike to building my own mountain bike, a road bike, getting a trials bike and almost having enough parts left over to build a singlespeed! My shins now have more scars and gouges than I had as a kid! It has been awesome riding with you all. I will never forget the century

we rode in the rain and Lynch crashing into me in Belmont. I did my first road and mtb race and I came to love NY for its beauty.

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And how can I forget the team trivia gang! JM and DW! It burns when I pee? 22 pitchers of beer and paying for only 5? Breaking into your old apartment? Winning, not winning, drawing on my windows. uggh.

I want to thank JP for being a good friend. JP is a great listener and a huge MH advocate. Thanks dude. Frouch? MH? Monster-slapping? Pint of Haggis?

I want to thank Kristin and Aubree for being such great friends. Kristin I really learned a lot from you about how to live. I find myself thinking "what would Kristin do" an awful lot. Your wedding was a turning point in my spiritual life. Thanks so much for including me in it. I love you guys.

I really want to thank my advisor and friend Scott Misture for putting up with me. It was a great privilege working for you and I learned so much. I think what I really learned is how to be a PhD. Hopefully someday I can know as much stuff as he does.

I guess lastly I need to thank my family... for being the biggest pain in the ass I could ever have. Well, not all the time, but your love and support over the past couple years has really helped. I love you guys. I was glad my dad and brother could see me defend. I was told that my grandfather always wanted to be a college professor. He worked his ass off with three jobs to care for his family. He isn't here anymore, but I wish I could have just one hour to talk with him and tell him I made it.

At this point I'd like to say something really profound, but I'm tired from the drinking we did last night and my fingers are sore from typing. So I'm going to sum things up. I'm going to miss this place and the friends I've made here. But I will always hold Alfred dear in my heart.

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ABSTRACT

The three layer Aurivillius crystal structure was investigated for use as an ionic conductor. Sample synthesis was investigated using high temperature x-ray diffraction (HTXRD) for a range of compounds, using solid state synthesis and the polymerized complex method. Isothermal Avrami type kinetics studies were performed on $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ using *in situ* HTXRD and quantitative analysis performed via Rietveld refinements using TOPAS. The kinetics analysis yielded Avrami exponents of approximately 0.54, which fell in the range of the diffusion controlled reaction mechanisms. The activation energy over a range of temperatures was calculated to be on the order of 140kJ/mol. Crystal structure refinements were performed on the $\text{Bi}_2\text{Sr}_{2-x}\text{A}_x\text{Nb}_2\text{TiO}_{12}$ ($\text{A} = \text{Ca}, \text{Ba}$, $x = 0.5, 1$) series using combined x-ray and neutron diffraction Rietveld refinements. Refinements indicated a static disorder between the Bi and A sites, and between the Nb and Ti sites. A-site lattice strain investigated via the bond valence method reveals a linear increase in strain with the size of the substituted alkaline earth cation. Furthermore, large isotropic thermal parameters for the O1 and O4 oxygen sites reveal possible oxygen vacancy formation as a result of unresolved strain between the A and Ti layers of the structure. Oxygen stoichiometry is found to decrease as the size of the a lattice parameter decreases. Synthesis of non-stoichiometric three-layer phases was accomplished by aliovalent substitution and via forced site-mixing. Neither method produced samples with conductivities greater than $10^{-3} \frac{\text{S}}{\text{cm}}$ at 900°C . Non-stoichiometric compositions follow similar structural trends to those observed in the stoichiometric crystal structure refinements. Increased numbers of oxygen vacancies were recorded than anticipated from the dopants. The number of extra vacancies corresponds well with the amount shown in the stoichiometric compositions. Based on the conductivity and number of charge carriers, the mobilities of the charge carriers are very low, on the order of 10^{-7} to $10^{-10} \frac{\text{cm}^2}{\text{Vsec}}$ at 1000°C .

Chapter 1

Introduction

1.1 Aurivillius Crystal Structure

The purpose of this thesis was to investigate the potential of the Aurivillius crystal structure for use as an ionic conductor, specifically for use in the electrolyte layer of a solid oxide fuel cell.¹ The Aurivillius structure, being layered, showed similarities to the naturally oxygen deficient brownmillerites such as $\text{Ba}_2\text{In}_2\text{O}_5$ which are excellent oxygen ion conductors at higher temperatures. $\text{Ba}_2\text{In}_2\text{O}_5$ shows an order-disorder transformation on its oxygen sublattice where the oxygen vacancies become highly mobile and lead to the high conductivity. The Aurivillius structure had this potential due to its layered nature and its large number of available oxygen sites.

The Aurivillius crystal structure was discovered by Aurivillius in 1949.² It takes the form $\text{Bi}_2\text{A}_{n-1}\text{B}_n\text{O}_{3n+3}$ where n is equal to the number of octahedral layers in the structure. The structure consists of $n-1$ perovskite-like blocks of the form $(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2-}$ that are sandwiched between bismuth oxide $(\text{Bi}_2\text{O}_2)^{2+}$ sheets. The Bi^{3+} cations in the $(\text{Bi}_2\text{O}_2)^{2+}$ layer have a lone pair of electrons which extend towards the A site cation and exhibit stereochemical repulsion on the surrounding oxygen anions. The cubo-octahedral Aurivillius A site can be occupied by Sr^{2+} , Ba^{2+} , Ca^{2+} , La^{3+} , Bi^{3+} , Pb^{2+} , K^{+} . The octahedral B site is much more size restrictive and is typically occupied by Ti^{4+} , Nb^{5+} , Ta^{5+} , W^{6+} , Ga^{3+} , Al^{3+} , Mn^{3+} . Aurivillius phases have been reported in the 1-,2-,3-,and 4-layer variants. The three layer structure was studied in this work and is shown in Figure 1.1.

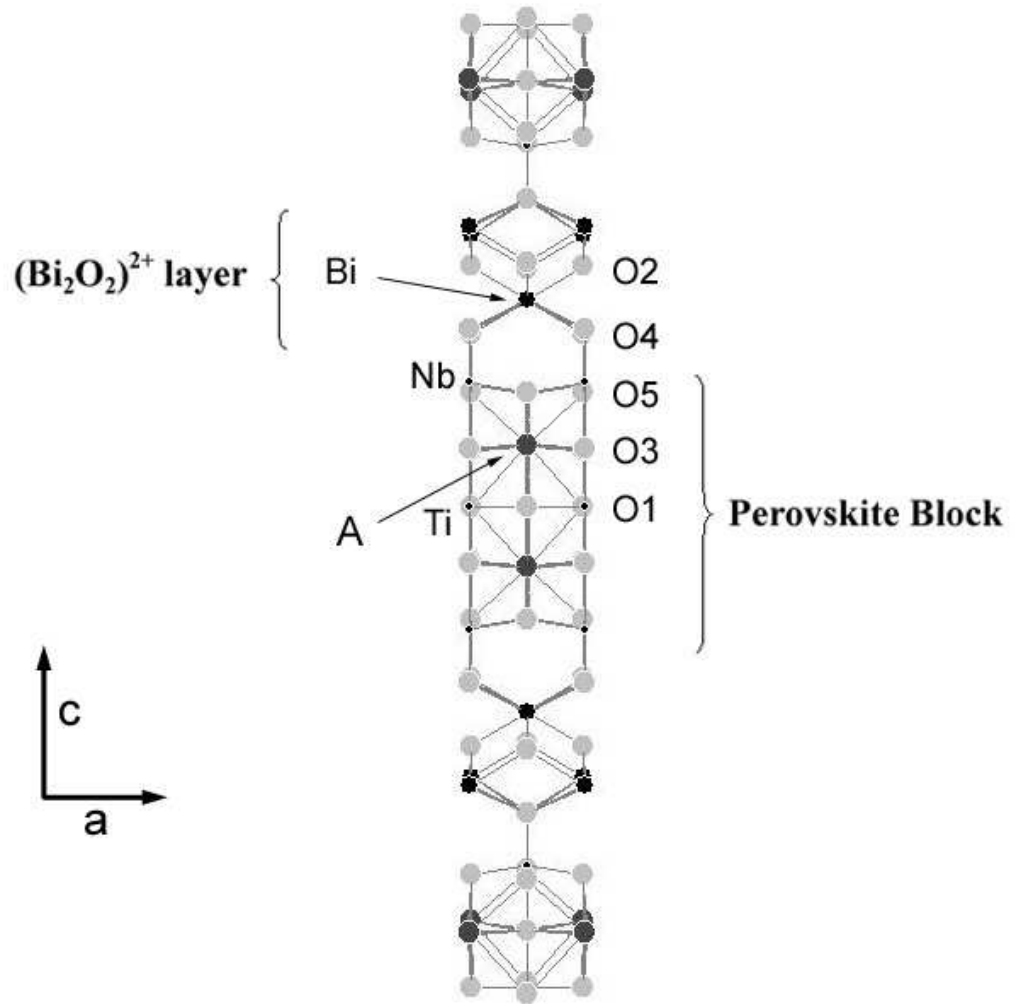


Figure 1.1: Schematic of three-layer Aurivillius structure $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$.

The style of this thesis is slightly different than the conventional thesis in that each chapter is written in the general format of a journal article. As such, no overall general literature review will be given, but rather each chapter will have its own relevant literature review. Chapter 2 was written and submitted to the Journal of Solid State Chemistry for publication and is currently in review. The general outline of this thesis is as follows.

1. **Synthesis of the three-layered Aurivillius phases.** Here, all of the synthesis steps involved in creating three-layer Aurivillius samples will be discussed. Synthesis methods, reaction characterizations and recommendations are given.
2. **Crystal structure refinement of the three-layer structure.** Here, a specific three-layer structure from Chapter one is chosen, $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$, and the crystal structure is refined from x-ray and neutron powder diffraction. Furthermore, the A site substituted with Ca^{2+} and Ba^{2+} in place of Sr^{2+} to investigate the effects of interlayer strain on structural stability.
3. **Synthesis of oxygen deficient phases, structural refinement, and electrical characterization.** Here, a range of oxygen deficient three-layer compositions are generated based on work done in Chapter three, and their crystal structures characterized. Electrical characterization reveals their potential as ionic conductors.
4. **Conclusions and recommendations for future work.** This section provides a summary of the entire body of work and recommendations.

Chapter 2

Synthesis and HTXRD

2.1 Introduction

Aurivillius ceramics have been synthesized by many groups, but by far the greatest degree of detail and the widest range of compositions have been investigated in the pioneering work of Subbarao and Newnham *et al.*³⁻⁶ They investigated the solid solubility ranges of various compositions and discovered most of the Aurivillius variants known today. However, the details of powder synthesis were apparently not as highly valued as the end properties of the materials and as a result, *the processing involved in powder synthesis* was not elaborated upon in the early publications pertaining to these materials. The lack of processing information is also observed in recent literature pertaining to Aurivillius based systems. The processing details typically include only the temperatures at which the samples were heated. In this thesis, the processing of the materials proved to be the most challenging and time consuming. There are two parameters required in any powder synthesis; these include the temperatures at which reaction will occur and the length of time required for reaction completion. Furthermore, the processing temperature must be kept out of phase diagram zones which lead to formation of secondary phases or melting, etc. The ideal instrument for studying both parameters is the high temperature x-ray powder diffractometer (HTXRD).⁷ This instrument is a conventional laboratory powder diffractometer with the addition of a furnace surrounding the sample holder. The real benefit of this instrument is the ability to perform real-time or *in situ* diffraction experiments of the sample at any temperature (within instrument capabilities) without removing the sample from the diffractometer for separate heat treatments. Ideally, one experiment could provide all the information necessary

to synthesize the desired phase in bulk form. Diffraction measurements could be made from room temperature to elevated temperatures and the resultant phase changes would be observed in the diffraction patterns. The reaction temperatures and times required to reach phase purity would be learned by noting when the desired diffraction peaks appear. There are, however, other factors involved which may not allow for complete reaction to occur in the relatively short time of the experiment. Most of the Aurivillius phases studied had more than four cations and as a result this opened the door for the formation of several intermediate phases, which were often nearly as stable as the desired phase. Furthermore, the sample powders react via solid state synthesis which is often a slow, laborious process where reaction occurs between two phases through a reaction zone of the product material. This process is often dictated by the slower diffusing species. As a result, observing a phase pure sample in a HTXRD measurement was usually the exception rather than the rule. It was our goal to take the knowledge obtained from HTXRD measurements and apply it directly to the bulk synthesis of the material. In this way, we could eliminate much of the guesswork and trial and error normally associated with the study and synthesis of a new composition. In this thesis, two synthesis methods were employed, conventional solid state synthesis and the polymerized complex method. Initially, all of the synthesis experiments were performed using solid state synthesis because it was relatively inexpensive, it did not require complicated laboratory ware, and it was relatively simple. However, one factor above all complicated this process, and it was the high volatility of Bi_2O_3 .⁸ This required a modification to the synthesis process. The polymerized complex method or Pechini process was attempted only after many repeated failures when using solid state synthesis.⁹ The solid state and polymerized complex methods are discussed in some detail below.

2.2 Solid State Synthesis Overview

Solid state synthesis is based on the idea that when you place two chemical species in contact and raise the temperature achieve sufficient mobility of ions such that a solid state reaction can occur. Given two particles, one of species A and the other of species B, species C will form via surface reaction on the region in contact between A and B. The rate of formation of C will be dictated by the diffusion of the slower moving species. After some

time, a given amount of C will have been produced between the two particles. However, unreacted A and B will still exist beyond the diffusion region. In order to allow the reaction to go further towards completion, a fresh A-B surface must be created and generally this is accomplished via grinding of the respective particles (In a fully three dimensional system, a central core of unreacted A and B remain, necessitating grinding to expose new A and B.). Solid state synthesis is normally a slow process requiring long times to obtain reaction completion. Elevation of the reaction temperature may promote the reaction, provided that the temperature is within the phase stability range of AB.

It is important to point out that the desired product will only form if all reactants are well mixed. Ball milling is the most widely used method for mixing of powder reactants. Essentially, the reactant powder is placed inside a cylindrical container along with a liquid medium and hard grinding media. This container is then sealed and placed on a belt which turns the container at a certain speed. While turning, grinding media collide with each other and the resultant collision energy is enough to break up particle agglomerates and with time will provide mixing of the powder. While simple to execute, this method has several key problems. The powder has to be reclaimed from the inside of the container, and from the grinding media. Furthermore, the energy with which the media collide is often enough to wear away at the grinding media and contaminate the reactant powder. Usually, a decreased mixing ability is seen over time, and longer milling times do not provide enhanced mixedness.¹⁰ Aside from ball milling, simply mixing the powders in a liquid medium using a mortar and pestle provides similar mixing results with less contamination.¹¹ Ultimately, the mixing provided by any type of milling will only be on a bulk scale and does not reach the atomic scale, thus long reaction times are required.

2.3 Polymerized Complex Synthesis Method Overview

The polymerized complex method of powder synthesis has several benefits over solid state synthesis. Most notably, if performed correctly, it provides atomic-scale mixing of the constituent cations. As a result of this much improved mixing, the resultant reaction times and processing temperatures will be dramatically decreased.

Originally developed by Pechini for production of bulk dielectrics, the polymerized complex method has been used to make various complex crystal structures, including per-

ovskites, pyrochlores, hexaferrites, and aurivillius phases.^{9,12-18} In short, a carboxylic acid is used to chelate a dissolved metal cation. (The original Pechini patent used citric acid, although other carboxylic acids such as polyacrylic acid (PAA) will work.¹⁹ Chelation does demand that the constituent cations be dissolved from various sources, such as oxides, carbonates, nitrates, chlorides, or from liquid sources such as butoxides. There is some work in the literature that makes use of citric acid alone to chelate the cations, then the chelate solution is heated to evaporate the solvents and leave an amorphous product which can then be heated to form the desired product. This process is simply called the citrate method.²⁰ However, despite the beneficial mixing, it is still possible for the cations to become segregated and fall out of solution during the reaction process. Therefore, if something is added to the system to lock everything in place, it would be beneficial. The addition of ethylene glycol to the citrate solution along with heat can cause a polymerization reaction which forms an ester (estrification). Heating to temperatures around 80-150°C will initiate the estrification reaction. Continued heating causes this ester to become extremely viscous, and ultimately if the reaction is taken to completion, a solid resin will be created. If the resin is then ashed at temperatures between 350-500°C, an amorphous powder product will be created.¹⁷ The final desired products are generally obtained by heating to temperatures as low as 600°C in only a few hours time.¹⁷ Estrification which is enabled by the chelate, holds ions suspended in a random arrangement which promotes atomic scale mixing upon pyrolysis. Figure 2.1 shows an example of a polymerized complex reaction where the initial amorphous reactants change to crystalline form upon heating. For this particular sample, a portion of the resin was placed directly on an alumina HTXRD sample holder while still fluid. The sample was heated from room temperature to 500°C in 50°C intervals, then from 500°C to 900°C in 100°C intervals. Note the conversion from amorphous to crystalline between 450-500°C. The initial amorphous nature of the diffraction pattern tells us that the sample has remained well mixed. If x-ray diffraction peaks appear when the sample is still in resin or ashed form, then it is an indication that some type of segregation has occurred. Furthermore, note the quick conversion from amorphous to crystalline form and the fast reaction to the desired phase.

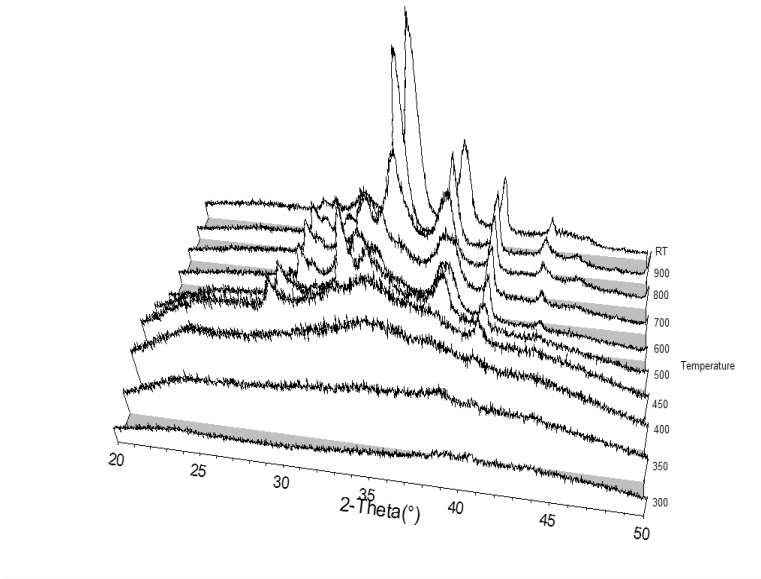


Figure 2.1: XRD patterns polymerized complex derived $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ from resin.

2.4 HTXRD-Motivation

Because no real knowledge of the synthesis variables existed for any of the three layer Aurivillius phases, we decided to start with the simplest Aurivillius compound $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, and then progress to the substitution of an isovalent cation (La^{3+}) for Bi^{3+} on the Aurivillius A site $\text{Bi}_2\text{La}_2\text{Ti}_3\text{O}_{12}$, then substitute onto the B site with Nb^{5+} , and A site with an aliovalent alkaline earth Sr^{2+} , $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$. These compositions were studied using HTXRD as mentioned previously. The HTXRD studies were performed on the above compositions having been synthesized by the solid state and polymerized complex method. The results of these studies are shown below.

All three solid state derived samples used the same sample preparation procedure. A 2g powder batch was generated consisting of the precursor powders Bi_2O_3 , La_2O_3 , SrCO_3 , Nb_2O_5 , and TiO_2 (all powders of at least 99.9% purity from Alfa-Aesar) was mixed into a slurry using isopropanol in a diamonite mortar and pestle. A small portion of the resulting slurry was deposited on a sample holder which consisted of a 20x20x1mm thick alumina plate. This plate was subsequently placed on an 100x20x1mm thick alumina strip. Platinum paste was used to secure the sample plate to the alumina strip. The slurry was added until a meniscus of material formed. A slight puff of air washed the slurry across

the alumina plate thus creating a uniformly thick and relatively flat powder sample surface. The slurry was dried before placing in the instrument.

Samples obtained from the polymerized complex method were initially ashed to 350°C prior to depositing on the alumina strip for the x-ray diffraction experiments. It was not possible to perform x-ray diffraction on the *as reacted* resin, as it would not conform to the shape of the sample holder (it was rubbery). As a result, it was never possible to truly see whether the sample was completely amorphous after reacting completely to the polymer resin. In retrospect, a method to observe this would be to dip a sample holder in the resin while it is still liquid, then perform *in situ* HTXRD measurements. After ashing at 350°C, the sample was crushed to a hard, shiny, black powder. Larger than normal amounts of the powder were loaded because upon heating, as the remainder of the organics would volatilize from the sample on heating.

The HTXRD instrument used for these experiments was constructed at Alfred University by my advisor, Dr. Scott T. Misture.⁷ The instrument is a Siemens D500 diffractometer with a vertical theta-theta goniometer. Figure 2.2 shows a picture of the tube-goniometer-furnace-detector assembly. Either Cu or Co radiation was used for the solid state measurements. Chromium radiation was used for the polymerized complex measurements. A fast mBraun position sensitive detector (PSD) with a 10°2θ window was used. The sample sits horizontally on two alumina pins which are located in the center of the furnace. The furnace itself consists of two machined blocks of alumina insulation with platinum wire wound in a hemispherical manner such that when the two parts of the furnace are combined, the sample sits in the center of a spherical cavity. As such, the heating zone around the sample is quite uniform and temperature gradients are minimized. A beryllium window is cut in the top of the furnace to allow passage of the x-ray beam.

2.5 HTXRD Analysis, Solid State Method

2.5.1 Bi₄Ti₃O₁₂ HTXRD Reaction Sequence

As mentioned previously, it was our intention to start with relatively simple compositions with few cations, then progress to systems containing multiple cations. Bi₄Ti₃O₁₂ is a perfect composition to start with because it only has two cations. Figure 2.3 shows the HTXRD patterns for Bi₄Ti₃O₁₂ formed via solid state precursors. Table 2.I shows the

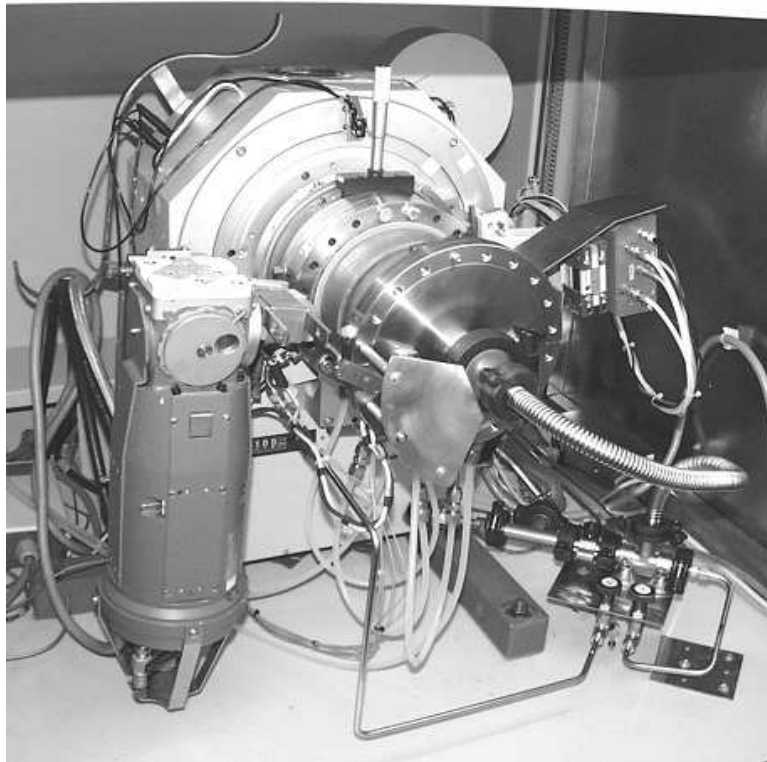


Figure 2.2: HTXRD used for these experiments.

Table 2.I: Phases present in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ sample prepared from Bi_2O_3 and TiO_2 powders.

Phase	PDF Card #	Temperature Range
Bismite (Bi_2O_3)	41-1449	RT - 700°C
$\text{Bi}_{12}\text{TiO}_{20}$	34-97	625°C- 880°C
Anatase (TiO_2)	21-1272	RT - 870°C
$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	35-795	525°C- 1150°C
$\text{Bi}_2\text{Ti}_2\text{O}_7$	34-97	1150°C- ?

phases present at the different temperatures. Initial measurements over a broad temperature range indicated several regions of interest. These regions included the formation temperature of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, the decomposition of Bi_2O_3 , etc. A second set of measurements were performed over 25° temperature intervals with 5° intervals used over the specific regions of interest. Measurements were taken to 1150°C to show the onset of melting of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. The two phases that exist over the entire temperature range are bismite Bi_2O_3 (PDF 41-1449) and anatase TiO_2 (PDF 21-1272). Bi_2O_3 remains in the monoclinic symmetry. The almost imperceptible broad peak at $29.7^\circ 2\theta$ in the 525°C pattern shows the first presence of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ in the sample. The 100% peak of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ increases in intensity slowly and continuously until about 625°C where the growth increases sharply. Transformation of bismite to $\text{Bi}_{12}\text{TiO}_{20}$ (PDF 34-97) occurs at approximately 625°C. The 100% peak of $\text{Bi}_{12}\text{TiO}_{20}$ exists at approximately $28^\circ 2\theta$, however it is still strongly overlapped by the bismite peak at 650°C. By 700°C, bismite has completely converted to $\text{Bi}_{12}\text{TiO}_{20}$. The 100% peak of TiO_2 decreases slowly and continuously until about 570°C where the intensity decreases at a larger rate. TiO_2 peaks are visible in the patterns until approximately 870°C. The $\text{Bi}_{12}\text{TiO}_{20}$ peak intensity is constant until about 825°C where it begins to fall off sharply. By 880°C, there is no sign of $\text{Bi}_{12}\text{TiO}_{20}$ in the pattern as seen in Figure 2.4. The 100% $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ peak reaches a maximum intensity by 860°C, and then begins to decrease at 1000°C. It decreases continuously until $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ melts between 1140 and 1150°C. A clear jump in background or amorphous hump is observed in the 1150°C pattern which indicates melting. Furthermore, a new phase appears out of the melt at 1150°C which is $\text{Bi}_2\text{Ti}_2\text{O}_7$ (PDF 32-118).

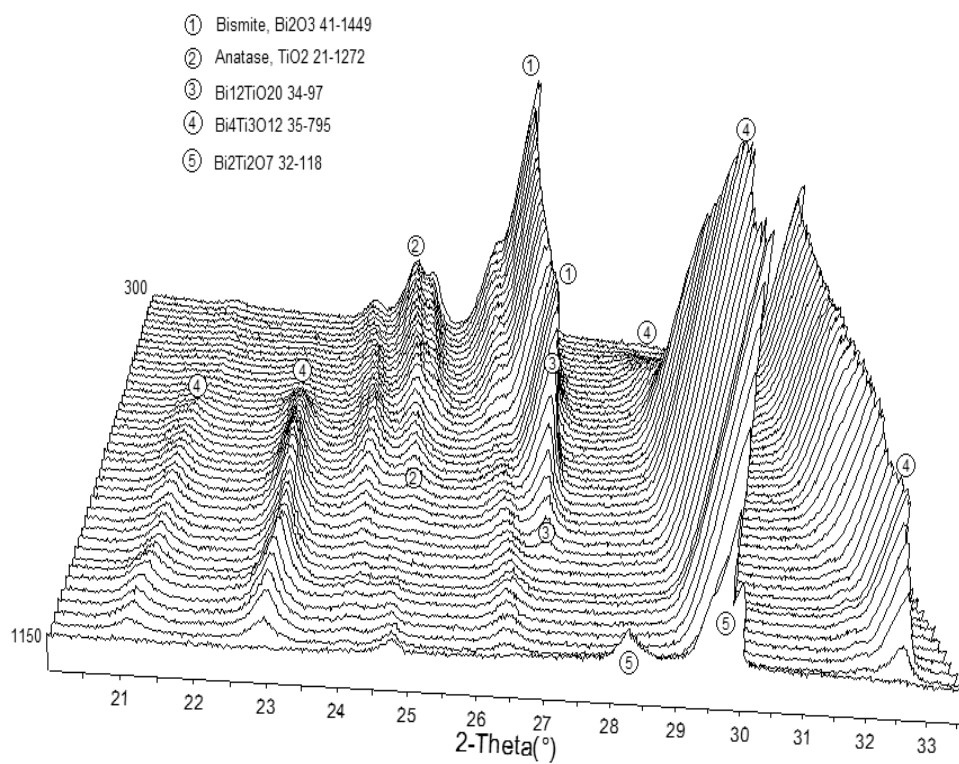


Figure 2.3: HTXRD patterns for Bi₂O₃ and TiO₂ powders in stoichiometric ratio of Bi₄Ti₃O₁₂ from 300°C to 1150°C.

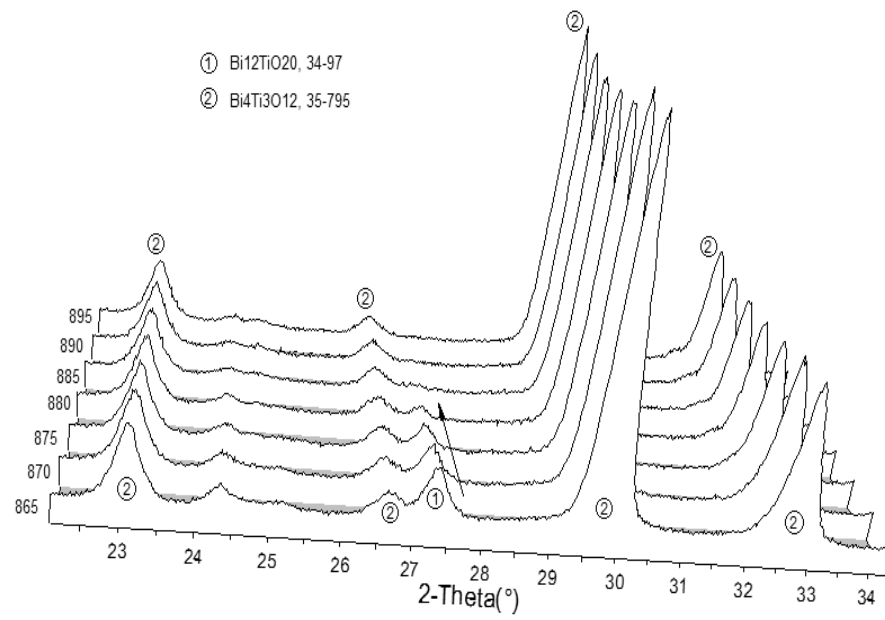


Figure 2.4: HTXRD patterns for Bi₂O₃ and TiO₂ powders in stoichiometric ratio of Bi₄Ti₃O₁₂ from 865°C to 895°C, highlighting the decomposition of Bi₁₂TiO₂₀.

2.5.2 Bi₄Ti₃O₁₂ HTXRD-SEM Analysis

In order to verify the phases present at each temperature without solely relying on diffraction data, samples were analyzed with the scanning electron microscope (SEM). Individual samples were heated to a specific temperature in the HTXRD, held for one hour, then a diffraction pattern was collected. The sample was cooled and prepared for SEM analysis. Sample temperatures were chosen to highlight specific reaction sequence events as were observed previously. Samples were heated to four temperatures; 525°C, 540°C, 850°C, and 900°C. Each sample was sputtered with a gold-palladium coating for an approximate 300Å coating thickness. A Phillips 515 SEM with LaB₆ filament was used to obtain secondary electron and backscattered electron images of the samples. A Kevex energy dispersive spectrometer (EDS) attachment was used to obtain elemental information.

Diffraction patterns for the four additional temperatures are seen in Figure 2.5. As expected, the same phases are present at the same temperatures as were observed in Figure 2.3. However, as Figure 2.6 shows, some growth is observed in the Bi₄Ti₃O₁₂ peak after the one hour hold at 540°C. A similar effect is seen for the other three temperatures. While it was not the intent of this experiment to reach equilibrium, it is interesting to note that further reaction does occur.

The samples used for SEM analysis were not polished, but rather retained the form they had when they were placed on the alumina strip sample holder. As such, the microscopic image shows a rough surface. Figure 2.7 shows typical secondary (SE) and backscattered (BSE) electron images from the 525°C sample. The sample topography generally consists of approximately 10μm agglomerates which themselves are composed of approximately 0.5μm grains. Note the contrast difference in Figure 2.7 between the light and dark areas. Since this sample initially consisted of Bi₂O₃ and TiO₂ and the reaction temperature was still low, the light areas most likely represent Bi₂O₃ and the darker areas TiO₂. EDS measurements performed on the light and dark areas are shown in Figure 2.8. While both spectra show evidence of bismuth and titanium, the light area is clearly rich in bismuth whereas the dark area is rich in titanium. Therefore, the light area is most likely Bi₂O₃ or Bi₁₂TiO₂₀ and the dark area is TiO₂.

Little difference if any was noted between the 525°C and 540°C micrographs. It was not possible to identify the Aurivillius phase in any region of either sample. However, a

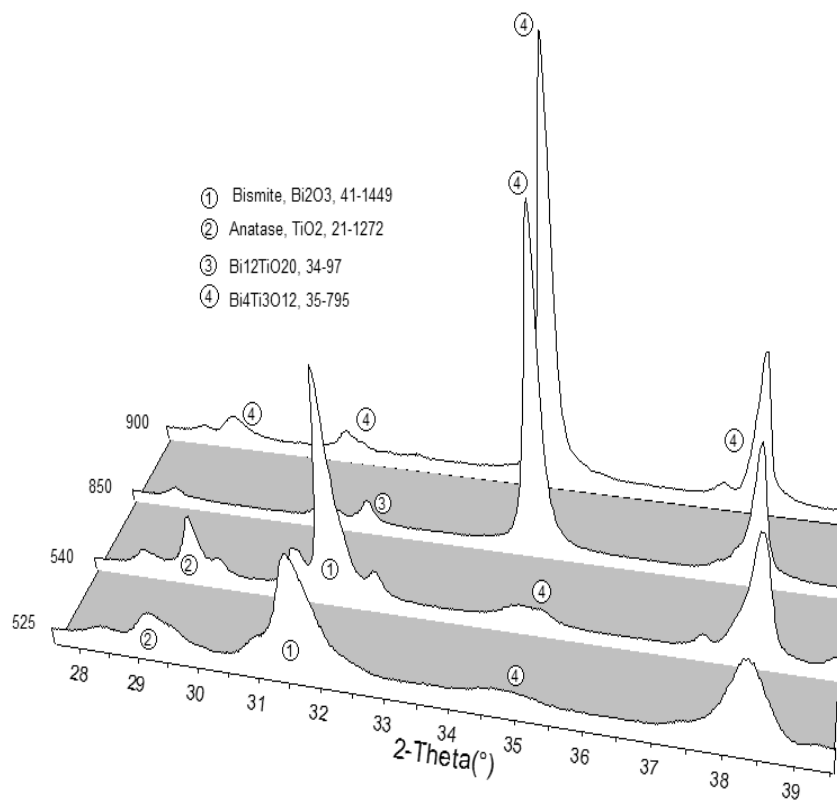


Figure 2.5: HTXRD patterns for the individual temperature diffraction measurements at 525°C, 540°C, 850°C, and 900°C after one hour hold at each temperature.

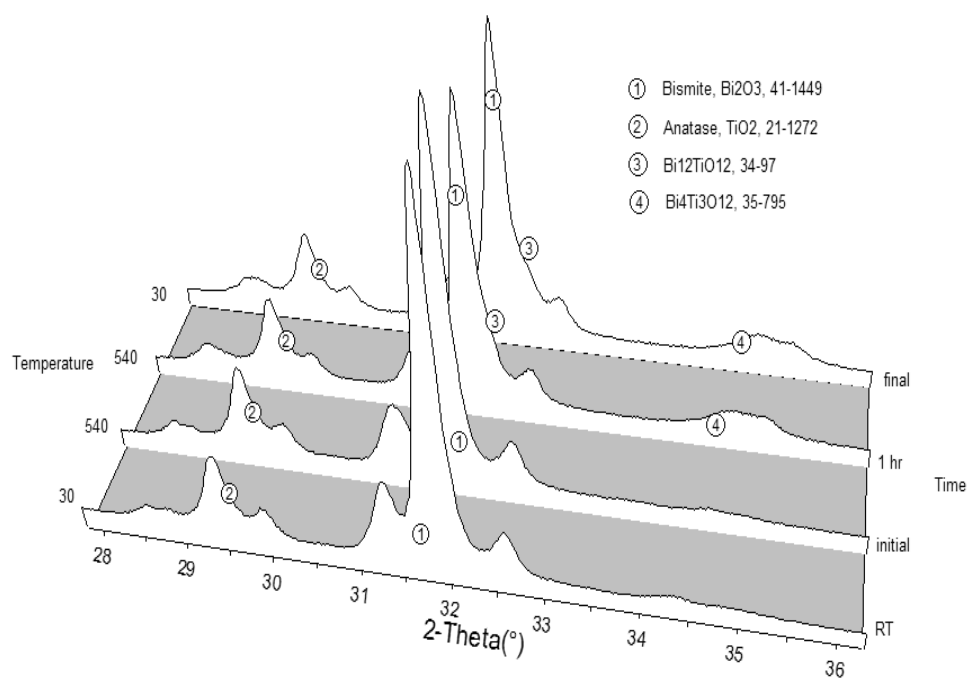
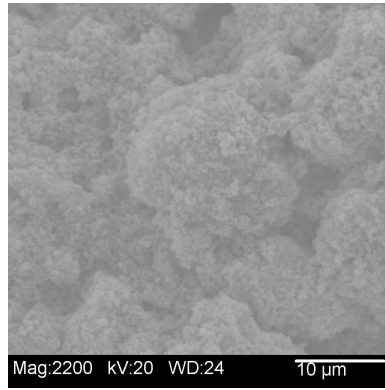
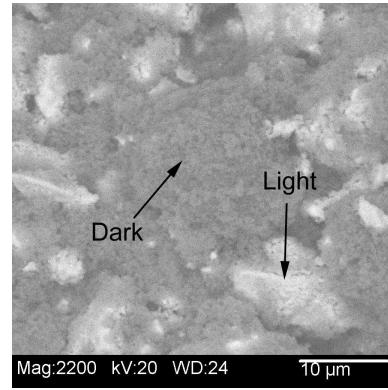


Figure 2.6: HTXRD pattern for the 540°C individual temperature scan. Times are indicated in the figure.

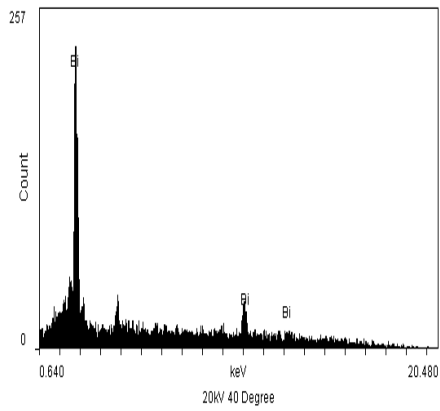


(a)

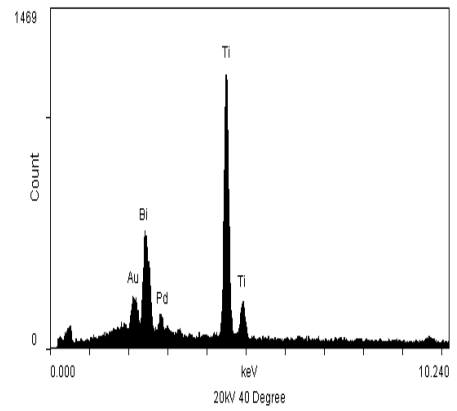


(b)

Figure 2.7: Secondary (a) and backscattered electron (b) SEM images of the 525°C $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ sample.



(a)



(b)

Figure 2.8: EDS spectra for the 525°C $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ sample focused on the bright (a) and dark areas (b) of the image in Figure 2.7.

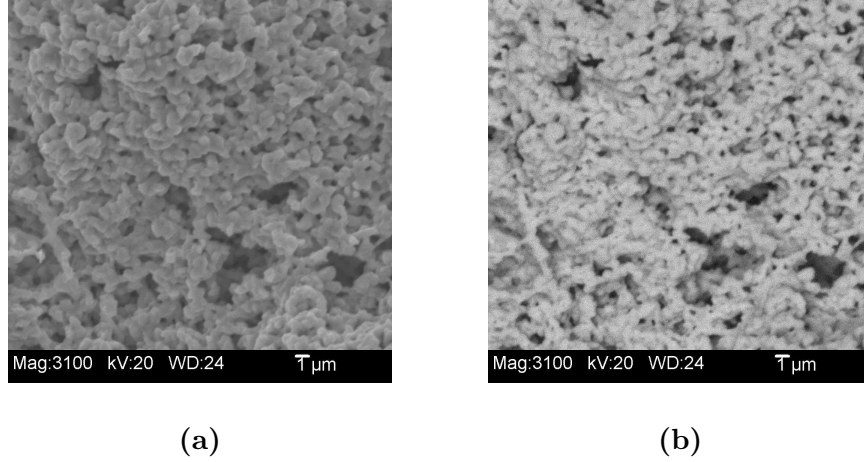


Figure 2.9: Secondary (a) and backscattered electron (b) SEM images of the 850°C sample.

dramatic difference in microstructure was observed in the micrographs of the sample heated to 850°C. Figure 2.9 shows the SE and BSE images for the 850°C sample. The large agglomerates as observed at lower temperatures do not exist, but rather grains with sizes on the order of $1\mu\text{m}$. The grains appear to have sintered uniformly. Note the lack of contrast in BSE mode in Figure 2.9. According to Figure 2.3, by this temperature, most of the sample has transformed to $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and only a small amount of $\text{Bi}_{12}\text{TiO}_{20}$ is supposed to remain. Figure 2.10 shows the EDS spectra for the sample area shown in Figure 2.9. While bismuth and titanium are present, it was not possible to rule out the presence of $\text{Bi}_{12}\text{TiO}_{20}$. On closer inspection, some areas of the image, especially in BSE mode, appeared to be slightly brighter than the surroundings. Figure 2.11 shows a BSE micrograph and the EDS spectra for this bright area. A slightly higher bismuth content is observed for this area as opposed to other areas, therefore, $\text{Bi}_{12}\text{TiO}_{20}$ is probably still to be found in the material.

The 900°C sample showed very little difference from the 850°C samples except that of microstructure. The grains appear to have coalesced further due to sintering, but still remain approximately $1\mu\text{m}$ in size. Figures 2.12 and 2.13 show the SE and BSE images and the EDS spectra for this sample.

In summary, the SEM images, coupled with the individual temperature diffraction measurements verify unambiguously, the phases present at each temperature. It was not possible to identify any presence of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ at the 540°C temperature in the SEM, nor

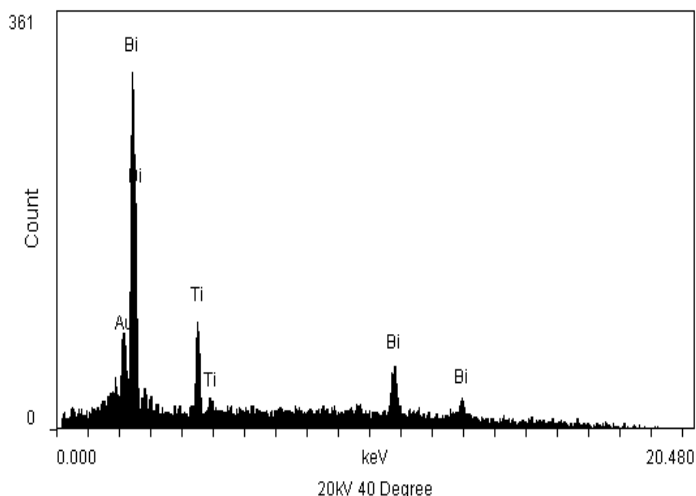


Figure 2.10: EDS spectra for the region shown in Figure 2.9 at 850°C.

was it possible to identify $\text{Bi}_{12}\text{TiO}_{20}$ at 850°C in the SEM. It is interesting to note that the microstructure followed suit with the expected reactions and temperatures. Little microstructural change was observed until higher temperatures. It is not known whether the more compact, sintered microstructure observed at 850°C was due solely to sintering or possible melting of Bi_2O_3 . Liquid phase sintering is much faster than solid state sintering. If Bi_2O_3 melting was occurring then one would expect not to see rectangular shaped grains as observed in Figure 2.9.

2.5.3 $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ HTRXD Reaction Kinetics Study

Since the results of the HTRXD study of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ were so successful, it was decided to perform a kinetic based study in order to determine reaction rates of Bi_2O_3 and TiO_2 to form $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. Isothermal Avrami type kinetic studies have been performed in the Aurivillius system previously.^{21–24} Lu *et al.* performed isothermal kinetic studies on $\text{SrBi}_2\text{Nb}_2\text{O}_9$ by measuring the quantity SrCO_3 decomposed versus time.²² Because $\text{SrBi}_2\text{Nb}_2\text{O}_9$ formed during the heating process, they reasoned that if more SrCO_3 was decomposing, then more $\text{SrBi}_2\text{Nb}_2\text{O}_9$ must be forming. X-ray diffraction measurements were performed, however the results were not used in any sort of quantitative analysis. It is likely that they were simply measuring the rate of decomposition of SrCO_3 . Kwak *et al.* performed isothermal

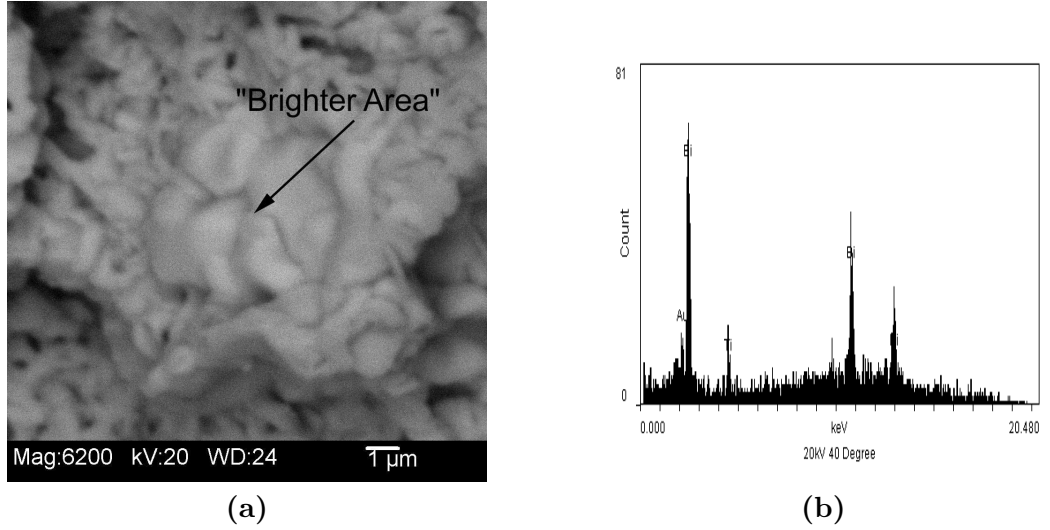


Figure 2.11: BSE (a) and EDS spectra (b) of brighter region in 850°C micrograph.

kinetic analysis of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin films using x-ray diffraction data to obtain quantities and ultimately the fraction Aurivillius phase transformed.²⁴ However, their quantitative analysis was standardless and based loosely on the method of Klug and Alexander.²⁵

Isothermal HTXRD measurements were performed using five different temperatures; 550°C, 575°C, 600°C, 700°C, and 800°C. It was desired to perform the measurement as fast as possible in order to minimize the amount of reaction occurring during the measurement itself, and therefore, a $10^\circ 2\theta$ scan range was used which happened to correspond with the window of the PSD. The $10^\circ 2\theta$ scan range, between 28-40° 2θ for cobalt radiation, allowed for the major Bi_2O_3 , TiO_2 , and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ peaks to be observed. Ideally, it would have been desired to fix the center of the detector at the middle of the $10^\circ 2\theta$ range, because this would have allowed significantly faster measurement times. However, this was not possible, and thus the detector had to scan the $10^\circ 2\theta$ range during the measurement. As a result, a $24^\circ 2\theta$ per minute scan rate was used to obtain a total measurement time of thirty seconds. Due to instrument electronics limitations, there was another thirty second wait between actual measurements. This meant that the minimum possible time between measurements was sixty seconds and as a result, the time profiles were adjusted accordingly. The values listed in Table 2.II show the times actually used between measurements and it also shows the total time elapsed per measurement.

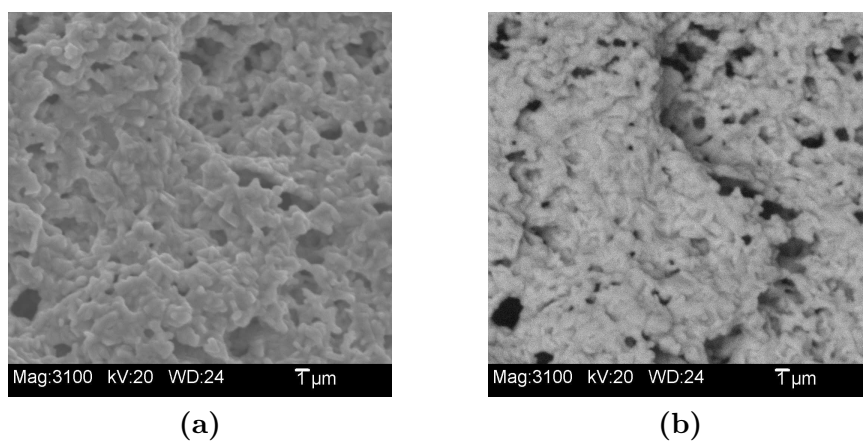


Figure 2.12: Secondary (a) and backscattered (b) electron SEM images of the 900°C sample.

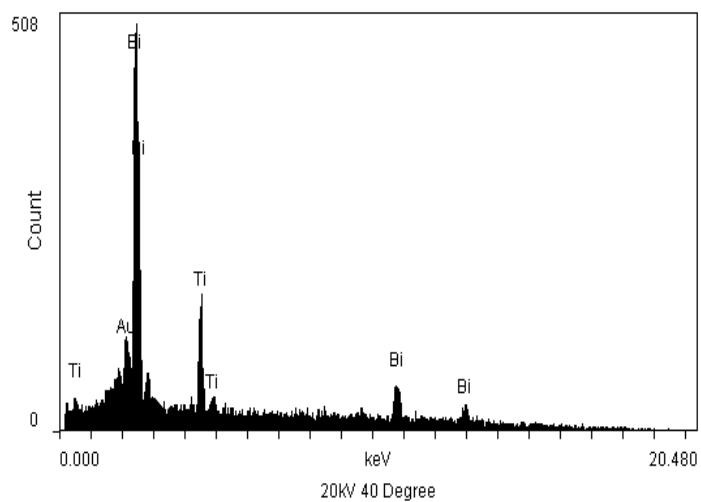


Figure 2.13: EDS spectra for the 900°C micrographs.

Table 2.II: Parameters Used in HTXRD Kinetics Studies.

Measurement	Hold time(sec)	Total time(sec)
1	0	0
2	0	60
3	0	120
4	60	240
5	180	480
6	420	960
7	900	1920
8	1620	3600
9	3500	7200

Figures 2.14- 2.18 show the HTXRD patterns for the five isothermal measurements. Note the increased amount of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ present especially from 600°C upwards. It is also interesting to note that a second form of bismuth oxide ($\text{Bi}_{12}\text{TiO}_{20}$) exists simultaneously with Bismite (Bi_2O_3). $\text{Bi}_{12}\text{TiO}_{20}$ is essentially the cubic form of Bi_2O_3 with a small amount of titanium doped into its structure. The amount of $\text{Bi}_{12}\text{TiO}_{20}$ increases the longer time the reaction proceeds at the given temperature and this occurs for all temperatures. However, at higher temperatures, most of the Bi_2O_3 has already converted to $\text{Bi}_{12}\text{TiO}_{20}$ by the time of the first measurement. The fact that $\text{Bi}_{12}\text{TiO}_{20}$ exists is not surprising. It is well known that bismuth oxide (Bi_2O_3) can be stabilized to the cubic symmetry by substitution of Bi^{3+} with another cation.^{26–28} Cations such as, Sr^{2+} , Ca^{2+} , La^{3+} , Ga^{3+} , Ti^{4+} , etc., are able to substitute at levels sufficient to stabilize the cubic symmetry.

Quantitative analysis was performed using the Rietveld method with TOPAS in order to extract concentrations of the constituents versus time.^{29,30} Diffraction profiles were fit using a fundamental parameters routine in place of the typical pseudo-Voigt or Pearson VII profiles. The instrumental and sample contributions to the peak profile were obtained via refinement of a powder sample of NIST standard Silicon (640c) on an alumina strip sample holder. Once a suitable refinement was obtained, the profile function was applied to all sample diffraction patterns. Quantitative data obtained for the three sample temperature used are the kinetics analysis is shown in tables 2.III, 2.IV, and 2.V.

The concentrations of all the phases were plotted as a function of reaction time as seen in figures 2.19 through 2.23. Note the increase in $\text{Bi}_{12}\text{TiO}_{20}$ concentration versus

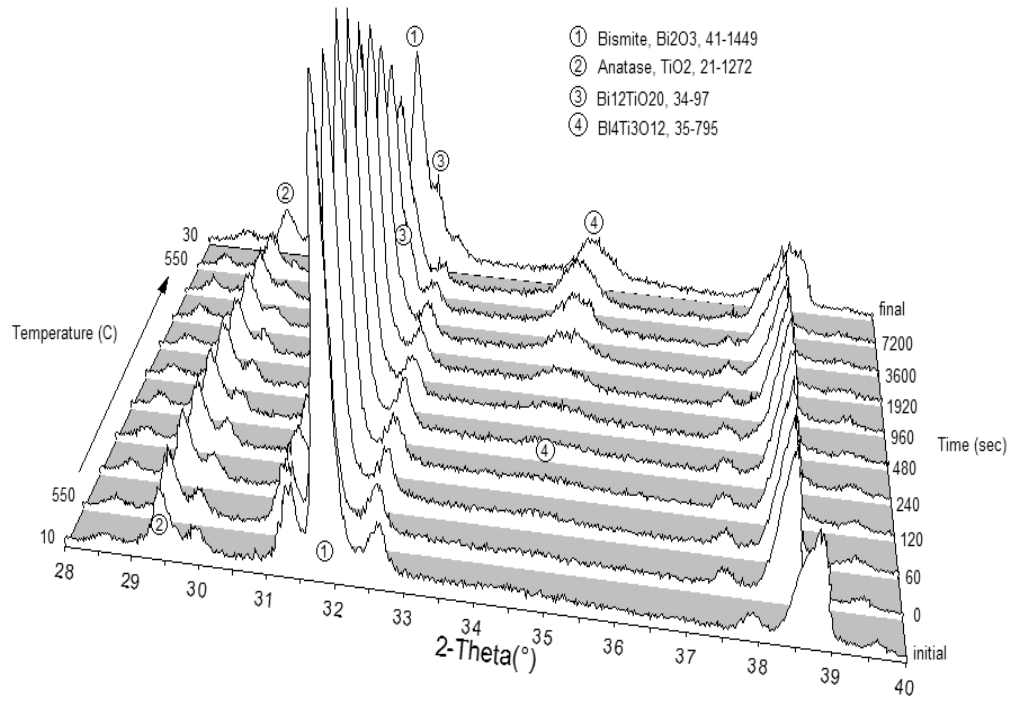


Figure 2.14: Isothermal HTXRD patterns for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ holding at 550°C .

Table 2.III: Rietveld-derived Concentrations from the 550°C HTXRD Kinetic Study.

Time (sec)	Bismite wt%	Anatase wt%	$\text{Bi}_{12}\text{TiO}_{20}$ wt%	$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ wt%	Frac. Trans. (Aurv/Tot wt%)
240	48.7 ± 0.6	42.8 ± 0.6	1.7 ± 0.05	6.8 ± 0.4	0.073
480	44.2 ± 0.5	41.6 ± 0.61	2.6 ± 0.06	11.7 ± 0.4	0.133
960	42.5 ± 0.5	39.7 ± 0.6	4.3 ± 0.07	13.6 ± 0.3	0.157
1920	37.1 ± 0.4	38.3 ± 0.6	7.1 ± 0.1	17.52 ± 0.3	0.213
3600	33.5 ± 0.6	35.5 ± 1.0	8.2 ± 0.2	22.8 ± 0.4	0.295
7200	27.1 ± 0.5	33.4 ± 1.1	11.1 ± 0.2	28.5 ± 0.5	0.398

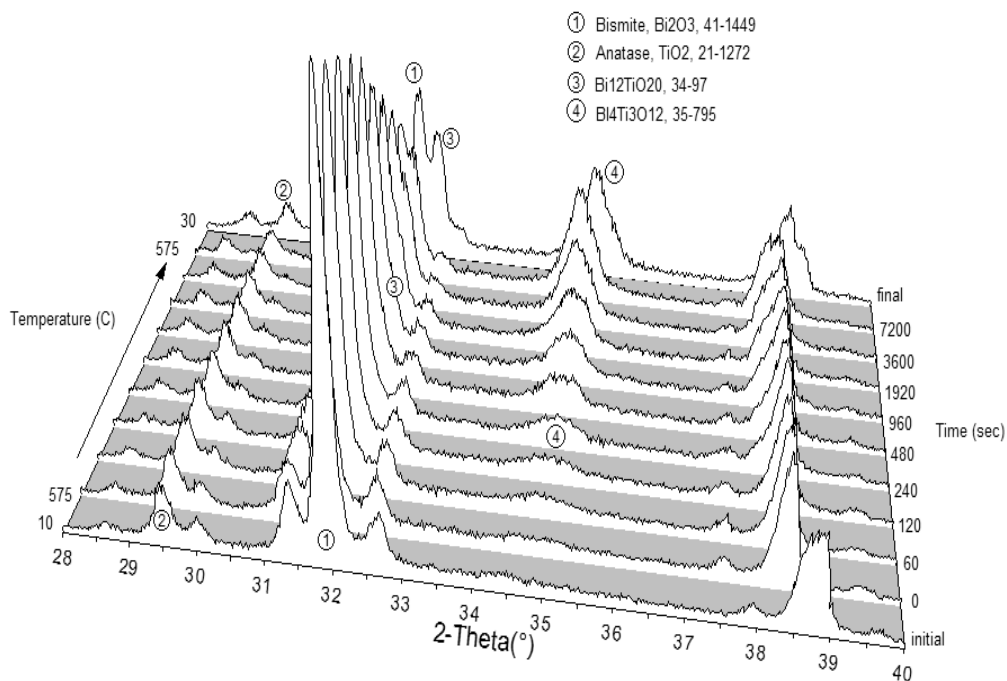


Figure 2.15: Isothermal HTXRD patterns for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ holding at 575°C .

Table 2.IV: Rietveld-derived Concentrations from the 575°C HTXRD Kinetic Study.

Time (sec)	Bismite wt%	Anatase wt%	$\text{Bi}_{12}\text{TiO}_{20}$ wt%	$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ wt%	Frac. Trans. (Aurv/Tot wt%)
0	52.2 ± 0.6	39.7 ± 0.6	1.7 ± 0.07	6.4 ± 0.16	0.064
60	48.3 ± 0.8	39.3 ± 1.0	3.6 ± 0.09	8.9 ± 0.2	0.088
120	44.7 ± 0.5	39.5 ± 0.6	4.6 ± 0.1	11.2 ± 0.2	0.112
240	42.2 ± 0.7	37.9 ± 0.8	5.1 ± 0.1	14.7 ± 1.1	0.147
480	38.1 ± 0.5	35.7 ± 0.7	8.3 ± 0.1	17.9 ± 0.3	0.179
960	32.7 ± 0.5	35.3 ± 0.7	11.8 ± 0.1	20.2 ± 0.3	0.202
1920	25.1 ± 0.5	35.0 ± 0.7	14.4 ± 0.2	25.5 ± 0.4	0.255
3600	20.3 ± 0.6	33.6 ± 1.3	16.0 ± 0.3	30.0 ± 0.6	0.300
7200	14.6 ± 0.4	31.9 ± 0.7	18.0 ± 0.2	35.5 ± 0.4	0.355

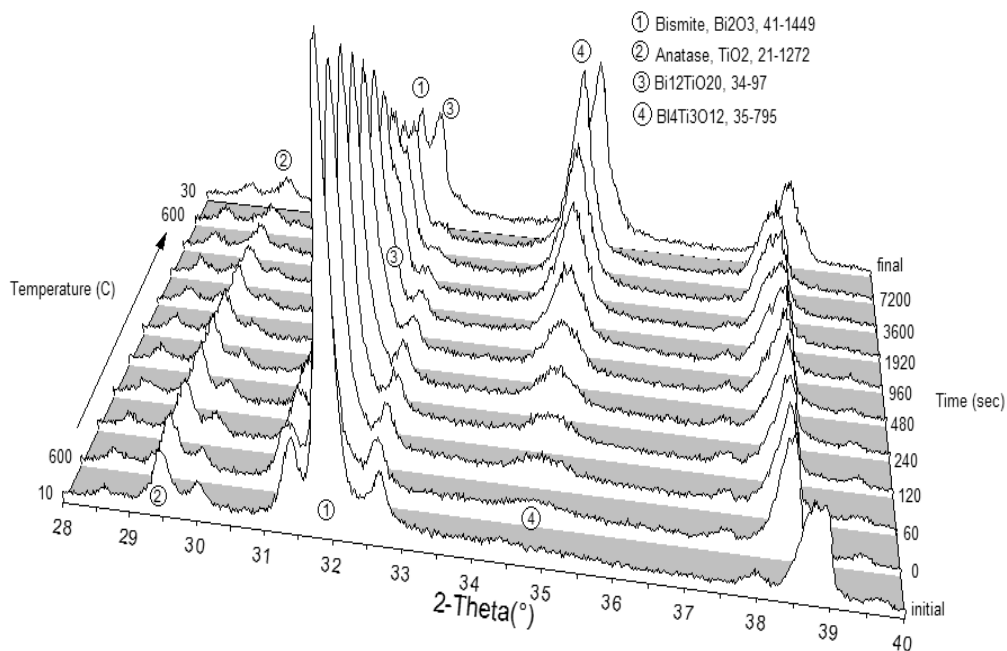


Figure 2.16: Isothermal HTXRD patterns for Bi₄Ti₃O₁₂ holding at 600°C.

Table 2.V: Rietveld-derived Concentrations from the 600°C HTXRD Kinetic Study.

Time (sec)	Bismite wt%	Anatase wt%	Bi ₁₂ TiO ₂₀ wt%	Bi ₄ Ti ₃ O ₁₂ wt%	Frac. Trans. (Aurv/Tot wt%)
0	52.5 ± 0.9	38.9 ± 1.0	1.5 ± 0.1	7.2 ± 0.3	0.072
60	47.0 ± 0.8	39.8 ± 1.0	3.6 ± 0.1	9.6 ± 0.3	0.096
120	45.2 ± 0.8	37.7 ± 1.0	4.7 ± 0.1	12.3 ± 0.3	0.123
240	43.9 ± 0.8	36.4 ± 1.0	5.1 ± 0.2	14.6 ± 0.3	0.146
480	31.6 ± 0.6	36.9 ± 1.1	9.4 ± 0.2	22.0 ± 0.5	0.220
960	27.5 ± 0.5	31.0 ± 0.7	9.8 ± 0.2	31.7 ± 0.5	0.317
1920	19.6 ± 0.5	27.2 ± 0.8	12.2 ± 0.2	41.0 ± 0.5	0.410
3600	16.1 ± 0.5	18.73 ± 1.8	13.7 ± 0.4	51.5 ± 1.2	0.515
7200	10.5 ± 0.6	12.7 ± 1.9	15.0 ± 0.4	61.8 ± 1.4	0.618

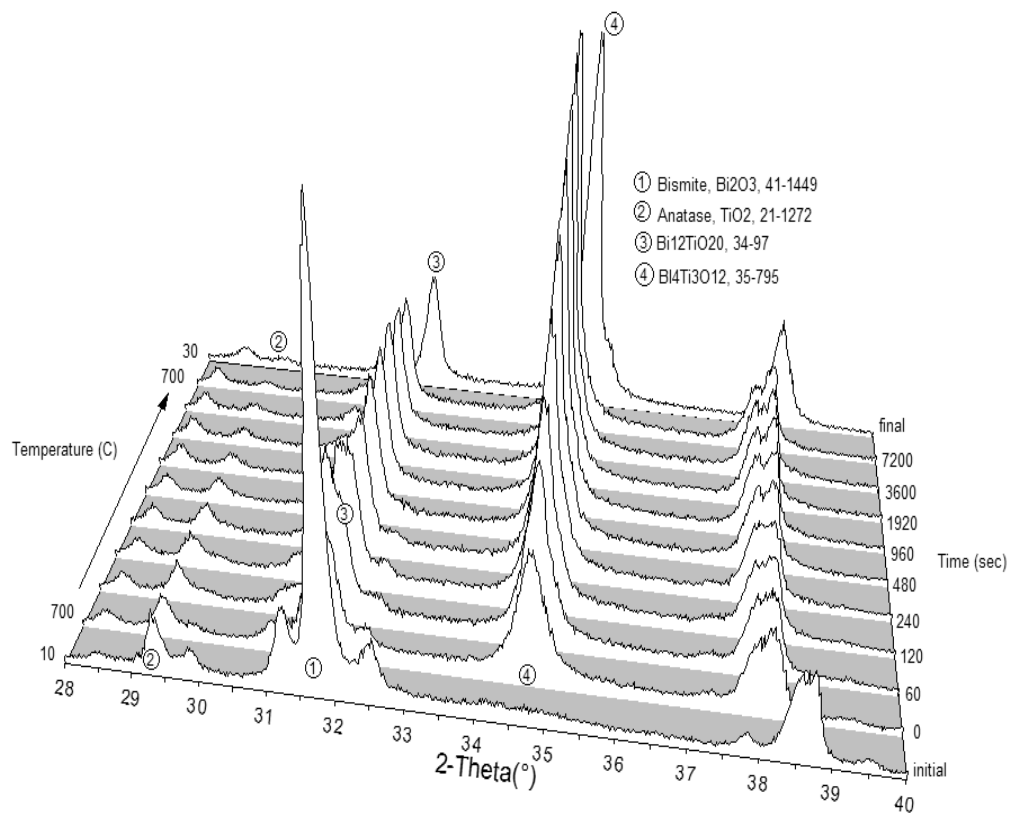


Figure 2.17: Isothermal HTXRD patterns for Bi₄Ti₃O₁₂ holding at 700°C.

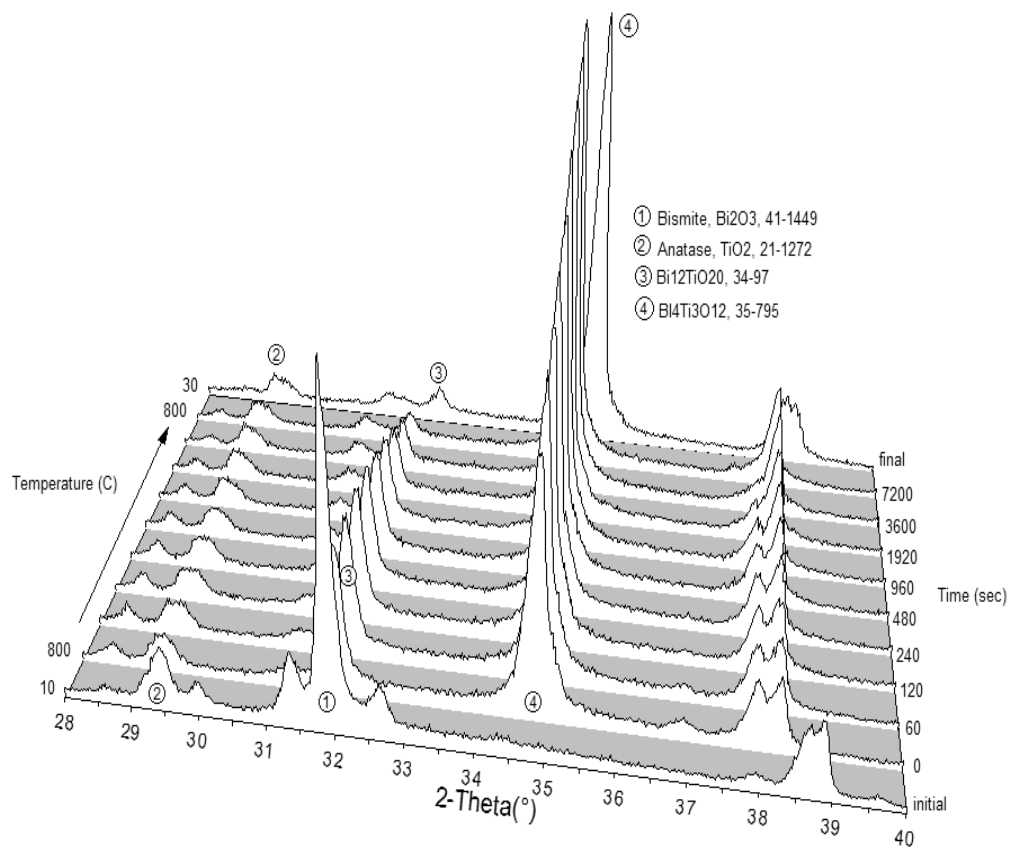


Figure 2.18: Isothermal HTXRD patterns for Bi₄Ti₃O₁₂ holding at 800°C.

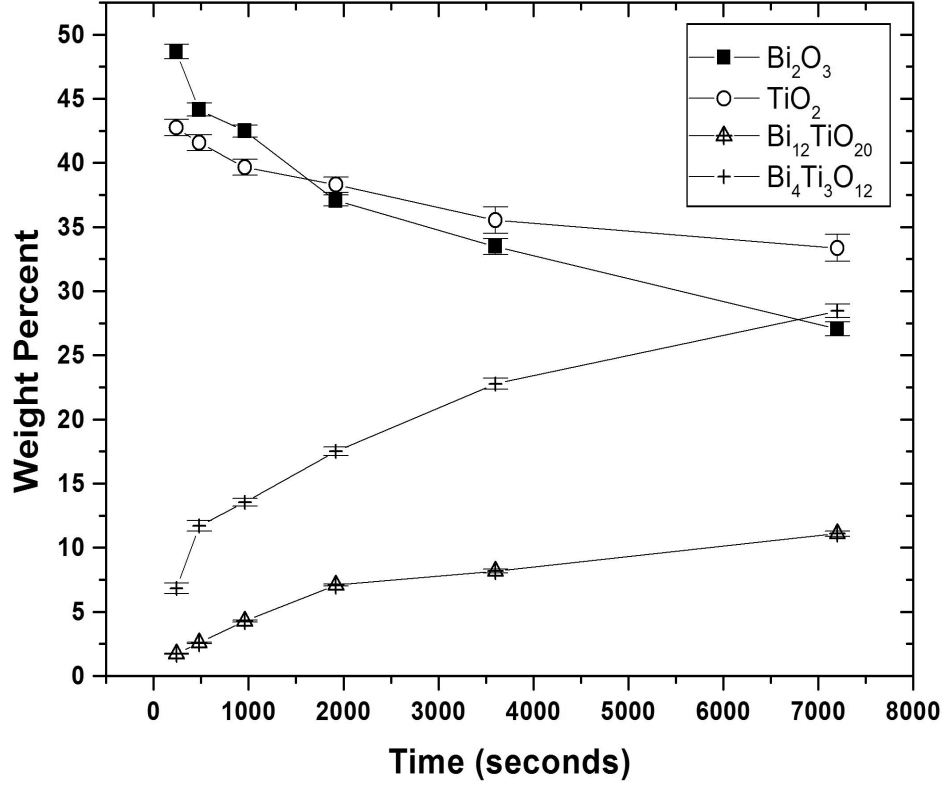


Figure 2.19: Weight percent versus time for reactants and products form HTXRD analysis of Bi₂O₃ and TiO₂ in the Bi₄Ti₃O₁₂ composition at 550°C.

Bi₂O₃ as the reaction proceeds. Furthermore, more Bi₁₂TiO₂₀ is present sooner at higher temperatures. At higher temperatures (700 and 800°C), most Bi₂O₃ has transformed to Bi₁₂TiO₂₀ by the first measurement. All samples show a decreasing reaction rate with time as equilibrium is approached. Most Bi₄Ti₃O₁₂ formation occurs within the first 2000 seconds regardless of temperature.

The concentration data was converted to fraction of Aurivillius phase transformed in accordance with the Avrami analysis. The fraction transformed data was reformatted in terms of Equation 2.1.

$$\ln(-\ln(1 - \alpha)) = \ln(k) + m\ln(t) \quad (2.1)$$

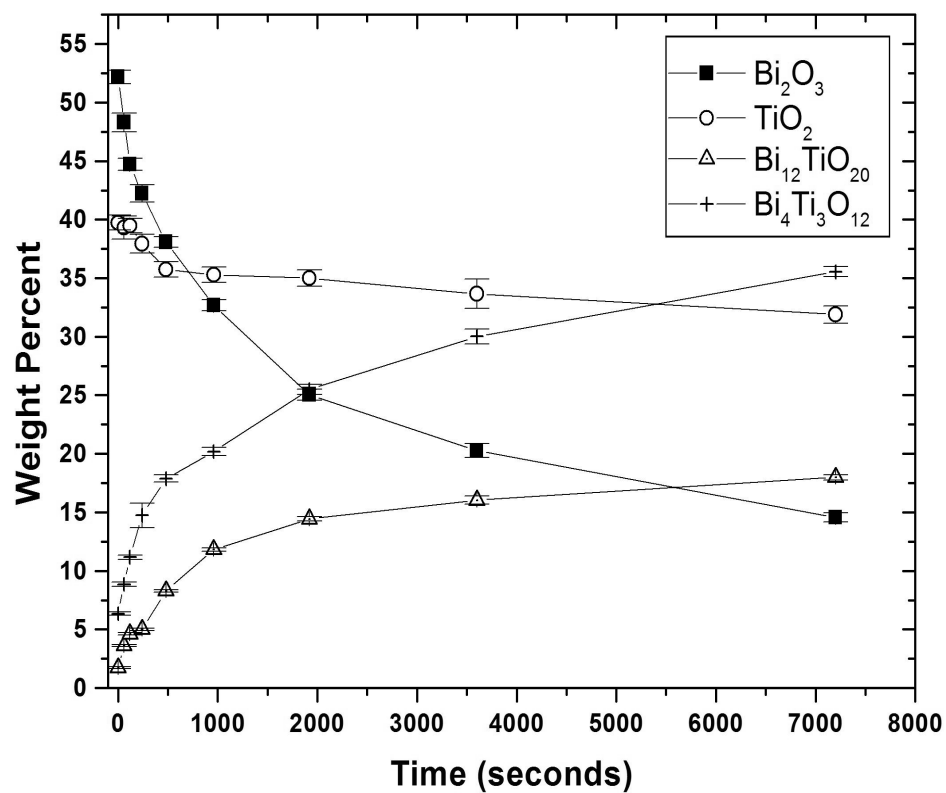


Figure 2.20: Weight percent versus time for reactants and products from HTXRD analysis of Bi_2O_3 and TiO_2 in the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ composition at 575°C .

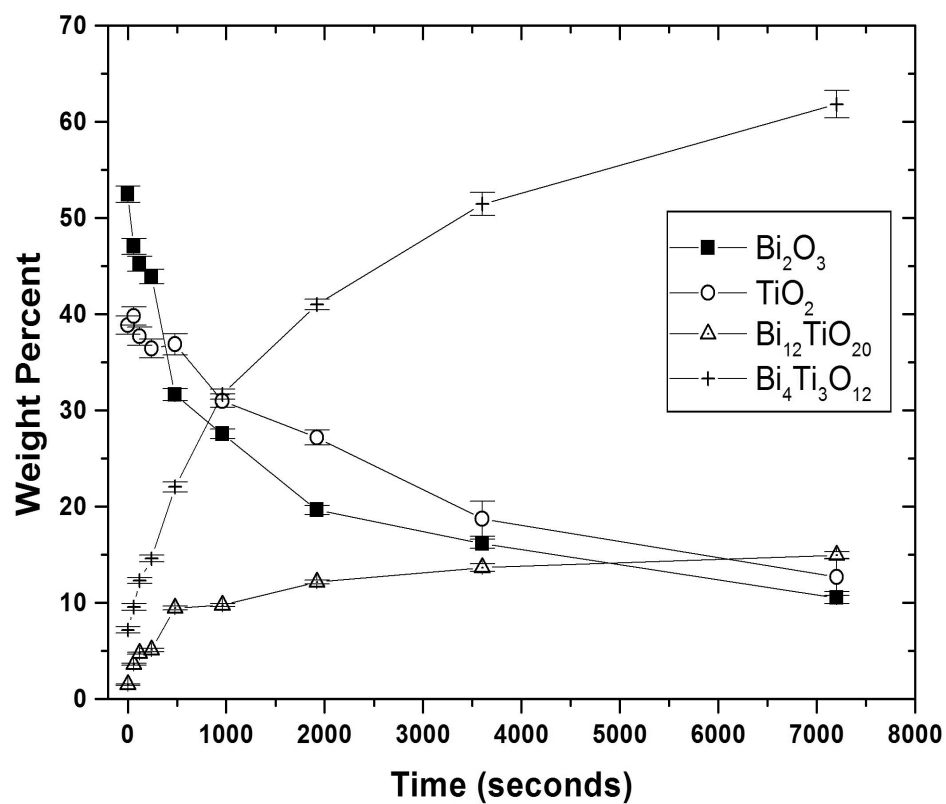


Figure 2.21: Weight percent versus time for reactants and products form HTXRD analysis of Bi_2O_3 and TiO_2 in the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ composition at 600°C .

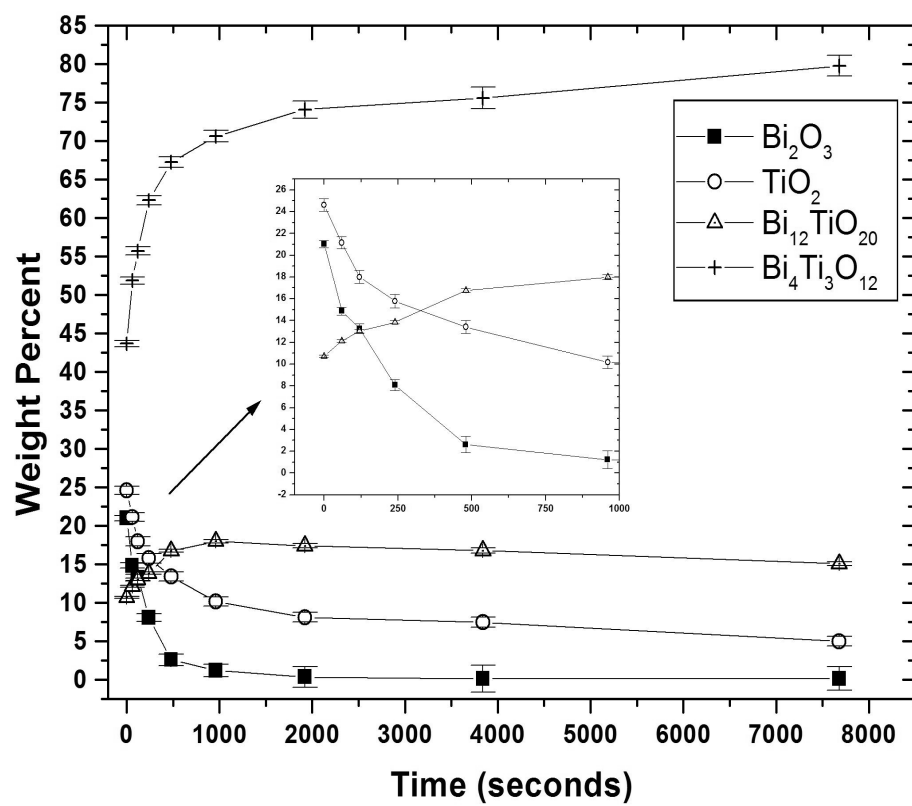


Figure 2.22: Weight percent versus time for reactants and products form HTXRD analysis of Bi_2O_3 and TiO_2 in the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ composition at 700°C .

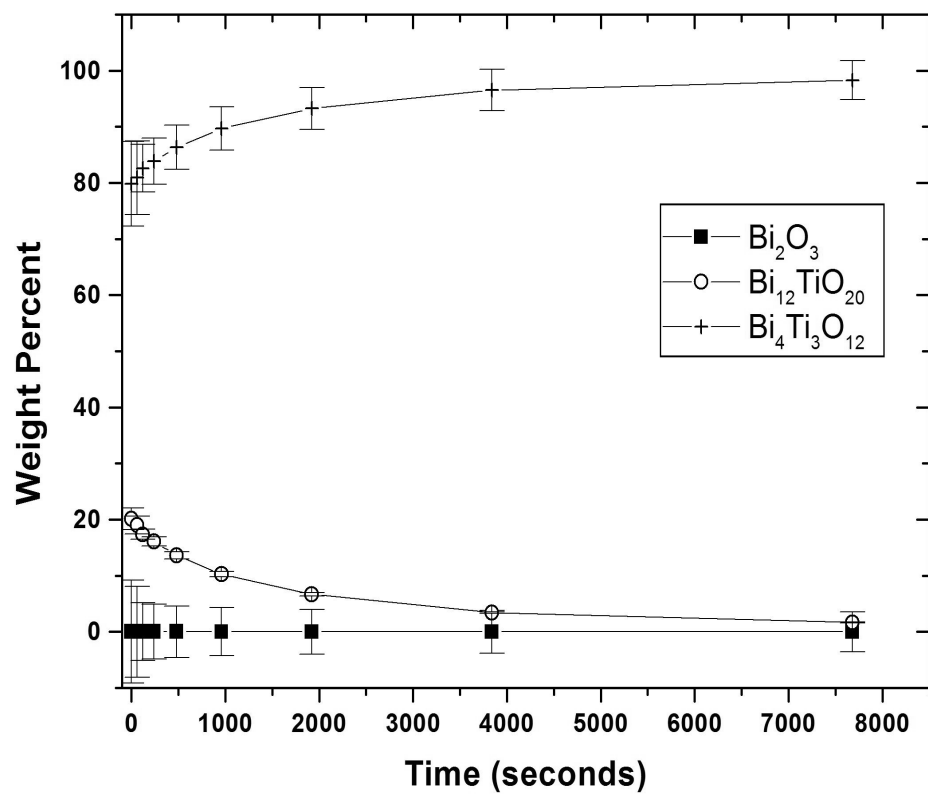


Figure 2.23: Weight percent versus time for reactants and products form HTXRD analysis of Bi_2O_3 and TiO_2 in the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ composition at 800°C .

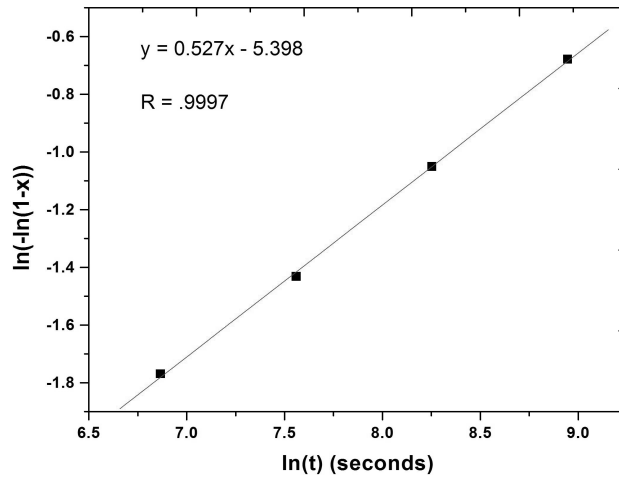


Figure 2.24: Plot of $\ln(-\ln(1 - \alpha))$ versus $\ln(t)$ for 550°C.

where k is the rate constant, m is the Avrami exponent, t is time, and α is the fraction transformed. If a plot of $\ln(-\ln(1 - \alpha))$ versus $\ln(t)$ is made, the slope will yield the Avrami exponent m . However, this analysis is only valid within fraction transformed ranges of $0.15 < \alpha < 0.5$ as stated by Hancock *et al.*^{31,32} Only the 550°C, 575°C, and part of the 600°C temperatures had α values within the prescribed range. The fraction transformed in the 700°C and 800°C measurements fell completely outside the high side ($\alpha > 0.5$) of this range. It was observed that (especially in the 575°C and 600°C measurements), valid results were only obtained when using the data within the prescribed regions. For example, if all of the data points were used for the 600°C measurement, then the slope of the line changed from 0.54 to 0.45. Plots of $\ln(-\ln(1 - \alpha))$ versus $\ln(t)$ are seen in figures 2.24 to 2.26. Straight lines were fitted to the data, and the resulting equations as well as the R values are shown in the figures.

The 575°C, 700°C, and 800°C plots failed to produce an Avrami exponent that fell within guidelines. The Avrami exponent is supposed to indicate the manner of reaction, be it diffusion controlled or interface controlled.^{31,32} Table 2.VI lists the Avrami exponents and the related solid state rate equations pertaining only to the diffusion type models. In principal, once an Avrami exponent is found, we search for the appropriate rate equation then the rate equation is plotted as a function of time. All of the rate equations are based on

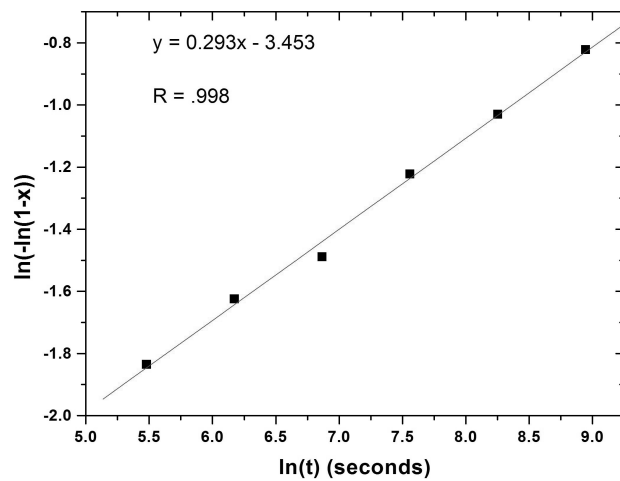


Figure 2.25: Plot of $\ln(-\ln(1 - \alpha))$ versus $\ln(t)$ for 575°C.

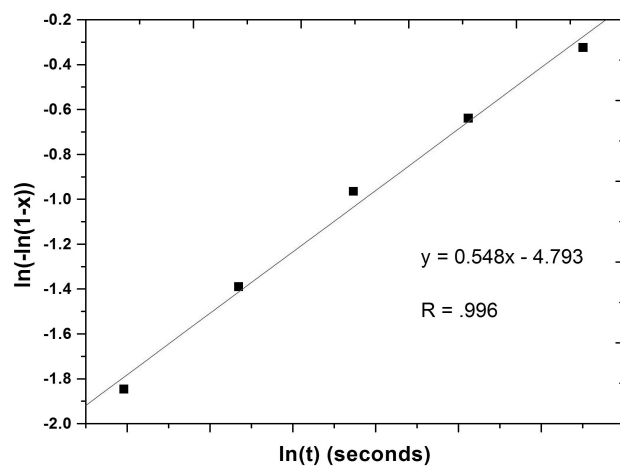


Figure 2.26: Plot of $\ln(-\ln(1 - \alpha))$ versus $\ln(t)$ for 600°C.

Table 2.VI: Diffusion Based Avrami Rate Equations and Exponents.

<i>Function</i>	<i>RateEquation</i>	<i>AvramiExponent(m)</i>
D_1	$\alpha^2 = kt$	0.62
D_2	$(1 - \alpha)\ln(1 - \alpha) + \alpha = kt$	0.57
D_3	$[1 - (1 - \alpha)^{\frac{1}{3}}]^2 = kt$	0.54
D_4	$1 - \frac{2\alpha}{3} - (1 - \alpha)^{\frac{2}{3}} = kt$	0.57

(2.4)

the fraction transformed (α). A plot of the rate equation versus time should ideally yield a line of which the slope is equal to the rate constant. Assuming that multiple temperatures have been investigated, this rate constant can then be expressed in the Arrhenius equation as seen in Equation 2.2 and then reformulated as Equation 2.3 plotted as $\ln$ (rate constant) versus $1/T$ to obtain a slope of $\frac{-E_a}{R}$ and ultimately obtain the activation energy (E_a) of the transformation.

$$k = k_0 \exp(-E_a/RT) \quad (2.2)$$

$$\ln k = \ln k_0 + \frac{-E_a}{RT} \quad (2.3)$$

The Avrami exponent for the 550°C and 600°C measurements were 0.53 and 0.548 respectively which fall within the range of the diffusion controlled type reactions (D1 through D4). Therefore, the four diffusion rate equations D1 through D4 were plotted versus time. Table 2.VII shows the results of linear fits to the plots of rate equation versus time as well as the R^2 values. Because it was the intention of this analysis to obtain activation energies, the 575°C data was used as well in this analysis even though the initial Avrami exponent fell outside the boundaries ($m=0.29$). In this way, three data points would be used for the Arrhenius plots. There did not seem to be a preference for any one type of rate equation. The 550°C data showed excellent fit to all equations, the 575°C data showed reasonably good fit to all equations, and the 600°C data showed good fits to all data, but gave a better fit to the D3 equation. As a result, the rate constants obtained from all four equations were used in the Arrhenius analysis. Figure 2.27 shows a typical Arrhenius plot using

Table 2.VII: HTXRD Kinetics Rate Constants and Activation Energies.

Rate Equation	550°C	575°C	600°C	E_a (kJ/mole)
D1	2.15E-5 (0.998)	1.5E-5 (0.96)	7.1E-5 (0.97)	140.4
D2	1.3E-5 (0.999)	9E-6 (0.96)	4.5E-5 (0.98)	145.98
D3	3E-6 (0.999)	2E-6 (0.97)	1.3E-5 (0.99)	172.5
D4	3E-6 (0.999)	2E-6 (0.97)	1.1E-5 (0.99)	152.7

the D1 data. Clearly, the fit was poor with an R value of 0.62. The highest R obtained was 0.61 with the D3 data. Note the low data point in the plot at the 575°C, all four plots had the low data point at the same temperature. Regardless of the quality of the fit, the results were tabulated as seen in Table 2.VII and activation energies on the order of 150kJ/mole were obtained. These data are on the same order of magnitude as those obtained by Kwak *et al.* (213-264kJ/mole), and Lu *et al.* (194-210kJ/mole).^{22,24} Both Kwak *et al.* and Lu *et al.* worked with the two layer Aurivillius phase $\text{SrBi}_2\text{Ta}_2\text{O}_9$.

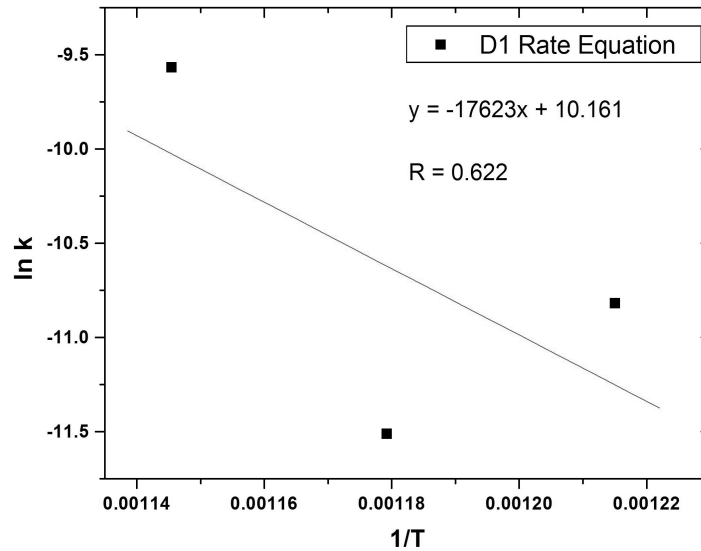
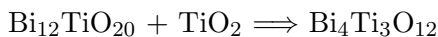
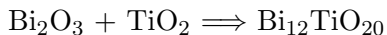
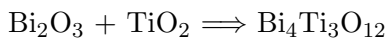


Figure 2.27: Arrhenius plot of rate constant for the D1 rate equation.

2.5.4 Bi₄Ti₃O₁₂ Solid State HTXRD Discussion

A number of conclusions can be drawn about Bi₄Ti₃O₁₂ as synthesized via solid state synthesis. The kinetics study really helps to solidify the understanding of the Bi₄Ti₃O₁₂ reaction mechanism. Based on the observations so far, the proposed Bi₄Ti₃O₁₂ reaction sequence is a three part process as seen below.



It is clear from the kinetics plots of weight percent versus time that the formation of Bi₁₂TiO₂₀ is not a critical step in the reaction. Figure 2.20 highlights this point well because it clearly shows that the Bi₂O₃ content is falling at a faster rate than TiO₂. Coupled with the fact that Bi₁₂TiO₂₀ increases much more slowly than as the Bi₂O₃ decreases, it is not a critical reaction step. If Bi₁₂TiO₂₀ were a critical step in the formation of Bi₄Ti₃O₁₂, then one would not expect Bi₄Ti₃O₁₂ to increase in quantity as fast as it does, rather, there would be a type of induction period where all Bi₂O₃ converts to Bi₁₂TiO₂₀, then formation of Bi₄Ti₃O₁₂ would commence. Ultimately, once enough Bi₄Ti₃O₁₂ has formed, as in the 700°C measurement (Figure 2.22), then Bi₁₂TiO₂₀ will react with TiO₂ to form Bi₄Ti₃O₁₂.

It is interesting however, to speculate on the actual mass transport mechanism during formation of Bi₄Ti₃O₁₂ be it vapor phase, liquid phase, or solid phase reactions. The vapor phase mechanism is a possibility due to the volatility of Bi₂O₃ however, it does not explain the Bi₄Ti₃O₁₂ formation at temperatures lower than the vaporization temperature of Bi₂O₃. Likewise, the liquid phase mechanism is not possible because of the low temperatures. A solid state mechanism is the last possibility and is strongly supported by the Avrami analysis. It was observed previously that reasonably good fits were obtained for the diffusion model rate constants at low temperatures. The crystal structures of the reactants Bi₂O₃ and TiO₂ are monoclinic and tetragonal, respectively, and do not share any features with the layered form of Bi₄Ti₃O₁₂. So some type of diffusion based structural formation is probably the way Bi₄Ti₃O₁₂ forms. It is interesting that Bi₁₂TiO₂₀ was not a critical step, because at least one author has speculated that the Aurivillius phase forms out a fluorite

Bi_2O_3 type phase. $\text{Bi}_{12}\text{TiO}_{20}$ is cubic and has a fluorite structure and the $(\text{Bi}_2\text{O}_2)^{2+}$ layer of the Aurivillius structure has a fluorite like structure. The fluorite material would then incorporate perovskite like layers during reaction at temperature.²³

2.5.5 $\text{Bi}_2\text{La}_2\text{Ti}_3\text{O}_{12}$ HTXRD Reaction Study

Based on the successful preparation of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, it would be interesting to note the effect on the reaction sequence with the substitution of an isovalent cation for Bi^{3+} . $\text{Bi}_2\text{La}_2\text{Ti}_3\text{O}_{12}$ involves complete substitution of La^{3+} onto the perovskite A site of the structure. Since La^{3+} is isovalent with Bi^{3+} , the structure would not be forced to create oxygen vacancies, say if A^{2+} were substituted. The starting precursor powders were Bi_2O_3 , TiO_2 , and La_2O_3 . The La_2O_3 powder was heated to 1000°C for 10 hours to remove any hydrated water.

The reaction sequence to synthesize $\text{Bi}_2\text{La}_2\text{Ti}_3\text{O}_{12}$ as observed via HTXRD shows relatively few phase changes and reactions during a high temperature cycle. Figure 2.28 shows the entire diffraction pattern from room temperature to 950°C . Table 2.VIII shows the phases present at each temperature. Little change is seen in the diffraction patterns until approximately 650°C . At about 650°C , the Bi_2O_3 precursor converts to either a δ Bi_2O_3 (PDF 45-1344) or a stabilized Bi_2O_3 -type phase $\text{Bi}_{12}\text{TiO}_{20}$ (PDF 34-97). The $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phase forms somewhere between 600 - 650°C , but its 100% peak is completely overlapped by that of La_2O_3 at $29.8^\circ 2\theta$. However, by observation of Figure 2.28 it can be seen that the prospective 100% peak of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ begins to increase in relative intensity after 600°C . According to the location of the diffraction peaks, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ forms first in place of $\text{Bi}_2\text{La}_2\text{Ti}_3\text{O}_{12}$. A slow decrease in the Bi_2O_3 and $\text{Bi}_{12}\text{TiO}_{20}$ relative peak intensity occurs until approximately 850°C where the peaks disappear completely. The TiO_2 and La_2O_3 peaks remain relatively constant in height until about 650°C , then they begin a slow decomposition until 950°C where they are still observed. Ultimately, at 950°C , the following three phases exist, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, La_2O_3 , and TiO_2 . The reaction to form $\text{Bi}_2\text{La}_2\text{Ti}_3\text{O}_{12}$ did not proceed to completion during the measurement time. Furthermore, no evidence of $\text{Bi}_2\text{La}_2\text{Ti}_3\text{O}_{12}$ can be observed from the diffraction patterns although it is not unreasonable to speculate that a small amount did form. Separate experiments did not reveal any new phase transformations and the reaction did not reach completion. It is interesting to note that TiO_2 and La_2O_3 existed in the sample even until high temperatures. It is clear that

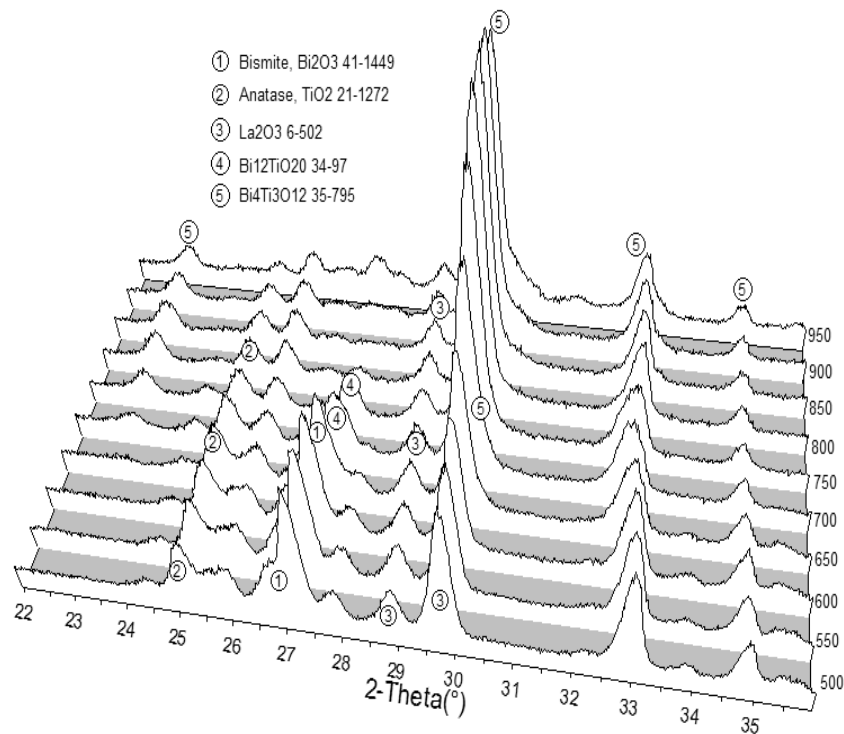


Figure 2.28: HTXRD patterns for the $\text{Bi}_2\text{La}_2\text{Ti}_3\text{O}_{12}$ composition as synthesized via solid state method from 500°C to 950°C.

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is forming due to the simultaneous growth of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and decomposition of Bi_2O_3 (we can see the diffraction peaks growing and decomposing), but it is truly unknown whether any La^{3+} was incorporated into the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ base structure. Bulk solid state synthesis of $\text{Bi}_2\text{La}_2\text{Ti}_3\text{O}_{12}$ proceeded to phase purity without complication, however, long times were required. We can speculate that La^{3+} is a slower diffusing species, and reacts more slowly.

2.5.6 $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ HTXRD Reaction Study

The attempt to synthesize $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ in the HTXRD represented the ultimate challenge in this series. In this compound, we are attempting to perform aliovalent

Table 2.VIII: Phases present in $\text{Bi}_2\text{La}_2\text{Ti}_3\text{O}_{12}$ prepared from Bi_2O_3 , La_2O_3 , and TiO_2 .

Phase		Temperature °C									
Phase	PDF	500	550	600	650	700	750	800	850	900	950
Bismite (Bi_2O_3)	41-1449	X	X	X	CNV	-	-	-	-	-	-
La_2O_3	5-602	X	X	X	D	X	X	X	X	X	X
Anatase (TiO_2)	21-1272	X	X	X	D	X	X	X	X	X	X
$\text{Bi}_{12}\text{TiO}_{20}$	34-97	-	-	-	X	X	X	X	D	-	-
$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	35-795	-	-	?	?	X	X	X	X	X	X

substitution onto the A site and B site with Sr^{2+} and Nb^{5+} respectively. Figure 2.29 shows the diffraction patterns for $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ as a function of temperature. The details of the reaction sequence are seen in Table 2.IX. Little change is observed until approximately 700°C where several intermediate phases appear, similar to what was observed in studying $\text{Bi}_2\text{La}_2\text{Ti}_3\text{O}_{12}$. The intermediate phases probably form initially at lower temperatures, but their diffraction peaks are hidden as a result of peak overlap by the other major phase diffraction peaks. The RT form of Bi_2O_3 converts to a cubic, stabilized δ Bi_2O_3 (PDF45-1344). Furthermore, BiNbO_4 (PDF16-295) and $\text{Sr}_{2.75}\text{Bi}_{6.75}\text{O}_{12.38}$ (PDF45-609) emerge as seen in Figure 2.30. It is possible that $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ forms at 700°C, but it is strongly overlapped with the SrO peak at $29.8^\circ 2\theta$. Note that $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ forms initially instead of $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$, however, it was difficult to clearly identify all phases due to the significant peak overlap in the pattern. It is possible to say this with confidence because there is enough difference between the diffraction peak locations of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ that this distinction can be made. The $\text{SrBi}_2\text{Nb}_2\text{O}_9$ phase forms at approximately 850°C. Figure 2.31 shows the $\text{SrBi}_2\text{Nb}_2\text{O}_9$ peak appearing at approximately $28.9^\circ 2\theta$ on the shoulder of a larger peak. Significant change occurs at approximately 900°C with a sharp decrease in the $\text{Sr}_{2.75}\text{Bi}_{6.75}\text{O}_{12.38}$ and the δ Bi_2O_3 peaks. At this point, the BiNbO_4 peak is the most dominant. By 950°C, as seen in Figure 2.32, the $\text{Sr}_{2.75}\text{Bi}_{6.75}\text{O}_{12.38}$ and δ Bi_2O_3 peaks are gone, and the $\text{SrBi}_2\text{Nb}_2\text{O}_9$ peak grows sharply. The TiO_2 and Nb_2O_5 phases exist until approximately 1000°C where they disappear completely. The 1000°C temperature shows the largest change in the diffraction pattern as the BiNbO_4 peaks drops sharply and the $\text{SrBi}_2\text{Nb}_2\text{O}_9$ peak becomes dominant. By 1050°C, the BiNbO_4 peak is nearly gone and a new phase $\text{Sr}_5\text{Nb}_4\text{O}_{15}$ (PDF 48-421) appears. From 1100-1200°C, only three phases

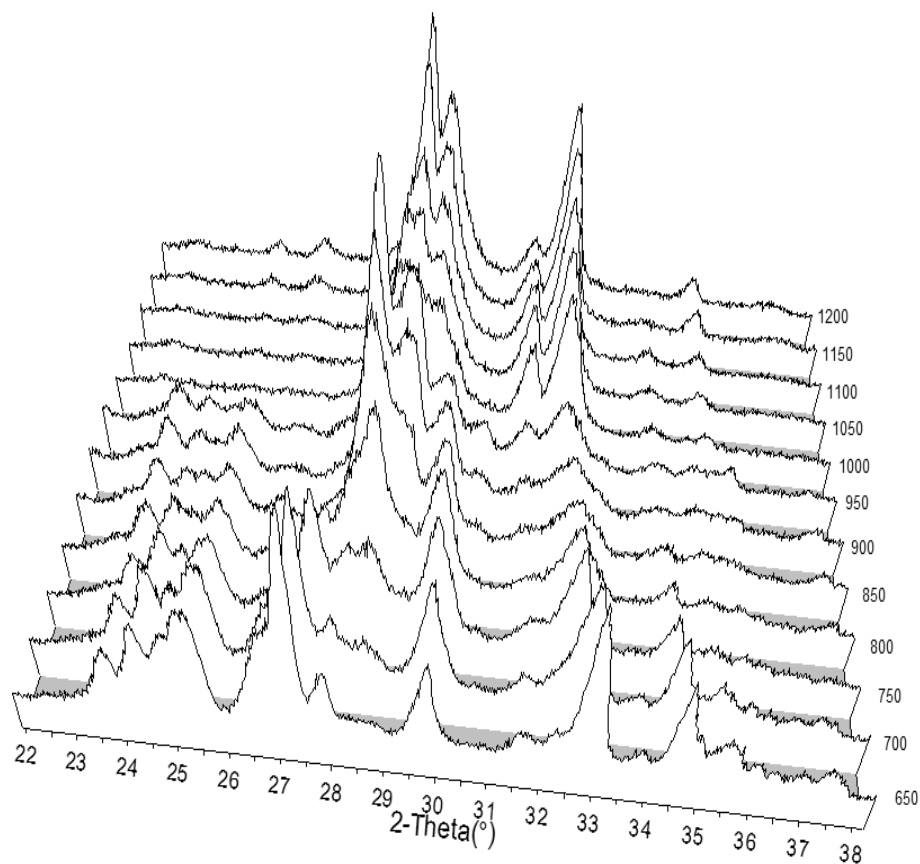


Figure 2.29: HTXRD patterns for $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ from 650°C to 1200°C . Sample heated at 5°C per minute, patterns collected every 100°C .

remain in the pattern, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $\text{SrBi}_2\text{Nb}_2\text{O}_9$, and $\text{Sr}_5\text{Nb}_4\text{O}_{15}$ as seen in Figure 2.33.

Subsequent experiments did not show different reaction sequences or any further progress toward reaction completion. At the time, it was speculated that a reason for this was that the sample was in powder form and therefore the individual grains were too far apart to actually react on a reasonable time scale. Therefore, a pressed pellet of the precursor material was created and placed on the sample holder using the temperatures and ramps as described previously. The entire series of diffraction patterns is shown in Figure 2.34. As noted, this sample does not reach reaction completion. Therefore, the pellet was held at 1100°C in the HTXRD for several hours as seen in Figure 2.35. Each diffraction scan represents one hour hold at 1100°C . No change at all is observed in the diffraction

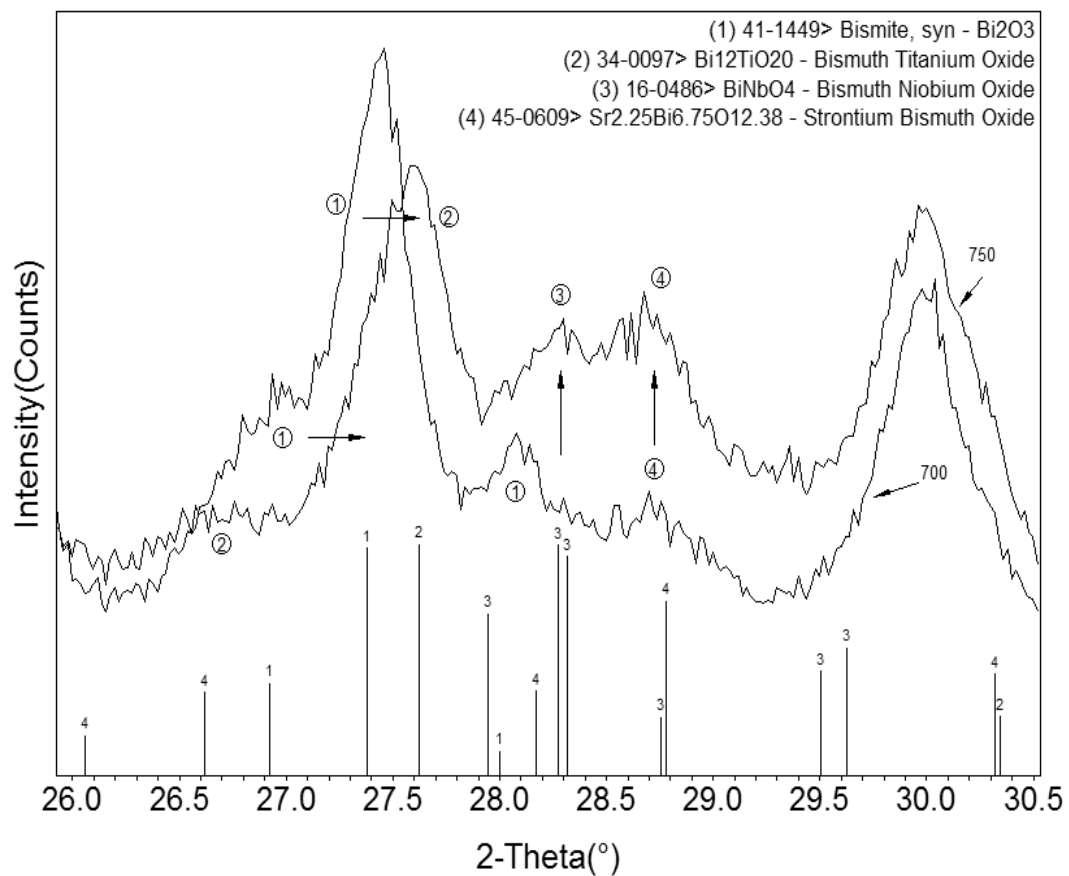


Figure 2.30: HTXRD patterns for 700°C and 750°C highlighting the intermediate phases and their locations.

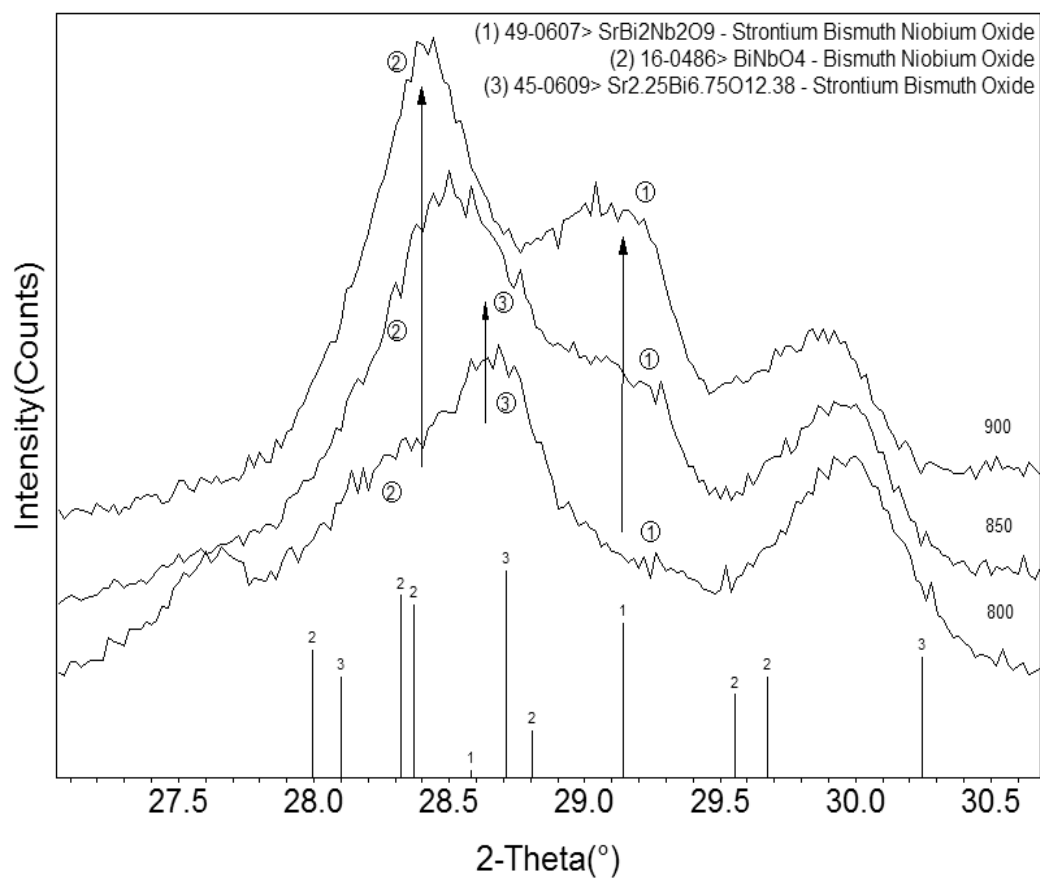


Figure 2.31: HTXRD patterns from 800°C to 900°C highlighting the intermediate phases and their locations.

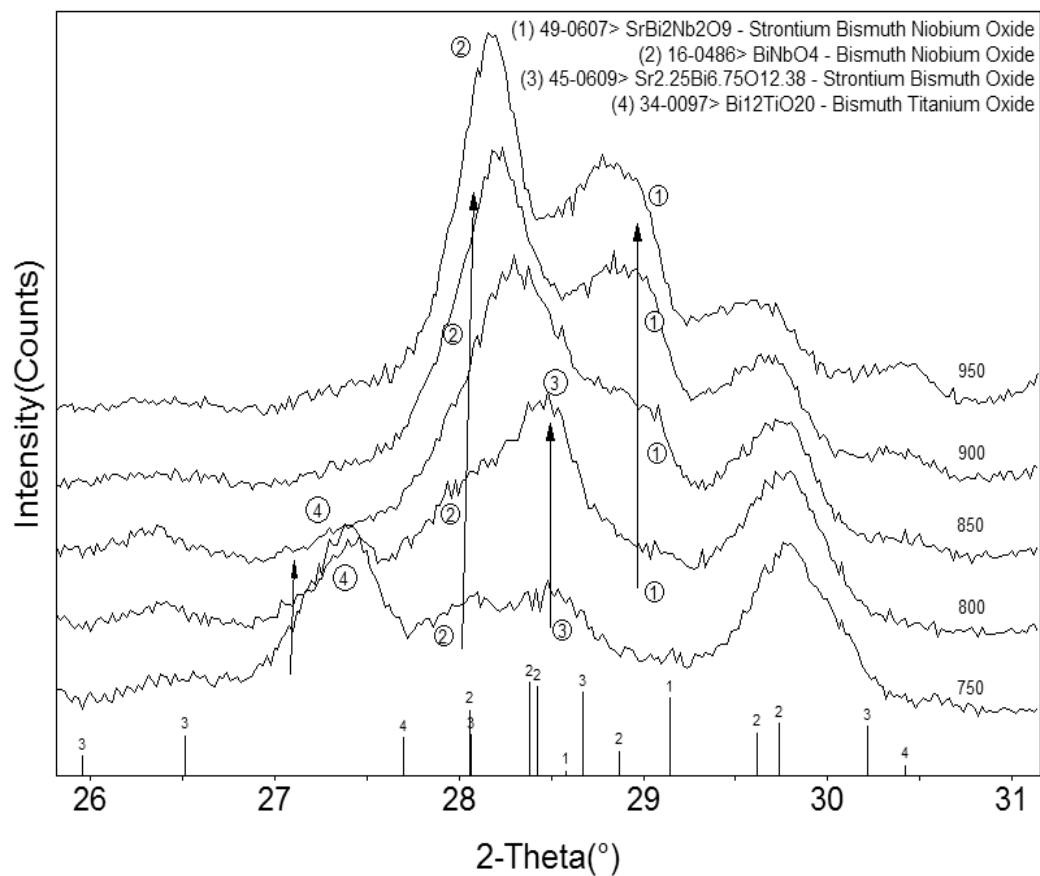


Figure 2.32: HTXRD patterns from 750°C to 950°C highlighting emergence of SrBi₂Nb₂O₉ and loss of Bi₁₂TiO₂₀ and Sr_{2.75}Bi_{6.75}O_{12.38}.

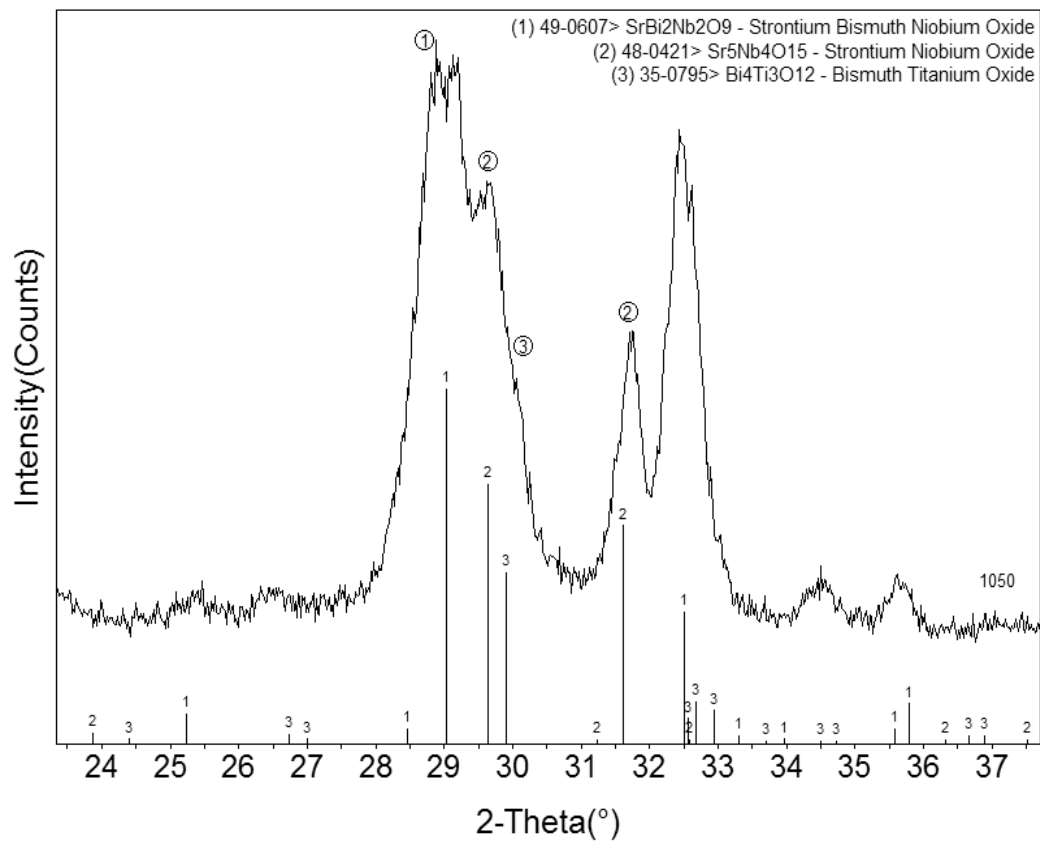


Figure 2.33: HTXRD pattern at 1050°C highlighting the three main phases; $\text{SrBi}_2\text{Nb}_2\text{O}_9$, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, and $\text{Sr}_5\text{Nb}_4\text{O}_{15}$.

Table 2.IX: Phases pres. in $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ prep. from Bi_2O_3 , SrO , Nb_2O_5 , and TiO_2 .

Phase		Temperature °C											
Phase	PDF	500	550	600	650	700	750	800	850	900	950	1000	1050
$\text{Sr}_{2.25}\text{Bi}_{6.75}\text{O}_{12.38}$	45-609	-	-	-	-	X	X	X	X	D	-	-	-
BiNbO_4	16-486	-	-	-	-	X	X	X	X	PR	PR	X	D
Bi_2O_3	45-1344	-	-	-	-	X	X	X	?	D	-	-	-
$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	35-795	-	-	-	-	?	?	?	?	?	X	X	X
$\text{SrBi}_2\text{Nb}_2\text{O}_9$	49-607	-	-	-	-	-	-	-	X	G	G	X	PR
$\text{Sr}_5\text{Nb}_4\text{O}_{15}$	48-421	-	-	-	-	-	-	-	-	-	-	-	X
Bismite (Bi_2O_3)	41-1449	X	X	X	CNV	-	-	-	-	-	-	-	-
Anatase (TiO_2)	21-1272	X	X	X	X	X	X	X	X	X	X	D	-
Nb_2O_5	37-1468	X	X	X	X	X	X	X	X	X	X	D	-
SrO	6-520	X	X	X	X	?	?	?	?	?	-	-	-

patterns. Therefore, several possibilities exist; the intermediate phases that form are nearly as stable than the desired product and require extremely long times to actually react, the intermediate phases have lower free energy than the desired phase, or a reaction zone of product material has formed around a central shell of reactant material and the entire sample must be crushed to expose fresh reactant surface. In reality, it is probably a combination of the two which occurs in this sample.

Despite the fact that complete powder synthesis was not successfully demonstrated in the HTXRD experiments, valuable processing knowledge was obtained that could be directly applied to bulk powder synthesis and these can be summarized as follows: 1. More cations bring more complex reactions, 2. Longer reaction times are required to achieve phase purity, 3. Good powder mixing is required, and furthermore, intermediate regrindings are required to expose fresh reactant.

2.6 HTXRD Polymerized Complex Method

2.6.1 $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ HTXRD Reaction Study

In a similar manner to the solid state experiments, samples were made via the polymerized complex method, then placed in the HTXRD for analysis. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ was chosen first because of its simple composition. A complete description of the polymerized complex method is shown later. Figure 2.36 shows the high temperature x-ray diffraction patterns for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ synthesized via the polymerized complex method. Table 2.X shows the phases present versus temperature. Diffraction measurements were taken at room temperature, then from 300°C to 1000°C over 100°C intervals. The room temperature pattern consists primarily of tetragonal Bi_2O_3 (PDF 27-50) and a small amount of tetrago-

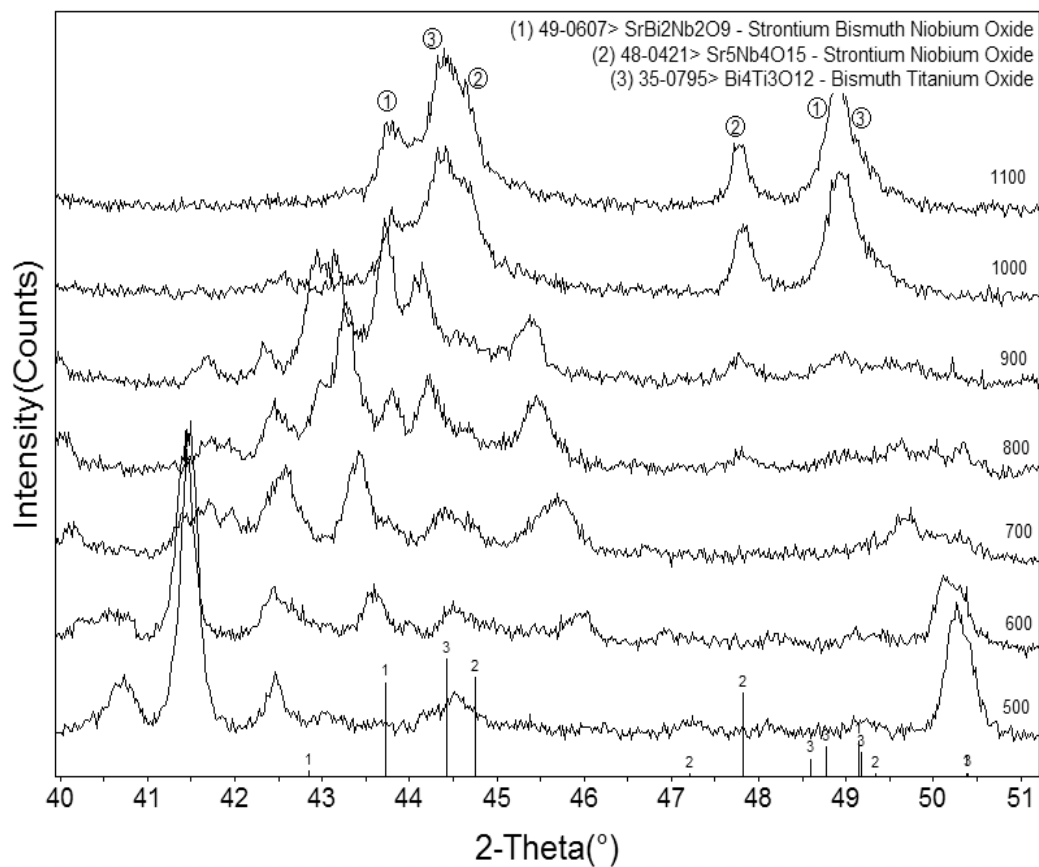


Figure 2.34: HTXRD pattern of Bi₂Sr₂Nb₂TiO₁₂ composition pellet from 500°C to 1100°C.

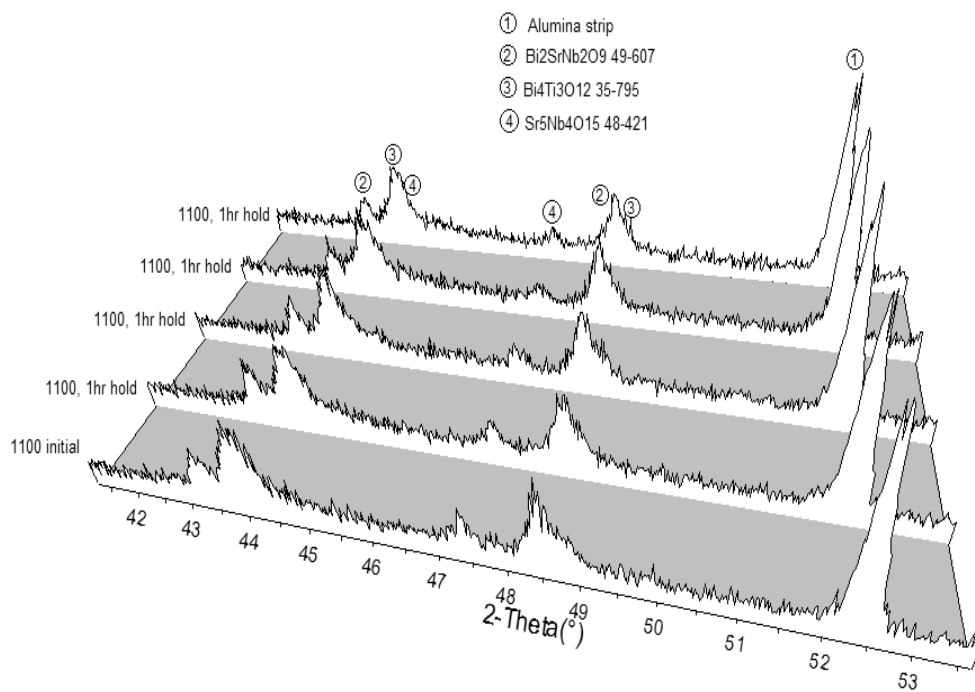


Figure 2.35: HTXRD pattern of $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ composition pellet held at 1100°C for 5 hours.

Table 2.X: Phases Present for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ synthesized via Polymerized Complex method.

Phase		Temperature °C							
Phase	PDF	300	400	500	600	700	800	900	1000
Bi_2O_3	27-50	X	DR	X	DR	-	-	-	-
$\text{Bi}_2\text{O}_{2.33}$	27-51	X	GR	X	X	-	-	-	-
$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	35-795	-	-	X	GR	X	X	X	X

nal $\text{Bi}_2\text{O}_{2.33}$ (PDF 27-51). Note that these are different Bi_2O_3 phases than what appeared in the solid state analysis. The $\text{Bi}_2\text{O}_{2.33}$ grows sharply by 400°C while the tetragonal Bi_2O_3 peak decreases in relative intensity. The $\text{Bi}_2\text{O}_{2.33}$ phase likely grows at the expense of Bi_2O_3 . By 500°C, a small broad peak appears which belongs to the Aurivillius phase, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (PDF 35-795). The $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ peak grows sharply by 600°C along with the sharp decrease in height of the tetragonal Bi_2O_3 peak. The $\text{Bi}_2\text{O}_{2.33}$ is not affected by the reaction at this temperature. By 700°C, all peaks belonging to Bi_2O_3 and $\text{Bi}_2\text{O}_{2.33}$ disappear, leaving $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ as the only phase. The titanium source peaks were not observed at any temperature. It is possible that because of the nature of the polymerized complex method that the TiO_2 crystal sizes were extremely small or amorphous, and therefore difficult to see their presence in the diffraction pattern. It is interesting to note that the reaction sequence of the polymerized complex method favors the creation of bismuth oxide prior to Aurivillius phase formation. Furthermore, the bismuth oxide phases do not persist past 700°C whereas the cubic Bi_2O_3 phase in the solid state samples persisted until after 880°C. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ peak formation was observed at slightly lower temperatures in the polymerized complex method as compared to solid state. This is quite likely due to the fact that the polymerized complex method creates extremely good mixing which will lead to faster reactions at lower temperatures.

2.6.2 $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ HTXRD Reaction Study

Figure 2.37 shows the high temperature diffraction patterns for $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ as synthesized via the polymerized complex method. This pattern shows temperatures starting from 300°C to 1200°C in 100°C intervals. The room temperature pattern (not shown) depicts three phases; bismuth metal (PDF 44-1246), tetragonal Bi_2O_3 (PDF 27-50) and

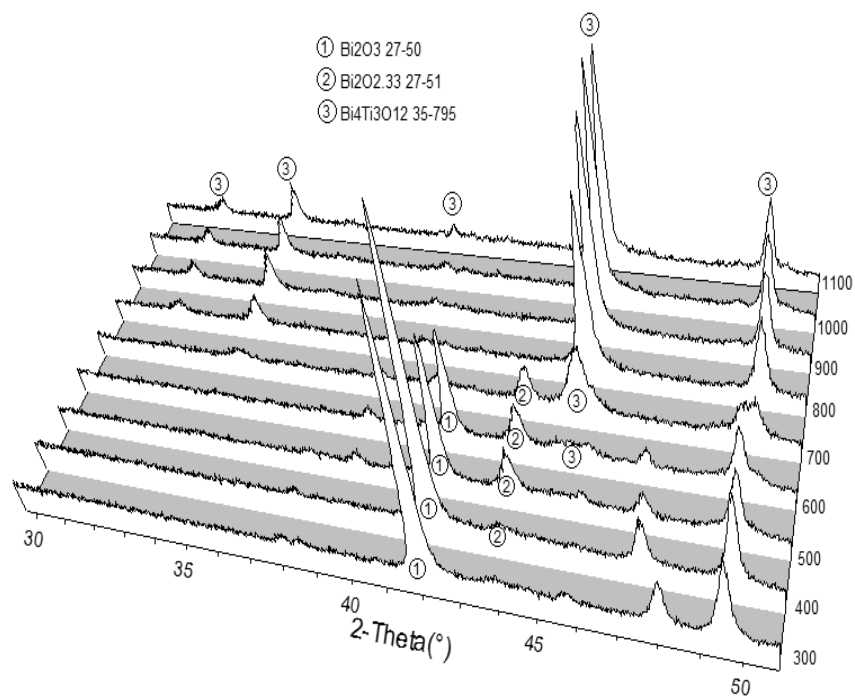


Figure 2.36: HTXRD pattern of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ as synthesized via the polymerized complex method.

Bi₂O_{2.33} (PDF 27-51). Bismuth metal disappears by 300°C accompanied by a large increase in background centered around 44°2 θ . The peak splitting at 44°2 θ in the 500°C pattern is possibly due to the formation of Bi₂Sr₂Nb₂TiO₁₂ but the resolution is extremely poor. However, by 600°C, it is clear that the Bi₂O₃-type phases have nearly disappeared and two broad peaks have replaced them which belong to Bi₂Sr₂Nb₂TiO₁₂. Relatively sharp growth of Bi₂Sr₂Nb₂TiO₁₂ is observed at the 700°C temperature. Bi₂Sr₂Nb₂TiO₁₂ continues to grow and reaches a maximum at 900°C. However, note the rather broad peak widths, even in the 1100°C measurement. One would expect that broad peaks would sharpen at higher temperatures as the grain size increases or residual strain anneals out. However, the peaks remain of similar width. Successive reheating of the same sample at 900°C for four one hour intervals did nothing to change the peak width. Figure 2.38 shows the HTXRD patterns for the sample that was reheated. Therefore, it is likely that the peak width is not the result of small crystallites, but rather of stacking faults. Similar work done in this system by Luisi showed broad peaks analogous to this work.³³

2.6.3 Polymerized Complex HTXRD Discussion

The polymerized complex sample HTXRD analysis posed several interesting problems: How does one compensate for the organic burnoff during the measurement? How does one quantify the relative rates of reaction. The use of Cr radiation resulted in peak intensities that were dramatically lower than if Cu or Co radiation were used. The use of Cu or Co radiation is recommended for future studies. While no kinetic studies were performed on the polymerized complex samples, they were observed to faster than the solid state samples. This is especially evident in the analysis of Bi₂Sr₂Nb₂TiO₁₂ where it was shown that the phase formed quickly without prior intermediates.

2.6.4 HTXRD Analysis Conclusions

The most important thing obtained from the HTXRD analysis was that we had a first glimpse into the processing direction to take with a particular material. Instead of wasting countless hours in a trial and error type synthesis attempt, we learned firsthand exactly the type of problems we would run in to when processing bulk material. Furthermore, when comparing the results between the solid state and polymerized complex methods, we confirmed that the polymerized complex method led to a faster synthesis of the desired

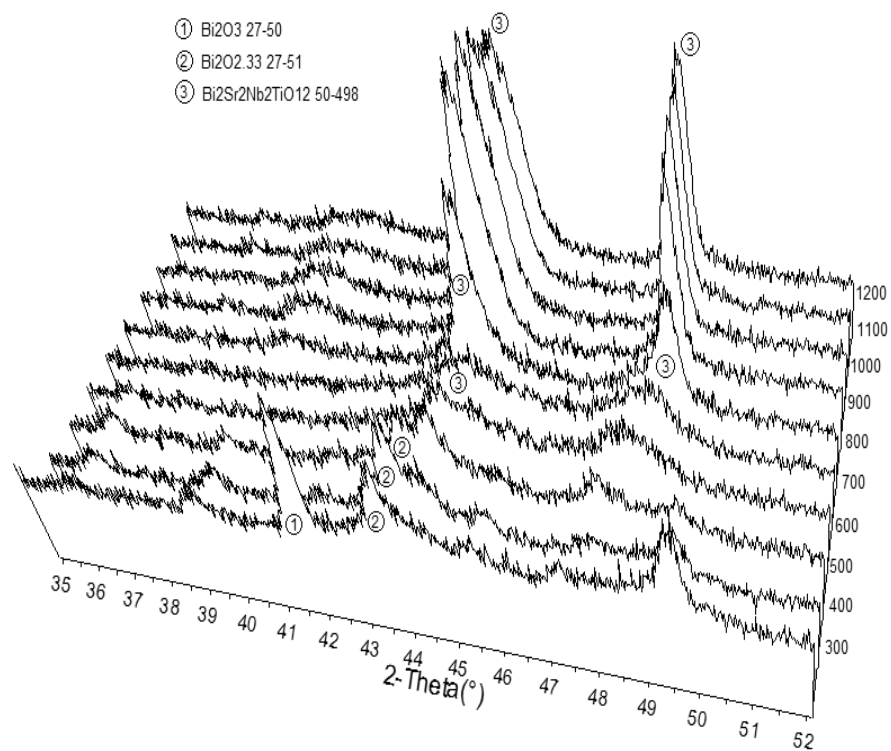


Figure 2.37: HTXRD pattern of Bi₂Sr₂Nb₂TiO₁₂ as synthesized via the polymerized complex method.

material. We also identified broadened peaks, probably due to stacking faults, which led us to avoid this method of preparation.

2.7 Bulk Powder Synthesis

Powder synthesis was accomplished via two methods as described previously, solid state synthesis, and polymerized complex method. Both methods ultimately produced phase pure powders once a suitable synthesis recipe was determined.

2.7.1 Solid State Synthesis

All solid state synthesis experiments were performed using covered MgO crucibles. MgO crucibles were used exclusively as they did not react with the precursor powders, nor would the Mg^{2+} cation be incorporated into the Aurivillius structure. Al_2O_3 and porcelain type crucibles all showed measurable reaction with the reactant powder when they were used. All reactant powders were obtained from Alfa-Aesar and were of at least 99.9% purity. The following powders: Bi_2O_3 , SrCO_3 , BaCO_3 , CaCO_3 , La_2O_3 , TiO_2 , Nb_2O_5 , Al_2O_3 , Ga_2O_3 were weighed on a Metler-Toledo balance in stoichiometric proportions. The powders were ground in acetone using a diamonite mortar and pestle until a homogeneous slurry was obtained. Ball milling was not used due to the likelihood of contamination from the milling media.

Initial solid state synthesis attempts were performed using only powder based samples. In other words, once the reactant powders were suitably mixed, the precursor powder mass was simply placed inside a crucible, and the sample heated to the desired temperature. This method had only minor success. It was later learned that it did not provide for the necessary close contact of the reactant powders required for reaction, nor did it account for the volatility of Bi_2O_3 . Furthermore, initial experiments involved heating the samples directly to high temperatures instead of pre-reacting the samples at a lower temperature. It was later determined that initial heating to a lower temperature, preferably below the melting temperature of Bi_2O_3 , helped prevent the volatilization and melting of this powder.

Powder samples that were pressed into pellets were found to react faster and achieved phase purity with greater success. However, these samples always displayed some type of secondary phases in addition to the desired Aurivillius phases. The volatility of Bi_2O_3

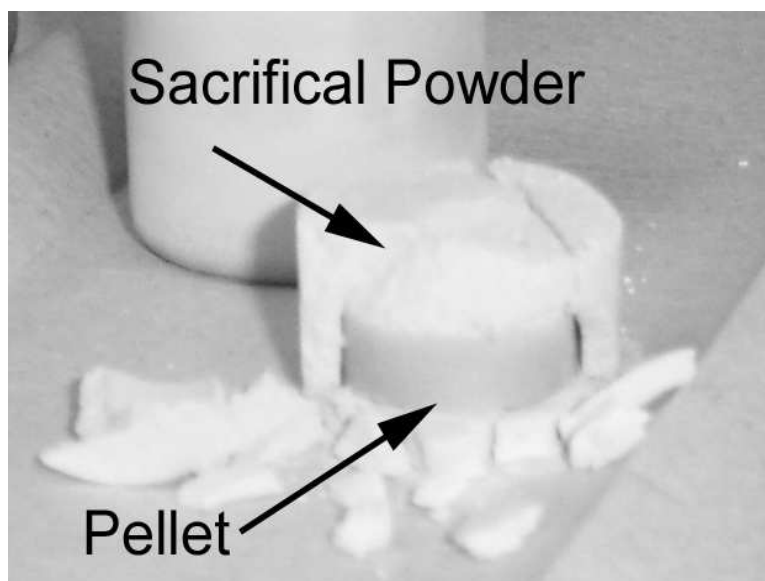


Figure 2.39: Schematic of a pellet inside a powder bed.

was not being taken into account even in pellet form. As the pellet reacted at high temperatures, a small amount of Bi_2O_3 evaporated from the pellet surface and left a thin surface layer of Bi_2O_3 depleted material. Often, the quantity of this second phase was not great enough to be visible in the diffraction pattern. Ultimately, the most reliable solid state synthesis method was found to be in both pressing a pellet of the material followed by surrounding the pellet in a bed of sacrificial powder, then placing both pellet and powder inside a covered Mgo crucible. In other words, the pellet was literally buried inside a powder mound of the same material. Figure 2.39 shows a photograph of the pellet inside a powder bed. The Bi_2O_3 in the sacrificial powder would evaporate at elevated temperatures and provide a bismuth rich atmosphere surrounding the pellet thus raising the bismuth vapor pressure and minimizing any bismuth loss from the pellet. This method produced the most reliable, reproducible results, however, it did require large amounts of powder.

It was determined that the length of time in the furnace was not a critical step, but rather the number of times the sample was ground. Grinding the reactant pellet into a powder was mandatory in order to expose fresh reactant surface. Figure 2.40 shows a set of experiments performed on a single sample. The sample was pressed into a pellet and fired four times with intermittent regrindings. Only after over 100 hours of furnace time

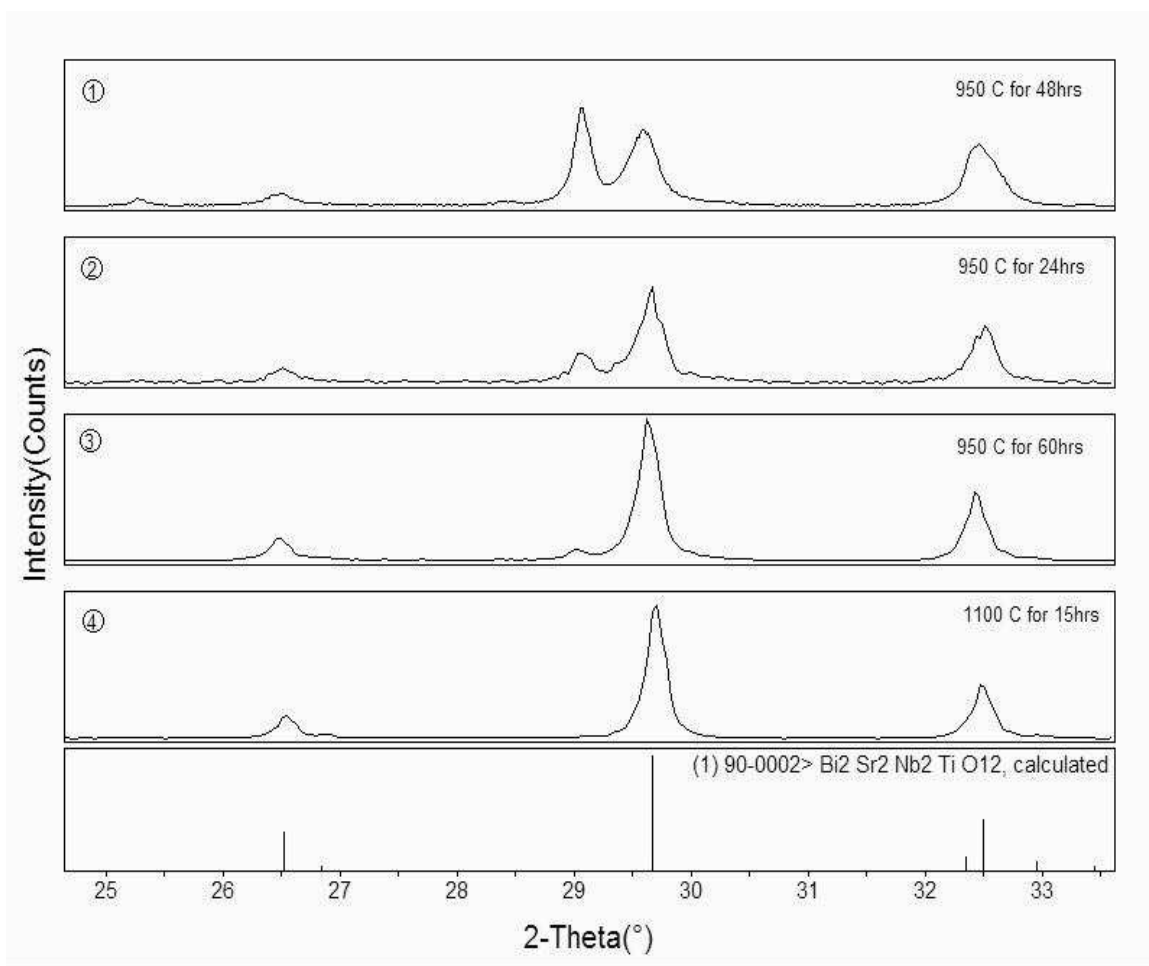


Figure 2.40: X-ray diffraction patterns taken for a sample of $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ that had been heated four times for multiple hours with intermittent regrinding.

did the sample reach phase purity.

2.7.2 Samples Generated

A wide range of three layer Aurivillius phase samples were attempted for synthesis via the solid state method described previously. Table 2.XI summarizes the compositions attempted and the success of the attempt. The reason some samples were investigated will be described in chapters 3 and 4. Solid solubility limits were investigated for most samples.

Table 2.XI: Compositions Generated via Solid State Synthesis.

Composition	Phase Pure ?
$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	Yes
$\text{Bi}_{3.95}\text{Ca}_{0.05}\text{Ti}_3\text{O}_{12-x}$	Yes
$\text{Bi}_{3.9}\text{Ca}_{0.1}\text{Ti}_3\text{O}_{12-x}$	No
$\text{Bi}_{3.85}\text{Ca}_{0.15}\text{Ti}_3\text{O}_{12-x}$	No
$\text{Bi}_{3.8}\text{Ca}_{0.2}\text{Ti}_3\text{O}_{12-x}$	No
$\text{Bi}_{3.75}\text{Ca}_{0.25}\text{Ti}_3\text{O}_{12-x}$	No
$\text{Bi}_{3.95}\text{Sr}_{0.05}\text{Ti}_3\text{O}_{12-x}$	Yes
$\text{Bi}_{3.9}\text{Sr}_{0.1}\text{Ti}_3\text{O}_{12-x}$	No
$\text{Bi}_{3.95}\text{Ba}_{0.05}\text{Ti}_3\text{O}_{12-x}$	Yes
$\text{Bi}_{3.95}\text{Pb}_{0.05}\text{Ti}_3\text{O}_{12-x}$	No
$\text{Bi}_2\text{La}_2\text{Ti}_3\text{O}_{12}$	Yes
$\text{Bi}_2\text{LaSrTi}_3\text{O}_{12-x}$	No
$\text{Bi}_2\text{La}_2\text{Ti}_2\text{GaO}_{12-x}$	No
$\text{Bi}_2\text{Ca}_2\text{Nb}_2\text{TiO}_{12}$	No
$\text{Bi}_2\text{SrCaNb}_2\text{TiO}_{12}$	Yes
$\text{Bi}_2\text{Sr}_{1.5}\text{Ca}_{0.5}\text{Nb}_2\text{TiO}_{12}$	Yes
$\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$	Yes
$\text{Bi}_2\text{Sr}_{1.5}\text{Ba}_{0.5}\text{Nb}_2\text{TiO}_{12}$	Yes
$\text{Bi}_2\text{SrBaNb}_2\text{TiO}_{12}$	Yes
$\text{Bi}_2\text{Ba}_2\text{Nb}_2\text{TiO}_{12}$	No
$\text{Bi}_2\text{Sr}_2\text{Ta}_2\text{TiO}_{12}$	Yes
$\text{Bi}_2\text{Ca}_2\text{Ta}_2\text{TiO}_{12}$	No
$\text{Bi}_2\text{Ba}_2\text{Ta}_2\text{TiO}_{12}$	No
$\text{Bi}_2\text{Sr}_2\text{Ti}_2\text{NbO}_{12-x}$	No
$\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{GaO}_{12-x}$	No
$\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{AlO}_{12-x}$	No
$\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{Al}_{0.5}\text{Ti}_{0.5}\text{O}_{12-x}$	No
$\text{Bi}_2\text{Sr}_{1.5}\text{Ca}_{0.5}\text{Nb}_2\text{Al}_{0.5}\text{Ti}_{0.5}\text{O}_{12-x}$	No
$\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{Al}_{0.25}\text{Ti}_{0.75}\text{O}_{12-x}$	No
$\text{Bi}_2\text{Sr}_{1.5}\text{Ca}_{0.5}\text{Nb}_2\text{Al}_{0.25}\text{Ti}_{0.75}\text{O}_{12-x}$	No
$\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{Al}_{0.05}\text{Ti}_{0.95}\text{O}_{12-x}$	Maybe
$\text{Bi}_2\text{Sr}_{1.5}\text{Ca}_{0.5}\text{Nb}_2\text{Al}_{0.05}\text{Ti}_{0.95}\text{O}_{12-x}$	Maybe
$\text{Bi}_{1.85}\text{Sr}_{2.15}\text{Nb}_2\text{TiO}_{12-x}$	No
$\text{Bi}_{1.9}\text{Sr}_{2.1}\text{Nb}_2\text{TiO}_{12-x}$	No
$\text{Bi}_{1.95}\text{Sr}_{2.05}\text{Nb}_2\text{TiO}_{12-x}$	Yes
$\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_2\text{TiO}_{12-x}$	Yes
$\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ca}_{0.525}\text{Nb}_2\text{TiO}_{12-x}$	Yes
$\text{Bi}_{1.975}\text{Sr}_{1.75}\text{Ca}_{0.275}\text{Nb}_2\text{TiO}_{12-x}$	Yes
$\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ba}_{0.525}\text{Nb}_2\text{TiO}_{12-x}$	Yes
$\text{Bi}_2\text{Sr}_2\text{Nb}_{1.9}\text{Ti}_{1.1}\text{O}_{12-x}$	No
$\text{Bi}_2\text{Sr}_2\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{12-x}$	Yes
$\text{Bi}_2\text{Sr}_{1.5}\text{Ca}_{0.5}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{12-x}$	Yes
$\text{Bi}_2\text{Sr}_{1.5}\text{Ba}_{0.5}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{12-x}$	Yes
$\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{12-x}$	Yes
$\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ca}_{0.525}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{12-x}$	Yes
$\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ba}_{0.525}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{12-x}$	Yes

2.7.3 Polymerized Complex Method

Despite the success of the solid state method in producing phase pure samples, it was extremely time consuming and labor intensive. It could take up to two weeks to produce a single 10 gram powder sample. Even then, there was still the chance, after even 100 hours of furnace time, that the sample would not be phase pure. Thus, it was desired to find another method which could reliably produce samples in less time with less work. The polymerized complex method was investigated because it had the potential to produce phase pure samples at temperatures as low as 700°C in as little as an hour of furnace time.³⁴ If the method was done correctly, the atomistic mixing would virtually eliminate the chance for stable intermediates.

Several excellent synthesis articles existed in literature describing the polymerized complex method.^{12–17,19,34–37} Most articles list some type of flowchart detailing the ingredients, and when in the process those components are to be mixed. However, a frustrating aspect of these articles was that most of the processing steps were all simply slight modifications of a single recipe and no real scientific reason was given for a specific processing additive or molar ratio, etc. There was no other literature to fall back on when something in the process went wrong or when a question came up on whether something would adversely affect the reaction. In fact, it is surprising how little scientific explanation is given in the initial patent.⁹

One thing above all was generally ignored in the polymerized complex literature, the degree of dissociation of the chelating agent. Citric acid is the most commonly used chelating agent for this process. Polyacrylic acid has also been used, but any other carboxylic acid would work. Only a small percentage of dissociation is realized when actually dissolving the citric acid in water. As a result, one must add considerably more citric acid into the batch to allow for complete chelation of the constituent cations. The molar ratio of citric acid to ethylene glycol was also rarely discussed in literature. However, according to leChatlier's principle, an excess of one component would cause the reaction to be driven to completion and thus the reason for the excess of ethylene glycol. Varying the ratio of citric acid to ethylene glycol (CA:EG) drastically affected the outcome of the reaction, i.e., the solution would foam with some CA:EG ratios and would form a dense resin with others.

Initial experiments were conducted without the knowledge of the dissociation problem of citric acid and as a result, incomplete chelation almost always led to the formation of a precipitate prior to polymerization. The final recipe for sample synthesis using the polymerized complex method took some time to figure out and is described below.

The following chemicals were used when applicable: Bi_2O_3 , $\text{Sr}(\text{NO}_3)_2$, CaCO_3 , BaCO_3 , SrCO_3 , titanium butoxide, and NbCl_5 using the following general procedure. All laboratory ware used in these experiments were first cleaned with Alconox, then rinsed with acetone and allowed to dry. Deionized water was used exclusively. Bi_2O_3 (and) $\text{Sr}(\text{NO}_3)_2$ were dissolved in an aqueous solution of HNO_3 or HCl until a clear solution was obtained. Once dissolved, the appropriate amount of citric acid (anhydrous) was added and dissolved. Dissolution was aided via stirring using a magnetic stir bar while heating to about (80°C) . A thermometer was placed inside the main beaker and held in place using a stand and clamps. The bottom of the thermometer touched the bottom of the beaker. Then, titanium butoxide was separately dissolved in a small quantity of ethylene glycol. Titanium butoxide had to be added in this fashion, otherwise a precipitation reaction would occur when it was placed in contact with water. Finally, the titanium butoxide/ethylene glycol mixture was added drop-wise to the Bi_2O_3 - $\text{Sr}(\text{NO}_3)_2$ - H_2O - HNO_3 (or HCl) solution until a clear solution of approximately 40-50 ml total volume was obtained. The titanium butoxide-ethylene glycol beaker was rinsed with ethylene glycol, and the rinsate was added to the total solution. When using NbCl_5 , the powder had to be dissolved separately in HCl in order to prevent reaction. NbCl_5 has been shown to form a gel and it did so on several occasions in this system. The Nb-HCl solution was then added dropwise to the entire solution. The Nb-HCl beaker was rinsed with HCl and the rinsate poured into the total solution. Nonetheless, once complete dissolution was obtained in all systems, the solution was placed in a 50 ml Pyrex beaker, heated under constant stirring on a hot plate to 80°C for approximately 3 hours or enough time to evaporate the extra water added to the solution. Once evaporation stopped, the temperature was slowly increased to approximately 130°C to initiate the reaction. Above 130°C , an esterification reaction occurs between the citric acid and the ethylene glycol, ultimately yielding a hard, transparent solid polymer. The length of time required for complete reaction depended on how much water was used in the initial solution. Therefore, minimization of water content will decrease the time required. Generally, once the water “left” the system, approximately 3-5 hours were necessary for

complete formation of the polymer. (Originally HNO_3 was used to dissolve Bi_2O_3 , and a strong exothermic reaction would occur simultaneously with the exit of the water yielding an unknown precipitate. This reaction did not occur when HCl was used.) Initially, the solution was clear, but gradually took on a yellowish, then tan, then brown color. The point at which most of the added water had left the system, the solution started to become viscous and foamed slightly. Much care was provided to control the temperature of the solution over the experiment because often, when the water had left the system, the temperature would spike up and it was possible to decompose the solution. It was difficult to accurately set the temperature on the laboratory hotplate, even with the use of a thermometer. At a certain point in the reaction, the entire beaker of solution would foam. At this point, the beaker was removed from the hot plate and placed in a drying oven which was preheated to 130°C , and the sample was left there often up to 24 hours in order to fully complete the reaction. It was important not to force the reaction to completion by heating but rather let it finish on its own time. If the temperature was increased too quickly, the resin would often burn. After this period, the sample was a hard, dense, brown, yet transparent resin. The beaker was placed in a furnace and the temperature slowly increased to 350°C for several hours in order to ash the sample. Often it was necessary to flow air into the furnace to fully oxidize the sample as the organic burnoff was highly reducing. The residual shiny black foam was easily ground into a powder. It should be noted that this powder was not completely free from the polymer at this point. Complete decomposition does not occur until approximately 500°C .

None of the experiments conducted using the polymerized complex method yielded completely amorphous materials. Instead, the bismuth chelate reduced to bismuth metal during the ashing process. Figure 2.41 shows a diffraction pattern taken from a material ashed at 350°C for several hours. Note the semi amorphous hump and the sharp peaks belonging to bismuth metal. Forcing oxygen gas into the ashing furnace did not alter the reduction process, rather it sped up the ashing process. The final carbon free material was a light, fluffy, white or yellow powder, resembling snowflakes. The powder did not pack well, even when pressed using a die. Figure 2.42 shows HTXRD diffraction patterns of $\text{Bi}_2\text{SrCaNb}_2\text{TiO}_{12}$ from 350°C to 900°C . Note the semi amorphous starting material with the bismuth metal peaks and the relatively quick evolution to the three layer Aurivillius phase. When performed extremely carefully, the polymerized complex method usually

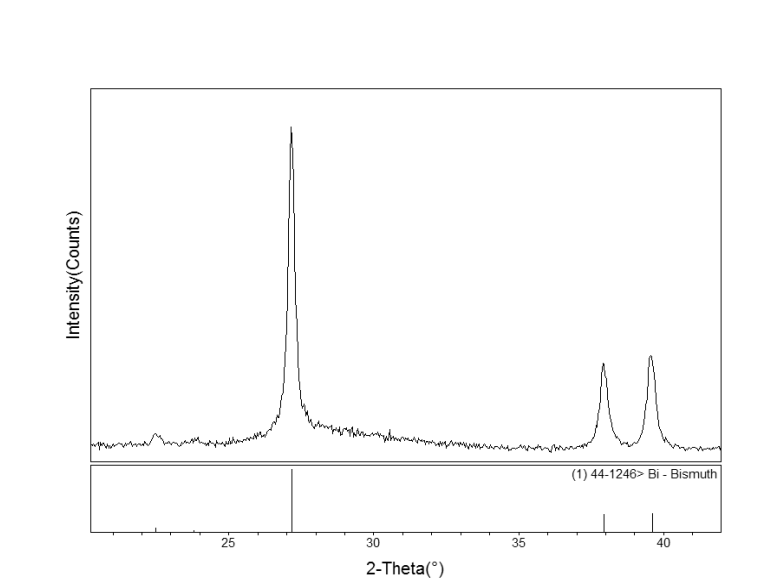


Figure 2.41: X-ray diffraction pattern for a polymerized complex sample that had been ashed at 350°C. Note the presence of bismuth metal.

produced very pure materials at temperatures as low as 700°C after only a few hour heat treatment. Figure 2.42 represents the exception to the rule of how the polymerized complex method worked for this thesis. However, as Figure 2.38 showed previously, in some cases, extremely broad diffraction peaks would occur for some peaks. The broad peaks did not sharpen during additional heat treatments and were thus an indication that stacking faults may have been occurring during structural formation. High resolution transmission electron microscopy (HRTEM) would be ideal for obtaining lattice fringe images and possibly highlighting the speculated stacking faults, however, no HRTEM was available. In the end, the polymerized complex method was passed up in favor of the ultimately more reliable, but more laborious solid state synthesis.

A modification to the polymerized complex method was employed in order to obtain greater chelation and possibly lead to increased phase purity. This involved raising the pH of the solution in order to force further dissociation of the citric acid.¹⁶ This would allow significantly less citric acid to be required but still provide the same degree of chelation. The pH of the solution was raised to three different levels, 3, 6, and 9 with the use of ammonium hydroxide. A Fisher Accumet pH meter calibrated using buffer solutions was used to monitor the pH. Complete dissolution of the ammonium hydroxide was observed

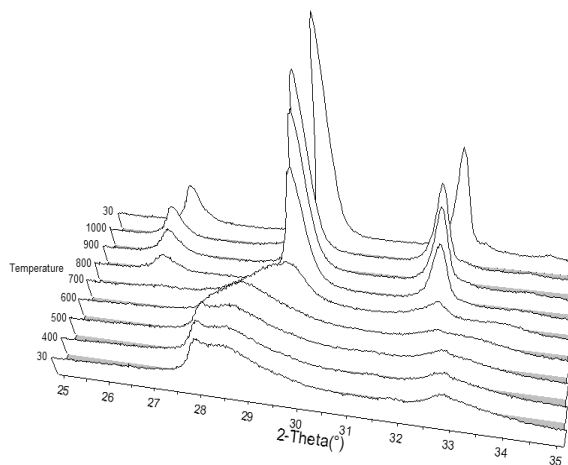


Figure 2.42: HTXRD patterns for a sample of $\text{Bi}_2\text{Sr}_{1.5}\text{Ca}_{0.5}\text{Nb}_2\text{TiO}_{12}$ synthesized via the polymerized complex method.

at all pH levels. The solution remained clear and colorless at temperatures and times where the unmodified solutions would have changed color to tan or brown. However, at a certain point, all of the pH modified samples began to precipitate a black substance until ultimately, the entire sample was a black gelatinous mass. Analysis of the black compound revealed that an amide had formed instead of the polyester. It was shown with IR spectra that ammoniolysis had occurred where the nitrogen from the ammonium hydroxide reacted with the carboxylic acid to form the amide.³³ The amide based samples were ashed in a manner similar to the unmodified samples. Completely ashed samples were extremely unhomogeneous and contained yellow, white and grey clumps of powder. The pH modification was attempted with pharmaceutical grade hydrogen peroxide, but the concentration was quite low as it was highly diluted with water. Other bases were not attempted, such as NaOH or KOH as the alkali earth elements have been shown to be easily incorporated into the Aurivillius structure.³⁸

There are a few things that we can speculate to be the cause of the problems in the polymerized complex method. One of which is surely the large number of precursor powders requiring dissolution. It was quite likely that part of the powders weighed out never actually made it into solution. Secondly, there was no way to monitor cations that may

have escaped during evaporation or during the ashing process. In fact, subsequent infrared spectroscopy experiments of ash residue found outside the ashing furnace revealed salts containing Sr^{2+} and Bi^{3+} . Thirdly, solid and liquid precursor powders were used. There was no solid titanium source available, and therefore some discrepancy between weighing powder masses and measuring liquid volumes may have occurred. Fourthly, the niobium source, NbCl_5 is highly reactive in ambient atmosphere and is quick to form niobium oxalates on the benchtop. All work in dissolution of NbCl_5 had to be performed in a glovebox under argon atmosphere. Lastly, even if the NbCl_5 was successfully dissolved, it had to be immediately poured into the total solution, otherwise a gelation would occur thus necessitating scrapping the mixture and repeating the dissolution. The HCl source is partly to blame for this as it did contain some water. However, higher molarity HCl is extremely dangerous, and thus it was worth taking the risk of gelation.

Samples Generated

A wide range of three layer Aurivillius phase samples were attempted for synthesis via the polymerized complex method illustrated previously. Table 2.XII shows the entire list of compositions attempted and the success of the attempt. None of the polymerized complex samples were ultimately used for later experiments due to the great deal of difficulty in obtaining reproducible samples.

Table 2.XII: Compositions Generated via the Polymerized Complex Method.

Composition	Phase Pure ?
$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	Yes
$\text{Bi}_3\text{CaTi}_3\text{O}_{12-x}$	No
$\text{Bi}_3\text{SrTi}_3\text{O}_{12-x}$	No
$\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{GaO}_{12-x}$	No
$\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{AlO}_{12-x}$	No
$\text{Bi}_2\text{Ca}_2\text{Nb}_2\text{TiO}_{12}$	No
$\text{Bi}_2\text{Ca}_{1.875}\text{Sr}_{0.125}\text{Nb}_2\text{TiO}_{12}$	Yes
$\text{Bi}_2\text{Ca}_{1.75}\text{Sr}_{0.25}\text{Nb}_2\text{TiO}_{12}$	Yes
$\text{Bi}_2\text{Ca}_{1.5}\text{Sr}_{0.5}\text{Nb}_2\text{TiO}_{12}$	Yes
$\text{Bi}_2\text{SrCaNb}_2\text{TiO}_{12}$	Yes
$\text{Bi}_2\text{Sr}_{1.5}\text{Ca}_{0.5}\text{Nb}_2\text{TiO}_{12}$	Yes
$\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$	Yes
$\text{Bi}_2\text{Sr}_{1.5}\text{Ba}_{0.5}\text{Nb}_2\text{TiO}_{12}$	Yes
$\text{Bi}_2\text{Sr}_{1.25}\text{Ba}_{0.75}\text{Nb}_2\text{TiO}_{12}$	No
$\text{Bi}_2\text{SrBaNb}_2\text{TiO}_{12}$	Yes
$\text{Bi}_2\text{Ba}_{1.5}\text{Sr}_{0.5}\text{Nb}_2\text{TiO}_{12}$	No
$\text{Bi}_2\text{Ba}_2\text{Nb}_2\text{TiO}_{12}$	No

Chapter 3

Characterization of $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$

Note, this chapter was originally written as a paper submitted to the Journal of Solid State Chemistry and is in the final revisions. Some parts of the paper have been modified to fit better in this thesis.

3.1 Introduction

Aurivillius ceramics have been shown to be excellent ferroelectrics and modest oxide conductors and a number of crystal structure models exist for these phases.^{4,38–42} An interesting feature of the Aurivillius structure is that it has the potential to display cation site mixing. Site mixing occurs when a cation from one crystallographically distinct site occupies another site in a static disorder. Site mixing is not uncommon in layered type materials and has been observed in alloys, pyrochlores, double-perovskites, and spinel type structures.^{43–47} Until recently (about 1997), most models of the Aurivillius structure did not include the site mixing parameter. Site mixing in the Aurivillius structure was initially discovered by Blake *et al.* for the two-layer ($n=2$) phases and later by Hervoches *et al.* in the three-layer ($n=3$) phases.^{48,49} In the Aurivillius structures, early theory suggested that only another cation with lone pair electrons such as Pb^{2+} could substitute for Bi^{3+} .⁵⁰ However, it was later determined that other cations lacking the lone pair such as the alkaline earths Sr^{2+} , Ba^{2+} , and Ca^{2+} , could occupy the Bi site.⁴⁸

Blake *et al.* used Rietveld refinements to show that in the two-layer Aurivillius structure $\text{BaBi}_2\text{Nb}_2\text{O}_9$, the Bi and A sites were of mixed occupancy.⁴⁸ Their Rietveld refinements converged to lower least squares residuals and chi squared values upon allowing this static

disorder to occur. Furthermore, they observed that the degree of static disorder increased as the size of the substituted A site cation increased from Ca^{2+} to Sr^{2+} to Ba^{2+} . Macquart *et al.* performed analogous work to Blake *et al.* in the $\text{ABi}_2\text{Ta}_2\text{O}_9$ system with similar results.⁵¹ Since the work of Blake *et al.* site mixing has been observed in the two, three, and four-layer Aurivillius systems.^{48,49,52,53}

It is important to ask why the static disorder occurs. Structural stability in the Aurivillius system is governed in large part by the lattice strain, therefore, static disorder is expected to play a role in mediating the stability. It is well known that perovskite-based structures are guided by geometric tolerance factors such as those developed by Goldschmidt which dictate radius ratio based regions of structural stability.⁵⁴ Tolerance factors were first used by Subbarao somewhat unsuccessfully to describe Aurivillius ceramics.⁴ Only a portion of the samples predicted to be stable by the tolerance factors actually formed. Suarez *et al.* were able to correlate tolerance factor with the paraelectric to ferroelectric phase transition but did not discuss structural stability.⁵⁵ A special set of tolerance factors specific to the Aurivillius structure were developed by Speakman which could predict with reasonable accuracy, structural stability in three-layer Aurivillius ceramics.⁵⁶ Armstrong *et al.* was the first to realize that the stable Aurivillius structure contains lattice strain particularly between the $(\text{Bi}_2\text{O}_2)^{2+}$ sheets and the perovskite blocks.³ Furthermore, they developed an empirical equation using the perovskite block cations to describe an ideal a lattice parameter. Equation 3.1 shows the Armstrong equation.

$$a = 1.33r_{\text{oct}} + 0.60r_{\text{A site}} + 2.36(\text{\AA}) \quad (3.1)$$

where a equals idealized a lattice parameter, r_{oct} is the octahedral site cation radius, and $r_{\text{A site}}$ is the A site cation radius. They reasoned that the $(\text{Bi}_2\text{O}_2)^{2+}$ layer in the ideal Aurivillius structure should have an a lattice parameter of $3.80\text{\AA}$ since the $(\text{Bi}_2\text{O}_2)^{2+}$ layer; similar to the fluorite type structure of PbO , is about 20% smaller than that of PbO . Applying the Armstrong equation to $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ using Shannon's ionic radii for 6 coordinated Ti^{4+} and 12 coordinated Sr^{2+} yields an ideal a lattice parameter of $4.06\text{\AA}$.⁵⁷ The actual a lattice parameter of $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ is $3.89\text{\AA}$, therefore some structural compromise has been made between the two competing layers. If a static disorder was introduced between the Bi and A sites, this could alter the $3.80\text{\AA}$ constraint and therefore explain the

compromised observed lattice parameter.

Blake *et al.* gave evidence in the form of bond valence sum (BVS) calculations to explain the static disorder.⁴⁸ They stated that the driving force behind the disorder was the overbonding of the Aurivillius A site. Since the ideal A site valence is two, a BVS greater than the formal cation valence indicates an overbonded condition where the bonds are in compression. BVS values less than the ideal value indicate bond tension or underbonding. They noticed that as the A site becomes overbonded by the larger alkaline earth, Bi^{3+} would occupy the A site to alleviate the overbonding. In other words, the static disorder occurred to relieve lattice strain. Analysis of the BVS studies pertaining to Aurivillius ceramics reveals two types of structures; those with underbonded A sites and those with overbonded A sites.^{18,48,49,51,52,58–62}

The structures with underbonded A sites generally resemble the prototype Aurivillius structures such as $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $\text{Bi}_3\text{TiNbO}_9$, and Bi_2WO_6 where alkaline earths have not been substituted for Bi^{3+} . While the ideal Aurivillius symmetry is tetragonal, the prototype structures are either orthorhombic or monoclinic. These structures appear to relieve the underbonding by structural distortions, such as octahedral tilting, octahedral rotation and atomic displacements, but not by site mixing. Withers *et al.* predicted that the reason for the structural distortions in the prototype structures was the large underbonding of the Bi^{3+} in the Aurivillius A site.⁶¹ A very interesting study by Lightfoot *et al.* analyzed $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ via high temperature neutron powder diffraction and validated the predictions made by Withers *et al.*⁶⁰ Rietveld refinements of the high temperature diffraction data indicated that on heating the structure transformed from orthorhombic to tetragonal symmetry. Furthermore, it was observed that the A site BVS decreased from a neutral valence of 3 in the orthorhombic symmetry to a strongly underbonded 2.22 (compared to 3) in the tetragonal symmetry.

The structures with overbonded A sites were those where an alkaline earth had been substituted for Bi^{3+} on the A site. $\text{SrBi}_2\text{Nb}_2\text{O}_9$ and $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ are two examples. Structures with overbonded A sites appear to relieve lattice strain predominantly by static disorder but can also display structural distortions. For example, $\text{SrBi}_2\text{Nb}_2\text{O}_9$ and $\text{CaBi}_2\text{Nb}_2\text{O}_9$ are orthorhombic while $\text{BaBi}_2\text{Nb}_2\text{O}_9$ has tetragonal symmetry.

While the effects of site mixing and lattice strain have been extensively studied in the two-layer Aurivillius analogues, only a few reports exist for the three-layer materials.

Therefore, the effects of systematic alkaline earth substitution of Ca^{2+} , or Ba^{2+} for Sr^{2+} in the base $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ composition were studied. Crystal structure refinements, site mixing effects, bond valence sum calculations were performed on the synthesized compounds via Rietveld refinements of combined x-ray and neutron powder diffraction.

3.2 Experimental Procedure

3.2.1 Powder Synthesis

Powder samples were made using solid state synthesis. A 30g batch was prepared for each compound. The initial powder reactants Bi_2O_3 99.99% (Alfa), SrCO_3 99.99% (Alfa), CaCO_3 99.99% (Alfa), BaCO_3 99.75% (Alfa), Nb_2O_5 99.99% (Alfa), and TiO_2 99.9% (Alfa) were weighed on a Metler-Toledo balance in stoichiometric proportions. The powders were ground in acetone using a diamonite mortar until a homogeneous slurry was obtained. The dried slurry was placed in a covered 2" by 3" MgO crucible (Ozark) and heated to 700°C for 5 hours at a rate of 150°C per hour. The powder was removed, re-ground and re-fired to 750°C using the same heating rate. This process was repeated for a third interval at 750°C. At this point, the powder appeared relatively homogeneous. In fact, the goal of these steps was to obtain a homogeneous precursor powder. A portion of the powder was pressed into a pellet using a 1.27cm steel die under 27.6MPa (4000psi) pressure using a Carver press. The pellet was placed in a large MgO crucible (30ml) and buried in the center of a sacrificial powder bed of the remaining powder. It is well known that Bi_2O_3 is volatile above 700°C and especially near its melting point, therefore, sacrificial powder beds are important for preventing Bi loss from the pellet. The crucible was covered and fired to an initial temperature of 1000°C for 12hr. The pellet was then ground to a powder under acetone, re-pressed into a pellet and buried in the sacrificial bed. The crucible was then placed back in the furnace for firing at 1100°C for three 30-hour intervals. At each interval, the pellet was removed, crushed and ground to a powder, re-pressed and re-buried in the powder bed.

Phase purity confirmation of the synthesized phases was achieved with laboratory powder x-ray diffraction, inductively coupled plasma (ICP) and x-ray fluorescence spectroscopy (XRF). Visual confirmation was obtained with secondary and backscattered SEM analysis. Figure 3.1 shows the x-ray diffraction patterns for the five samples. Although no exact

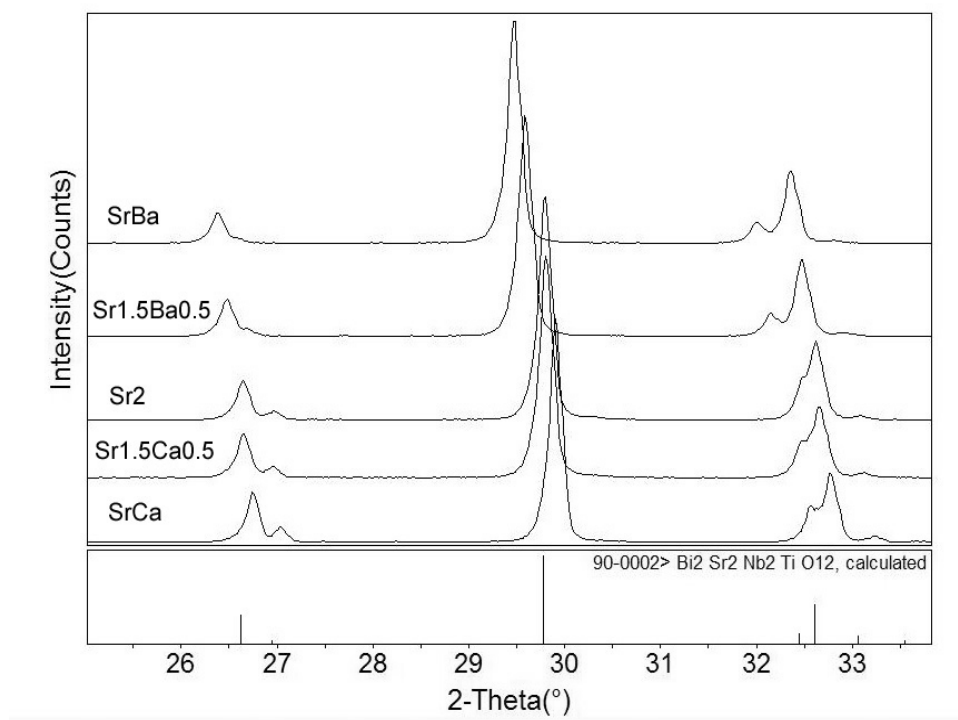


Figure 3.1: X-ray diffraction patterns taken for the three-layer Aurivillius compounds.

phase match exists in the powder diffraction file (PDF), all patterns match with the powder pattern calculated for the material. Secondary and backscattered SEM images indicate a single phase material. Powder from each sample was pressed into a pellet and sintered at 1050°C for 40 hours, mounted in vacuum impregnated epoxy mounts and polished to a 6 μm finish. Figure 3.2 shows a typical secondary and backscattered electron SEM image which shows a moderately dense (approximately 70% theoretical density) sample with rectangular shaped grains. No image contrast is seen in the backscattered indicating a single phase material. Bulk ICP/XRF analysis of the five samples shows that the phases formed as measured. Table 3.I displays the molar chemical composition for each sample obtained from ICP/XRF analysis. The slightly low Nb values from prescribed are most likely due to incomplete borate fusions.⁶³

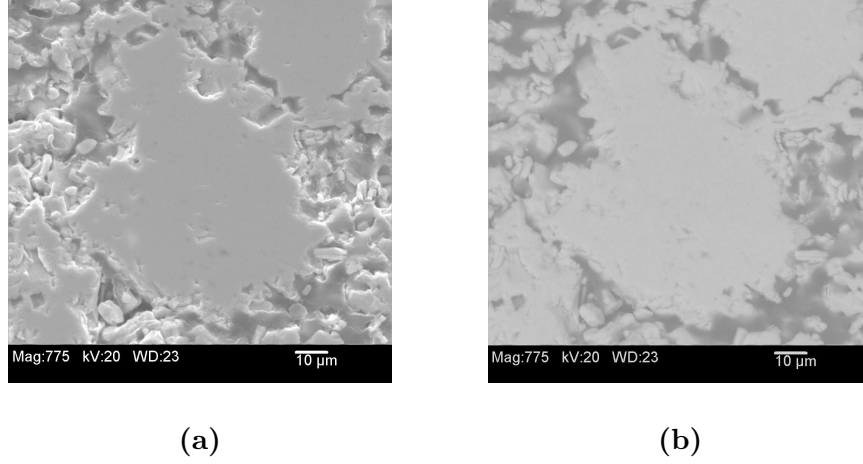


Figure 3.2: SE (a) and BSE (b) SEM images of $\text{Bi}_2\text{Sr}_{1.5}\text{Ba}_{0.5}\text{Nb}_2\text{TiO}_{12}$.

Table 3.I: Molar Chemical Composition Determined using ICP and XRF.

Sample	Bi	Sr	Ca	Ba	Nb	Ti
$\text{Bi}_2\text{SrCaNb}_2\text{TiO}_{12}$	2.0	1.0	1.1	0	1.9	1.1
$\text{Bi}_2\text{Sr}_{1.5}\text{Ca}_{0.5}\text{Nb}_2\text{TiO}_{12}$	1.9	1.5	0.5	0	1.8	1.0
$\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$	1.9	1.8	0	0	1.8	1.0
$\text{Bi}_2\text{Sr}_{1.5}\text{Ba}_{0.5}\text{Nb}_2\text{TiO}_{12}$	1.9	1.5	0	0.5	1.7	1.0
$\text{Bi}_2\text{SrBaNb}_2\text{TiO}_{12}$	1.8	0.9	0	1.1	1.8	1.0

Table 3.II: Neutron Scattering Lengths and X-ray Scattering Factors.

Where **Coh b** is the coherent bound neutron scattering length (fm),
Incoh b is the incoherent bound neutron scattering length (fm),
Coh XS is the coherent neutron scattering cross section (10^{-24} cm^2),
Incoh XS is the incoherent neutron scattering cross section (10^{-24} cm^2),
X-ray SF is the x-ray scattering factor (electrons).

Atom	Coh b	Incoh b	Coh XS	Incoh XS	X-ray SF
Bi	8.532	–	9.148	0.0084	83
Sr	7.02	–	6.19	0.06	38
Ba	5.07	–	3.07	0.15	58
Ca	4.70	–	2.78	0.05	20
Nb	7.054	-0.139	6.235	0.0024	41
Ti	-3.438	–	1.485	2.87	22

3.2.2 X-ray and Neutron Diffraction

All x-ray diffraction experiments were performed using a Siemens D500 diffractometer in Bragg-Brentano geometry, with a graphite diffracted beam monochromator, using fixed 0.3° divergence slits. Powder diffraction measurements for Rietveld refinements were made at the power of 40kV and 30mA, from $2-150^\circ 2\theta$ with a $0.02^\circ 2\theta$ step size and a 10 second count time. Samples were loaded in top-loaded sample holders using a Siemens sample changer spinner and were spun at 50rpm during the diffraction measurement. Phase identification measurements were performed on the same instrument, but with a shorter count time.

All neutron diffraction experiments were performed using the Special Environment Powder Diffractometer (SEPD) located at the Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory.* Samples were pressed into pellets and stacked in a vanadium sample holder. Room temperature time of flight (TOF) diffraction measurements were collected over four detector banks; 22° , 44° , 90° , and 145° .

The x-ray and neutron scattering factors for the elements appearing in the samples are seen in Table 3.II. Good atomic contrast is observed between the Bi and Sr, Ba, and Ca. Furthermore, good contrast is observed between the Sr, Ba, and Ca atoms. The neutron data also provides good Nb and Ti contrast.

*SEPD, Special Environment Powder Diffractometer, Intense Pulsed Neutron Source at Argonne National Laboratory.

3.2.3 Rietveld Refinements

Combined x-ray and neutron diffraction Rietveld refinements were performed on the five synthesized phases. Only the 90° detector bank neutron data were used in the refinements. The other three data banks when included in the refinements tended to yield in higher residual errors and chi-squared values and therefore were not used. The low angle x-ray diffraction peak was excluded from all refinements due to the sharp direct-beam related intensity increase. Furthermore, in order to decrease the time required per refinement, the initial refinements were only taken out to 100°2 θ . The angle range was increased to the full 150°2 θ range after suitable profile functions and occupancy parameters were obtained.

Simultaneous x-ray and neutron diffraction refinements were employed. The initial structural model for the three-layer Aurivillius phase was taken from work by Hervoches and Lightfoot who characterized Bi_{1.8}Sr_{2.2}Nb_{2.2}Ti_{1.8}O₁₂ using combined x-ray and neutron diffraction refinements.⁴⁹ GSAS was used to perform the Rietveld refinements using the EXPGUI implementation.^{64,65} The cation coordinates were set to be uniform for all cations occupying a specific site. For the Bi site, the Bi³⁺ position was allowed to vary from the Sr²⁺ cation occupying it. Since the Sr²⁺ cation has no lone-pair of electrons, it is not constrained to occupy the same site as Bi³⁺. In order to test this, the cation positions for Bi³⁺ and Sr²⁺ were constrained to be the same, and instead the thermal parameter was varied. Each time this was tested, the thermal parameter for the Sr²⁺ cation refined to a negative value. Therefore, the positions were allowed to vary and the thermal parameters were constrained to be the same for each site. Initial thermal parameters were set at 0.025(Å²) for each atom and were varied during the course of the refinement.

Initially, all cation occupancies were set to unity. For example, in the Bi₂Sr₂Nb₂TiO₁₂ case, the Bi site occupancy and the corresponding A site Sr²⁺ occupancy were each set to unity. Refinement of the fractional occupancies in Bi₂Sr₂Nb₂TiO₁₂ was successful, however, refinement of the cation occupancies in the Ca²⁺ and Ba²⁺ compositions, resulted in refined values of less than one. Since about 15% static disorder of Sr²⁺ for Bi³⁺ was observed for Bi₂Sr₂Nb₂TiO₁₂, it was deemed reasonable to initially substitute a small fixed amount of the mixing cation on each site. In other words, in Bi₂SrBaNb₂TiO₁₂, the fraction of Bi³⁺ on the Bi site was set at 0.8 and this allowed 0.1 fraction of both Sr²⁺ and Ba²⁺ to be placed on the site as well. After allowing for this, the refinements produced

reasonable occupancies. During the course of the refinements, it was also discovered that allowing Nb and Ti site disorder produced significantly lower R_{wp} 's and therefore, these sites were initially allowed to mix to a small degree.

Refinement of the site mixing parameter proved daunting. It was not possible to set up occupancy constraints using only three atoms per site. In this situation, it was only possible to refine two different cations at a time, then refine a different set. This would eventually lead to a circular refinement were the three cation fractions would compete with each other. In order to solve this problem, a new constraint was introduced. One cation from the Bi site and the A site was split into two cations with identical occupancies, half of their original value but still retaining their original position.⁶⁶ For example, in the $\text{Bi}_2\text{SrBaNb}_2\text{TiO}_{12}$ case, it was now possible to refine the Bi-Sr-Ba fractions occupying the Bi site *and* the Bi-Sr-Ba fractions between the Bi and A sites simultaneously. Furthermore, the constraints could be set up in a way that forced the cation occupancies to add to unity. It is interesting to note that in earlier refinements where the fractions were *not* constrained to add to unity, the refined fractions still converged to values close to unity.

The peak profiles of all x-ray samples showed a large amount of asymmetry, especially at low angles. The low angle peaks are critical in order to correctly model the unit cell. In order to allow for their inclusion in the refinement, initial profile parameters were manually set to force the peak profiles to model the low angle asymmetry. Using the Thompson, Hastings and Cox profile model, the peak asymmetry parameters S/L and H/L were set to 0.04 and 0.03, as these typically allowed for a reasonable modelling of the asymmetry.⁶⁷ It was found that this was the only way to accurately model the peak asymmetry because the major profile parameters LX and LY tended to dominate the peak profile and would not allow for reasonable subsequent modelling of the S/L and H/L parameters. In those cases, the asymmetry could not be refined adequately. Initial values for LX and LY were set at 8 and 20 respectively as these tended to provide an adequate initial peak profile. The default values for LX and LY are zero, and if refined from the start from zero, the refinement tended to diverge.

The neutron diffraction patterns came with a set of recommended profile and histogram functions from Argonne. These variables provided an excellent initial fit and as a result, they were allowed to refine one by one. The “difA” and “zero” neutron corrections were not refined per recommendations.⁶⁸ A Debye-Scherrer absorption correction was refined

for the neutron data only.

Each refinement started with the initial parameters set as described previously. For each sample, it was desired to obtain an adequate profile shape before refining any atomic parameters. After initial refinement of the background and histogram scale factor, the lattice parameters were refined. This step was only possible if initial profile values LX and LY were set as described earlier. Then, the sample displacement parameter (shft) and sample transparency correction (trns) were refined along with lattice parameter. These parameters were “turned off” and LX and LY were refined separately. Preferred orientation using the March-Dollase function on a (001) axis was refined. Generally, due to the method of sample loading, this proved to be a major correction, especially for the very low angle (001) reflections. Polarization correction was refined. Generally, refinement of the base profile values yielded R_{wp} values on the order of 16 and chi-squared values of about 7. The profile parameters were fixed and refinements of the atomic-based parameters were refined. Ultimately, it was determined that refining the Nb-Ti occupancies first yielded the most stable refinements. Next, the Nb and variable oxygen positions were refined, followed by the oxygen thermal parameters. During the course of the refinement, it was determined that the Bi site positions tended to refine to unreasonable values. Ultimately, this led to unstable occupancy values. Therefore, the Bi site positions were initially set to mimic the $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ refinements. The Bi site position was set to 0.215 and the A site cation mixing onto this site was set to 0.205 for all samples. The Bi and A site occupancies were refined next. Afterwards, their positions were allowed to refine, and then fractions and positions refined simultaneously. Bi and A site thermal parameters and then lastly the Nb-Ti site thermal parameters. The above refinement procedure was worked out such that the Nb-Ti thermal parameters would refine to positive values.

3.3 Results

3.3.1 Phase Stability

Five different samples were synthesized to phase purity. Table 3.III shows all of the samples attempted. It was not possible to completely substitute Ca^{2+} or Ba^{2+} for Sr^{2+} . It is interesting to note that the $\text{Bi}_2\text{SrCaNb}_2\text{TiO}_{12}$ and $\text{Bi}_2\text{SrBaNb}_2\text{TiO}_{12}$ compositions represent rough solubility boundaries for Ca^{2+} and Ba^{2+} respectively.

Table 3.III: Three-layer Aurivillius Compositions Attempted.

Sample	Phase Purity
$\text{Bi}_2\text{Ca}_2\text{Nb}_2\text{TiO}_{12}$	NO
$\text{Bi}_2\text{Ca}_{1.5}\text{Sr}_{0.5}\text{Nb}_2\text{TiO}_{12}$	NO
$\text{Bi}_2\text{SrCaNb}_2\text{TiO}_{12}$	YES
$\text{Bi}_2\text{Sr}_{1.5}\text{Ca}_{0.5}\text{Nb}_2\text{TiO}_{12}$	YES
$\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$	YES
$\text{Bi}_2\text{Sr}_{1.5}\text{Ba}_{0.5}\text{Nb}_2\text{TiO}_{12}$	YES
$\text{Bi}_2\text{SrBaNb}_2\text{TiO}_{12}$	YES
$\text{Bi}_2\text{Ba}_{1.5}\text{Sr}_{0.5}\text{Nb}_2\text{TiO}_{12}$	NO
$\text{Bi}_2\text{Ba}_2\text{Nb}_2\text{TiO}_{12}$	NO

3.3.2 Structure Refinement

Figure 3.3 shows a schematic of the refined three layer Aurivillius structure for $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ indicating the atomic sites and important layers in the structure. Figure 3.4 shows a typical combined x-ray and neutron diffraction Rietveld refinement difference pattern for the $\text{Bi}_2\text{Sr}_{1.5}\text{Ba}_{0.5}\text{Nb}_2\text{TiO}_{12}$ composition. Slight mismatch is observed between the calculated and experimental pattern at low angles due to difficulties in modelling peak asymmetry. Tables A.I through A.V show the refined atomic coordinates, fractional site occupancies and isotropic thermal parameters for the five samples and these are found in the appendix. Table 3.IV displays all of the refined bond lengths. The three-layer Aurivillius unit cell changes dimension based on the size of the substituted alkaline earth cation. Figure 3.5 shows the change in the a and c lattice parameters respectively versus alkaline earth content. Since Ca or Ba is substituting directly for Sr on the Aurivillius A site, the average A site cation radius (ACR) can be used to describe this change. Thus it can be seen that the a lattice parameter changes linearly with increasing ACR. The c lattice parameter increases nearly linearly with increasing ACR. All error bars are given in terms of one sigma, however it is likely that the ESD's are underestimated by the GSAS software.

Visual observation of the refined crystal structures reveals several interesting features. Figure 3.3 shows a calculated crystal structure using the Powdercell (PCW) code. The A site cations do not occupy the center of the cubo-octahedral position, but rather are displaced away from each other towards the extremities of the unit cell. Furthermore,

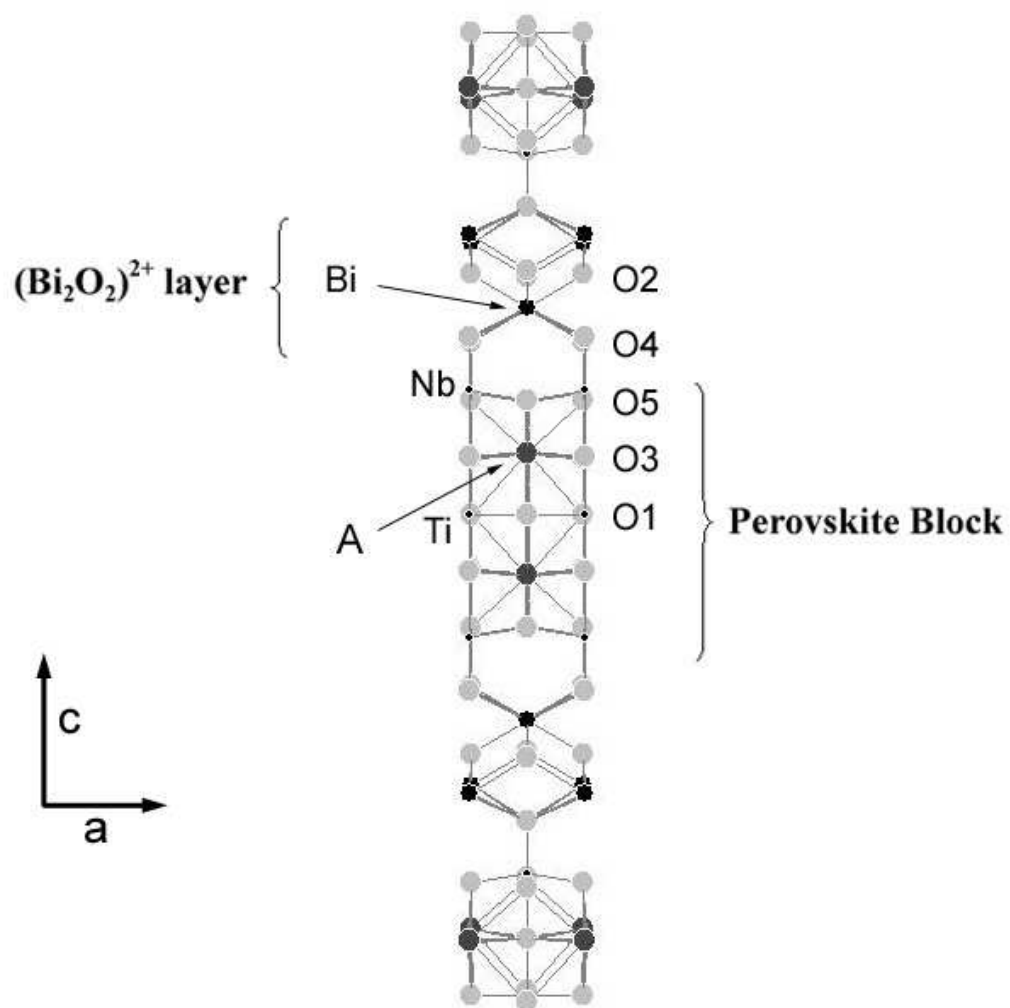


Figure 3.3: Refined three-layer crystal structure of $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$.

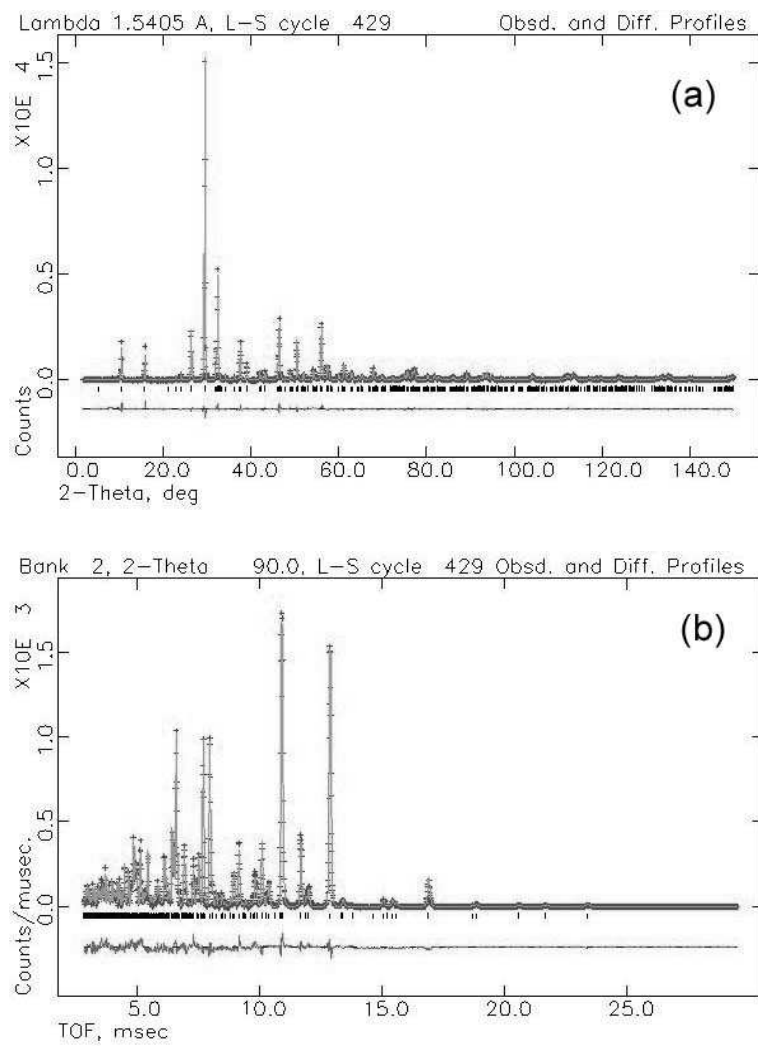


Figure 3.4: XRD (a) and neutron (b) Rietveld refinement plots for $\text{Bi}_2\text{Sr}_{1.5}\text{Ba}_{0.5}\text{Nb}_2\text{TiO}_{12}$.

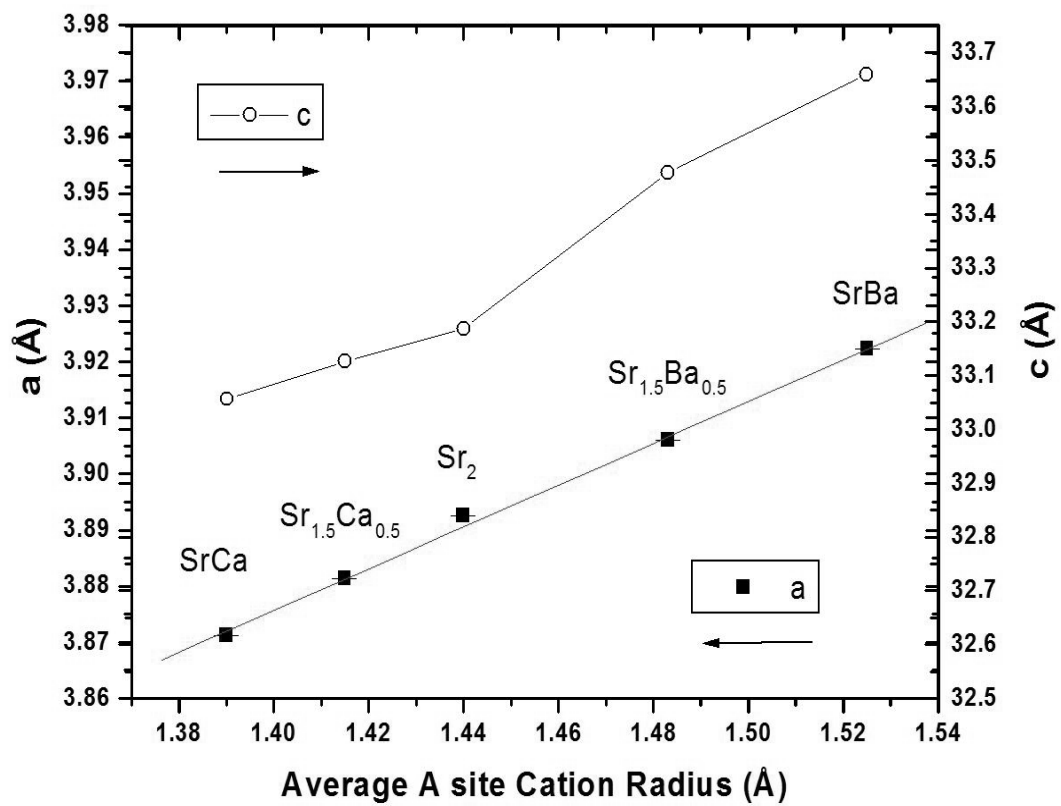


Figure 3.5: Refined a and c lattice parameters versus average A site cation radius.

Table 3.IV: Bond Lengths for the Five Samples.

Site	Bond	SrCa	Sr _{1.5} Ca _{0.5}	Sr ₂	Sr _{1.5} Ba _{0.5}	SrBa
	Bi-O2	2.28181(6)	2.28786(6)	2.27980(6)	2.27803(3)	2.282(2)
	Bi-O4	2.95008(6)	2.94704(6)	2.955(4)	2.98185(6)	3.003(4)
Bi	A-O2	2.63352(6)	2.61166(6)	2.61980(6)	2.59493(6)	2.64(2)
	A-O4	2.78631(6)	2.79665(6)	2.799(2)	2.82385(6)	2.8288(7)
	A-O5	3.27812(9)	3.29890(9)	3.273(4)	3.35588(9)	3.32(3)
	A-O1	2.84109(6)	2.84080(6)	2.85549(9)	2.87348(6)	2.896(3)
A	A-O3	2.74248(6)	2.74846(6)	2.7564(4)	2.76594(6)	2.7784(5)
	A-O5	2.60976(6)	2.64108(6)	2.666(3)	2.67213(6)	2.609(4)
	Nb-O3	2.25358(9)	2.26389(9)	2.273(9)	2.28842(9)	2.32(8)
Nb	Nb-O4	1.79032(6)	1.80513(6)	1.82(1)	1.82434(6)	1.82(1)
	Nb-O5	1.96442(6)	1.96767(6)	1.970(1)	1.97856(3)	1.985(1)
Ti	Ti-O1	1.93559(6)	1.94065(6)	1.94629(6)	1.95302(3)	1.96114(3)
	Ti-O3	1.91197(6)	1.92710(9)	1.943(8)	1.95995(6)	1.965(7)

the degree of displacement increases with ACR. The A-O bond lengths all increase with ACR as seen in Table 3.IV and Figure 3.6. The A-O1 bond is much larger than the A-O3 or A-O5 bonds and is indicative of the A site displacement. The Nb atoms follow a displacement similar to the A site in that they displace away from the center of the unit cell in a manner that leaves them offset to one side of the Nb-O octahedron. The Nb displacement increases with ACR. The Nb-O3 bond length testifies to this displacement as it increases to a larger degree than the Nb-O4 or Nb-O5 bonds. The Ti-O bond lengths also increase with ACR. The Ti-O3 bond is slightly smaller than the Ti-O1 in the Ca²⁺ compositions, but the Ti-O1 and Ti-O3 bonds approach the same length with increasing ACR. No offset is observed in the Ti cation. Figure 3.3 also depicts a displacement in the Bi and A cations occupying the Bi site as was described previously. The alkaline earth cation's lack of a lone pair of electrons allows it to occupy a more relaxed position than the host Bi cation.

A static disorder was observed between the Bi and A sites and between the Nb and Ti sites. In fact, simply allowing the Nb and Ti sites to disorder caused a substantial drop in residual error and chi-squared values. Figure 3.7 depicts the static disorder between the Bi and A sites. As mentioned previously, the Bi and A site cation occupancies were constrained to be the same. In general, the degree of site mixing between the Bi and A

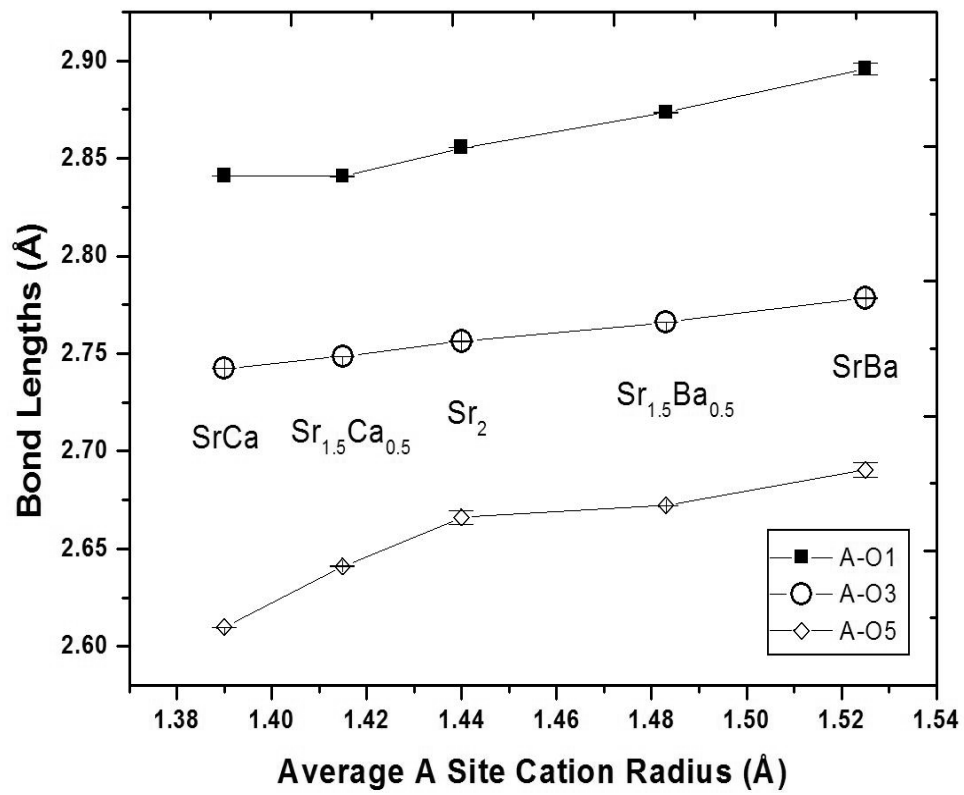


Figure 3.6: Bond lengths for the A-O bonds versus average A site cation radius.

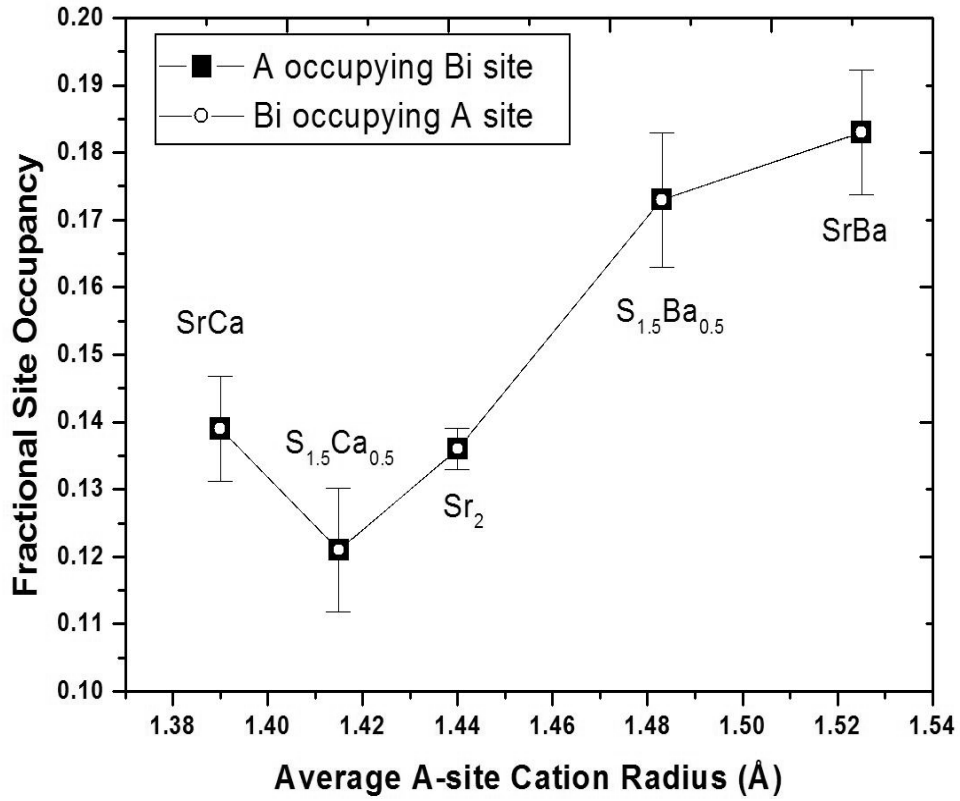


Figure 3.7: Fractions of A occupying Bi site, and Bi occupying A site versus average A site cation radius.

sites increases with ACR. All error bars are in terms of one σ . The $\text{Bi}_2\text{SrCaNb}_2\text{TiO}_{12}$ composition has a slightly larger Bi-A static disorder than the other compositions in that range and this is not well understood.

Figure 3.8 displays the total alkaline earth content occupying the Bi site along with the fraction of Ca^{2+} or Ba^{2+} occupying the Bi site. Of the total amount of alkaline earth occupying the Bi site, a substantial fraction comes from Sr^{2+} for the Ca^{2+} compositions. The Ca^{2+} cation prefers to remain on the A site. For the Ba^{2+} compositions, the alkaline earth cations occupying the Bi site appear to be completely Ba^{2+} , and Sr^{2+} remains on the A site along with the other portion of Ba^{2+} . The combined x-ray/neutron refinements allow this extra level of detail in the site mixing as refinements performed using only x-ray

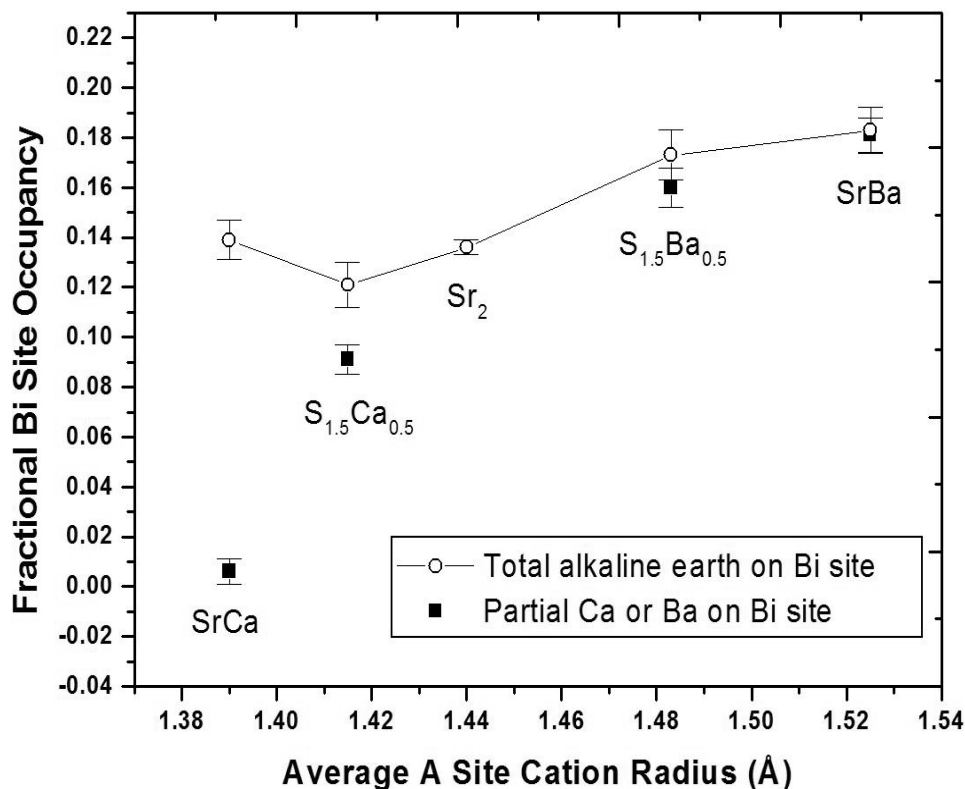


Figure 3.8: Fractions of Ca or Ba occupying Bi site and total fraction A occupying Bi site versus average A site cation radius.

data do not show any difference or preference in the Ca^{2+} or Ba^{2+} components.

Figure 3.9 depicts the fractional occupancy of the Nb site versus ACR. The degree of static disorder between the Nb and Ti sites does not appear to change significantly with ACR. Approximately 25% Ti^{4+} occupies the Nb site. An increase in the Ti^{4+} content on the Nb site was observed for the $\text{Bi}_2\text{SrCaNb}_2\text{TiO}_{12}$ composition, but the error bars (one sigma) indicate that the Nb-Ti disorder is probably static with ACR.

Bond valence sum (BVS) calculations were performed on the five samples using bond lengths generated by the refinements. BVS analysis describes the relationship between bond valences and bond lengths through Equation 3.2.⁶⁹

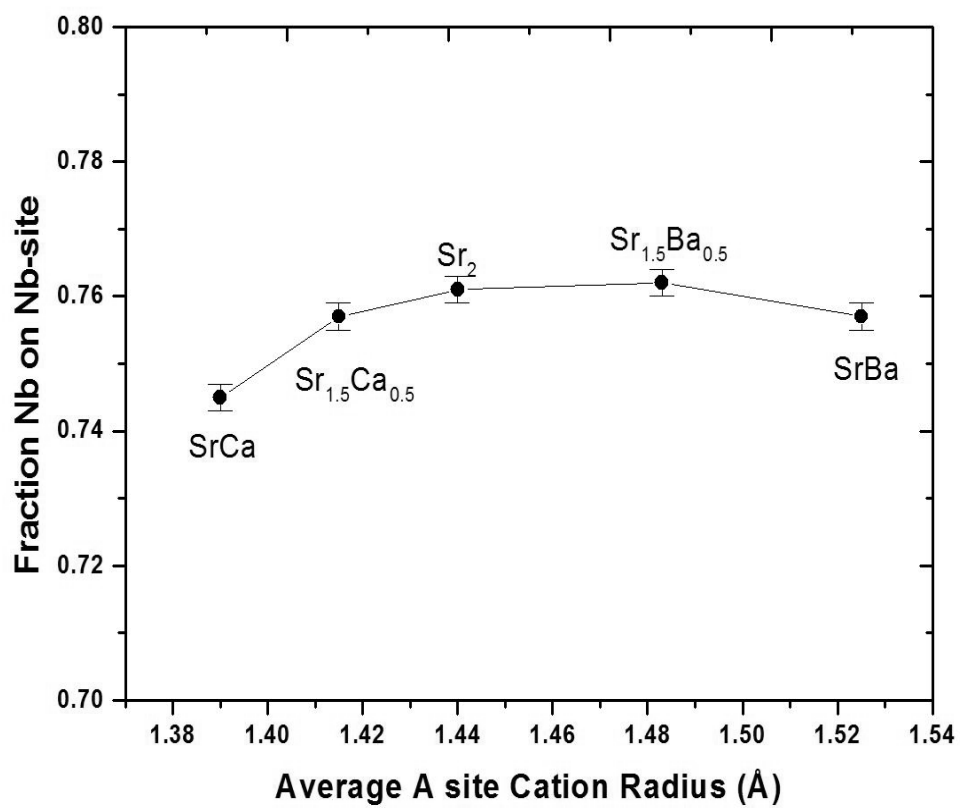


Figure 3.9: Fractions Nb occupying Nb site versus average A site cation radius.

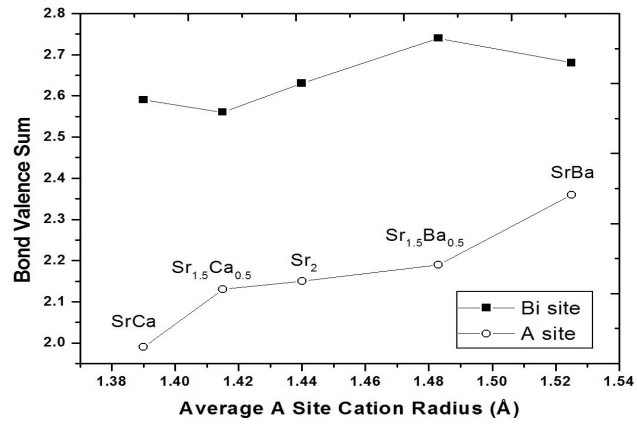
Table 3.V: Bond Valence Sum Values for the Five Samples.

Site	SrCa	Sr _{1.5} Ca _{0.5}	Sr ₂	Sr _{1.5} Ba _{0.5}	SrBa
Bi site	2.59	2.56	2.63	2.74	2.68
A site	1.99	2.13	2.15	2.19	2.36
Nb site	4.94	4.86	4.79	4.69	4.63
Ti site	5.10	4.95	4.82	4.68	4.61

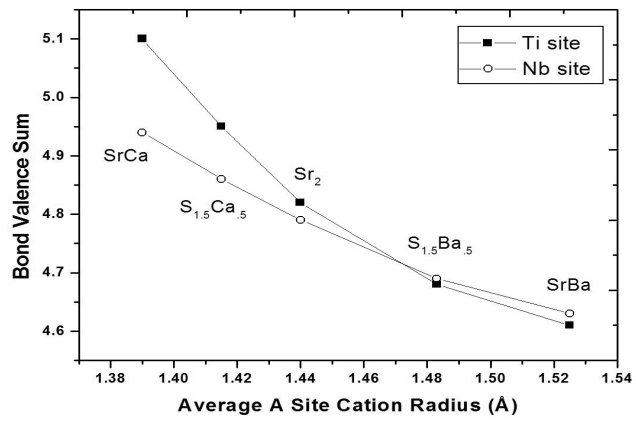
$$s_{ij} = \exp\left(\frac{R_0 - R_{ij}}{B}\right) \quad (3.2)$$

Where s_{ij} is equal to the bond valence, R_{ij} is the bond length of the respective cation-anion bond and R_0 , and B are cation-dependent constants. The value of B is generally set to 0.37Å for most cations. Values of R_0 and B have been calculated for most bond types and the values used for this work were taken from Brown and Altermatt.^{70,71} Despite the fact that BVS analysis has existed for some time, most of the initial work on the subject was done by I.D. Brown.^{69,70,72,73} Several other excellent references on BVS calculations exist by other authors.^{74–78} Furthermore, BVS calculations have also been performed in the Aurivillius system.^{48,49,51,53,60,62,74} The BVS for each site was calculated by multiplying Equation 3.2 for a given cation by the fraction of that cation on a specific site. For example, in the Bi₂Sr_{1.5}Ca_{0.5}Nb₂TiO₁₂ case, for the Bi cation on the Bi site, the BVS was generated via the Bi-O2 and Bi-O4 bonds, summing the BVS for the two bonds, then multiplying by the fraction of Bi on that site. The BVS was also calculated for the alkaline earths occupying the Bi site using the A-O2 and A-O4 bonds, multiplying by the respective fractions and summing the BVS to obtain a total. Table 3.V shows the calculated BVS for the four cation sites in the five compounds. The trends may be observed more clearly via Figure 3.10.

Different studies in literature of the three-layer Aurivillius ceramics show that because of the relaxation of the alkaline earth cation on the host Bi site, the alkaline earth relaxes enough to bond with the O5 oxygen. As seen in Table 3.IV, the A-O5 bond lengths range from 3.28Å in the Bi₂SrCaNb₂TiO₁₂ material to 3.35Å in Bi₂SrBaNb₂TiO₁₂. The ionic radius of Ca²⁺ is 1.34Å in eightfold coordination while that of O²⁻ is about 1.4Å giving a Ca-O bond length of 2.74Å which is much smaller than 3.35Å. Furthermore, the longest



(a)



(b)

Figure 3.10: Bond valence sum of the Bi and A sites (a) and Nb and Ti sites (b) versus average A site cation radius.

Ba-O bond length would be 3.01Å. Therefore, it is unlikely that an A-O5 bond forms and therefore this bond was not included in the BVS calculations.

The Bi site BVS remains relatively constant with ACR and is slightly underbonded for all compositions (BVS<3). The A site BVS increases with Ba²⁺ substitution and decreases with Ca²⁺ substitution and is overbonded (BVS>2) for all compositions except Bi₂SrCaNb₂TiO₁₂. It is interesting to note that the A site BVS increases with ACR despite the fact that the A-O bond lengths increase with ACR and the fraction of Bi³⁺ occupying the A site increases with ACR. Figure 3.6 shows the A-O bond lengths versus ACR. Normally, these two factors would cause a decrease in the A site BVS, however, Ba²⁺ is large enough to negate any decrease in BVS. The A site BVS increase is due solely to the type of alkaline earth occupying the A site and is not effected by bond length increases or site mixing. The Nb and Ti site BVS's decrease with increasing ACR. This is most likely due to the fact that most of the Nb-O bond lengths increase with ACR. However, the Ti BVS is extremely high for the Ca²⁺ compositions. Even though a portion of the Ti site is occupied by Nb⁵⁺, it is not enough to explain a Ti BVS greater than 4.5.

Thermal parameters for all elements were refined and nothing remarkable appears except the oxygen thermal parameters for the O1 and O4 sites. Figure 3.13 shows the O1 and O4 thermal parameters plotted as a function of ACR. The O1 thermal parameter is extremely large for the Ca²⁺ compositions, and moderately large for the Bi₂Sr₂Nb₂TiO₁₂ composition. The oxygen thermal parameters for the Ba²⁺ compositions appear normal. Furthermore, the O4 thermal parameter is larger than expected. The O1 oxygen site lies in the center of the unit cell and comprises the basal plane of the Ti-O octahedron. The O4 oxygen site connects the Bi and Nb sites. The large O1 and O4 oxygen thermal parameter and/or large BVS in the TiO6 octahedron has been observed in several three layer Aurivillius phases Bi_{1.8}Sr_{2.2}Nb_{2.2}Ti_{1.8}O₁₂, Bi₄Ti₃O₁₂, and Bi_{2.5}Na_{1.5}Nb₃O₁₂ and in Ruddleson-Popper phases.^{49,59,60,79,80}

In a particular study of Hervoches and Lightfoot, Rietveld refinements of high temperature neutron powder diffraction measurements indicate that the O1 thermal parameter becomes increasingly large and the Ti site BVS becomes more overbonded as the crystal symmetry increases.⁶⁰ The composition studied by Borg *et al.* has an overbonded NbO6 octahedra (Nb replaces Ti) as well as large O1 and O4 oxygen thermal parameters.⁵⁹ While not presented in their paper, BVS values were calculated for Bi_{1.8}Sr_{2.2}Nb_{2.2}Ti_{1.8}O₁₂ of Her-

vanches and Lightfoot from the bond lengths they provided and the Ti site was found to be highly overbonded with a BVS of 4.99.⁴⁹ In the latter study, Wright and Greaves discovered that rotations of the TiO6 octahedra were necessary to describe the structure. Additional refinements were therefore attempted using a model that allowed rotation of the TiO6 octahedra to determine if indeed the original structure model was correct. Any displacement of the O1 oxygen from its symmetry-fixed position resulted in additional peaks that were clearly visible in the calculated neutron diffraction patterns, thus eliminating the model used in the Ruddleson-Popper phases.⁸⁰

In order to investigate the potential for an oxygen vacancy on the oxygen sites, the oxygen fractional occupancies of all oxygen sites were refined. Prior to doing this, the isotropic thermal parameters were reset to default values for sites that had large thermal parameters on the initial refinements, specifically, the O1 and O4 sites. These were reset to the default value of $0.025\text{\AA}^2$. The fractional occupancies were refined for each oxygen site simultaneously, then the results evaluated. Any site that refined to an occupancy greater than one was reset to unity and the refinements repeated. Figure 3.11 shows the refined fractional occupancies for the O1 and O4 sites.

The O1 and O4 oxygen sites refined to a value less than one for all samples with the elevated oxygen thermal parameters. The degree of oxygen deficiency increased with decreasing ACR. The O1 site was fully occupied for the Ba containing compositions. Furthermore, the O4 occupancy shows a nearly linear trend with ACR. Figure 3.12 shows the total combined oxygen fractional occupancy plotted in terms of oxygen stoichiometry versus a lattice parameter. The oxygen stoichiometry approaches full occupancy as the unit cell size increases. Note, that this plot could have been made in terms of ACR, since ACR and a were shown to be linearly related. In order to validate the structural results, AC impedance spectroscopy measurements were performed at different temperatures to evaluate the possibility whether oxygen defects were present and whether they were mobile. Figure 3.14 displays the Arrhenius plots of the five compositions tested. Conductivities on the order of 10^{-4} to $10^{-3} \frac{S}{cm}$ were obtained at temperatures of approximately 900°C . DC conductivity measurements obtained over the same temperature ranges for the same samples validate the AC measurements. Details of the AC and DC measurements are seen in the appendix.

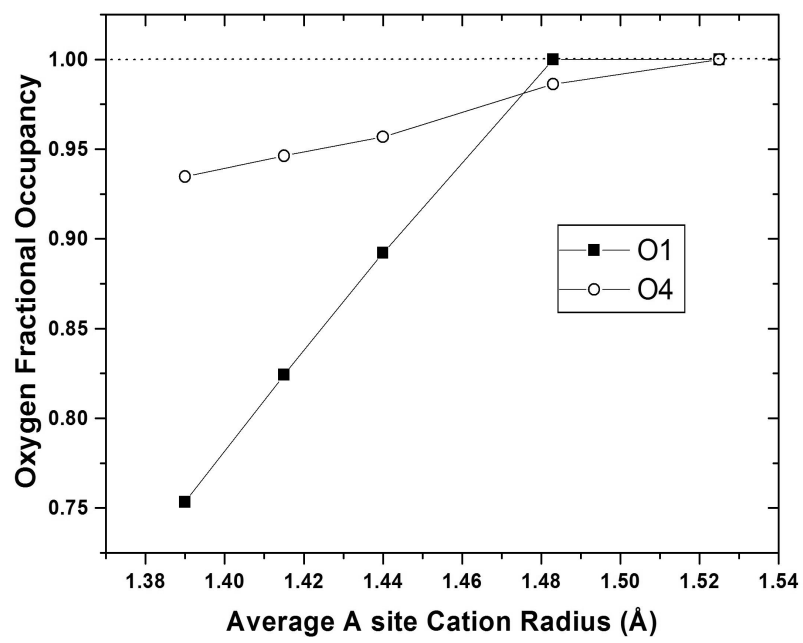


Figure 3.11: Refined fractional occupancies of the O1 and O4 oxygen sites for the five compositions.

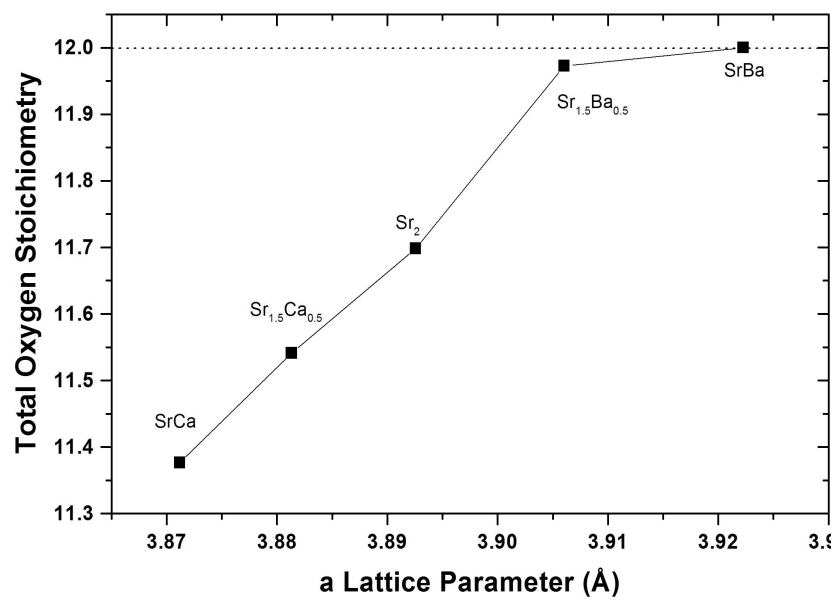


Figure 3.12: Total oxygen stoichiometry as a function of a lattice parameter for all five compositions.

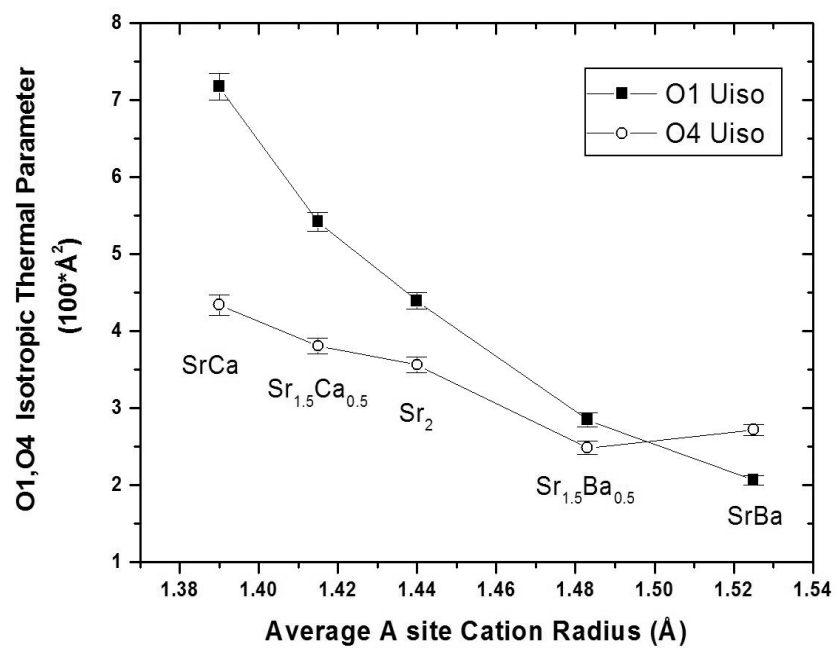


Figure 3.13: O1 and O4 oxygen isotropic thermal parameters for all five compositions.

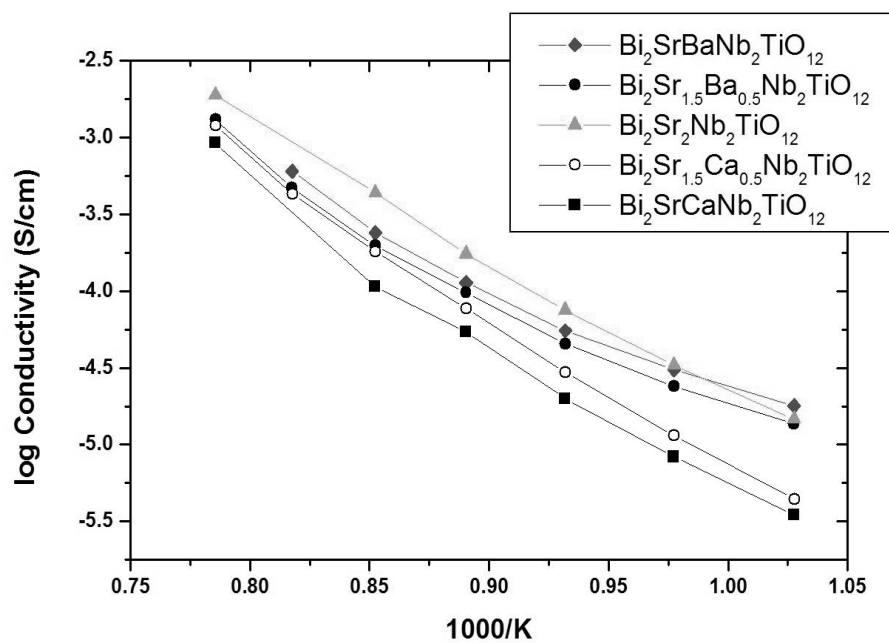


Figure 3.14: Arrhenius plot of log electrical conductivity versus $1000/T$ of the five compositions obtained from AC impedance spectroscopy.

3.4 Discussion

After careful examination of the refinement results, it is apparent that the three-layer Aurivillius structure is relatively tolerant to modification, but only to a limit after which the structure fails to form. The structure is sensitive to lattice strain and seeks to minimize undue strain by static disorder and possibly creation of oxygen defects. Furthermore, complex interrelationships exist between the static disorder, lattice strain and the oxygen stoichiometry.

3.4.1 Analysis of $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$

It is prudent to discuss the base, unsubstituted $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ composition first as this gives clues to understanding the static disorder and lattice strain results observed in the Ca^{2+} and Ba^{2+} compositions. It is interesting to note that the unsubstituted $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ composition exists with approximately 14% of the Bi site being replaced with Sr^{2+} and vice versa for the A site. Some driving force must exist in order to cause this stable static disorder. So far, two explanations exist in the literature that discuss the reason for the static disorder; the overbonding at the A site and the interlayer strain between the $(\text{Bi}_2\text{O}_2)^{2+}$ layer and the perovskite blocks.^{3,48} Therefore, we must ask ourselves which of these factors causes the static disorder in this compound. The A site overbonding in $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ appears to be stable and unaffected by site mixing as Figure 3.15 indicates because no change was observed in BVS when allowing for the static disorder. If A site strain was the dominant factor, then a decrease in A site BVS would have been observed when allowing the site mixing to occur. A word of caution must be inserted here because only one sample was used to obtain that specific data point. If more samples were collected, it is possible that we may observe a strain effect. But in any event, the interlayer strain must be more of a dominant factor. If the Armstrong *et al.* argument as posed previously is used here, then the $(\text{Bi}_2\text{O}_2)^{2+}$ layer is constraining the size of the perovskite block.³ The ideal $(\text{Bi}_2\text{O}_2)^{2+}$ layer has a lattice dimension of 3.80Å and the calculated Armstrong lattice parameter is 4.06Å. Therefore, the $(\text{Bi}_2\text{O}_2)^{2+}$ layer is approximately 6% smaller than the ideal perovskite block. The only way to decrease the strain between the layers would be to decrease the size of the perovskite block or increase the $(\text{Bi}_2\text{O}_2)^{2+}$ dimension. By allowing a static disorder between the two layers, smaller Bi^{3+} (1.17Å) can be substituted

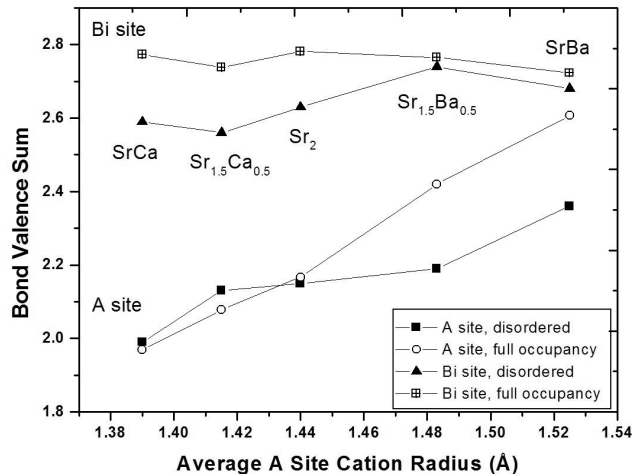


Figure 3.15: Full occupancy BVS versus ACR plots for the Bi and A sites. BVS for A and Bi sites *with* site mixing included for comparison.

for Sr^{2+} (1.44Å) on the A site and thus decrease the perovskite dimension and by subsequent substitution of Sr^{2+} for Bi^{3+} on the Bi site, increase the $(\text{Bi}_2\text{O}_2)^{2+}$ dimension.⁵⁷ In effect, the static disorder evens out the size difference between the two layers.

The nature of the static disorder between the Nb and Ti octahedral layers is not readily apparent although a simple layer strain argument similar to that described previously could be used. Nb^{5+} has an atomic radius of 0.64Å whereas Ti^{4+} has a radius of 0.605Å and thus the disorder could be the result of size balancing.⁵⁷ The Nb and Ti site influence on stability becomes more important when discussing the Ca^{2+} and Ba^{2+} compounds.

3.4.2 Alkaline Earth Substitution

Calling attention to Figure 3.8, it was observed that of the total amount of alkaline earth occupying the Bi site (Sr^{2+} and Ca^{2+} , or Sr^{2+} and Ba^{2+}), the Ca^{2+} cation showed a preference for remaining on the A site whereas the Ba^{2+} cation showed a very strong preference for occupying the Bi site. The Bi site is eight coordinated. Bi^{3+} in eightfold coordination has an ionic radius of 1.17Å whereas Ca^{2+} in eightfold is 1.12Å.⁵⁷ Despite the similarity of ionic radii, it is apparent from the previous discussion of interlayer strain that substituting a smaller cation on the Bi site would not favor the reduction of interlayer

strain. Therefore, it is not surprising that Ca^{2+} remains on the A site thereby allowing mostly Sr^{2+} to occupy the Bi site. On the other hand, it would be extremely favorable to substitute the larger Ba^{2+} cation for Bi^{3+} (1.42Å vs 1.17Å) on the Bi site as this would lead to a greater reduction of interlayer strain.

The degree of static disorder between the Bi and A sites increases from the Ca^{2+} to the Ba^{2+} compositions. In general, the degree of static disorder is dictated by two factors; interlayer strain and A site strain. The static disorder in $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ is controlled primarily by interlayer strain. Interlayer strain is also a factor in the Ba^{2+} compositions, but A site overbonding becomes a dominant factor in determining the degree of static disorder. Even though Ba^{2+} occupies most of the alkaline earth found on the Bi site, Ba^{2+} is still present on the A site, and therefore drives up the compressive strain on that site. As a result, the degree of static disorder must increase to alleviate this increased overbonding. Figure 3.15 shows this to be the case by the large decrease in A site BVS by allowing static disorder to occur. The A site BVS is actually decreased in the Ca^{2+} compositions due to the fact that Ca^{2+} is so much smaller than the A site host Sr^{2+} , and therefore, static disorder in the Ca^{2+} compositions is predominantly influenced by interlayer strain.

It is now possible to summarize a relationship between the degree of static disorder and the nature of the A site:

1. Static disorder occurs in an effort to reduce interlayer strain between the $(\text{Bi}_2\text{O}_2)^{2+}$ layer and the perovskite blocks,
2. The degree of static order is directly related to the average size of the A site cation, ie. interlayer strain is reduced with smaller average A site radii and therefore the degree of static disorder is reduced,
3. Interlayer strain is the predominant influence on the degree of static disorder until the A site strain becomes high enough that additional disorder is necessary to reduce the A site strain.

3.4.3 Octahedral - A Site Relationship

The unusually large lattice strain observed on the Ti site can be partially explained with the knowledge gained from the static disorder of the Bi and A sites. As seen in

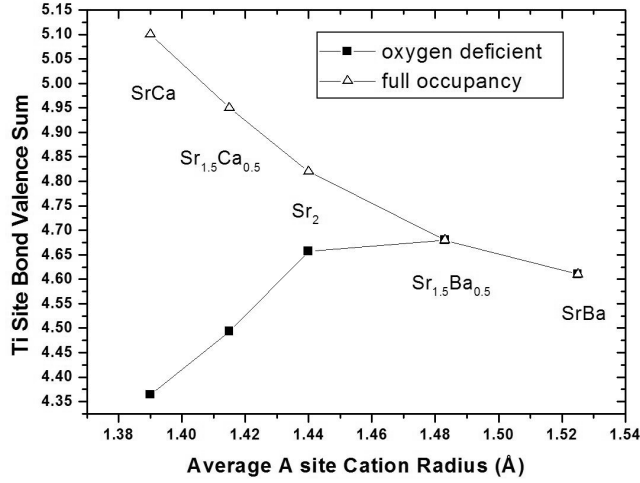


Figure 3.16: Ti site BVS and O1 isotropic thermal parameter plotted versus average A site cation radius.

Figure 3.10, the Ti site BVS is highly overbonded for the Ca^{2+} compositions with BVS values on the order of 5 compared to the ideal cation valence of 4 for Ti^{4+} . Furthermore, it was observed that the O1 oxygen site had a large thermal parameters for the Ca^{2+} compositions. Figure 3.16 plots the O1 thermal parameter and the Ti BVS versus average A site cation radius in a means to show the relationship between these parameters. The large Ti BVS can be explained as follows. It is known that Ca^{2+} prefers to remain on the A site. The smaller Ca^{2+} cation reduces the A site strain and decreases the A-O1, A-O3, and A-O5 bond lengths. The O1 and O3 oxygens are also bonded to the Ti^{4+} cation, therefore, the Ti-O bond lengths also must decrease. Since the static disorder between the Ti^{4+} and Nb^{5+} sites does not significantly change with respect to the cations occupying the A site, the Ti-O bond length reduction significantly increases the Ti site strain. The Nb site strain is only partially influenced by the A-O bond length decrease since the Nb^{5+} cation bonds the O3, O4, and O5 oxygens. Once the A site strain increases, the A-O bond lengths increase and the Ti site BVS decreases accordingly.

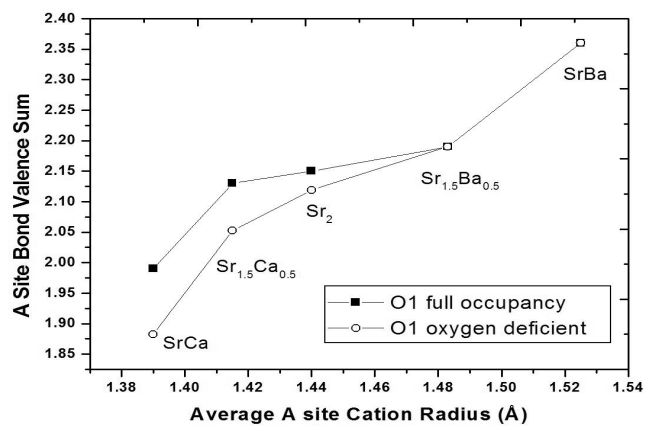
Even though the large Ti BVS can now be understood, the BVS is still too large to be reasonable despite the fact that it has been observed several times in literature, not only in the Aurivillius system, but in other layered perovskite-like materials.^{18,48,79,80} The fact

that the O1 thermal parameter also reaches unusually large values prompts one to think that oxygen may be leaving the structure thereby creating a strain induced oxygen vacancy. If the O1 oxygen was leaving the structure then only a fraction of the bond would contribute to the BVS and this would directly lead to a decrease in A and Ti site strain. The re-refinement of the oxygen occupancies as mentioned previously led us to discover that the O1 oxygen site was deficient in the Ca^{2+} compositions and $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$. Figure 3.17 shows the recalculated BVS values for the four cation sites by allowing the O1 oxygen deficiency. As can be seen, the A and Ti sites are affected by the oxygen deficiency. The A site BVS shows a moderate drop in BVS but the Ti site shows a significant decrease in BVS. In fact, the Ti site BVS approaches values to be expected for the level of Nb-Ti static disorder. The results of the AC impedance spectroscopy and DC conductivity experiments appear to indicate levels of electrical conductivity higher than expected in these materials. However, it is not known whether the conduction mechanism is via ionic or electronic means because platinum non-blocking electrodes were used. Electronic conduction is not expected in these materials and therefore, it is likely that these materials are ionic conductors and become oxygen deficient in an effort to reduce Ti site lattice strain.

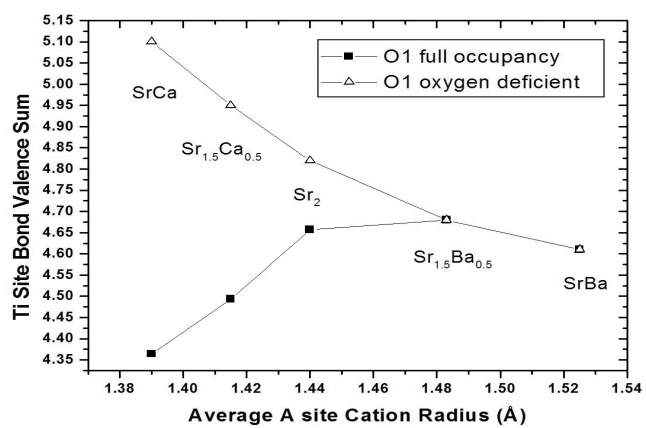
Also of considerable interest is the high O4 thermal parameter. The O4 oxygen site is another possible location for an oxygen vacancy. When the compositions were re-refined with a variable oxygen fractional occupancy, the O4 site also became oxygen deficient. Interestingly, the O4 deficiency remained with the Ba^{2+} compositions. It is not clear the structural benefit for an O4 deficiency as this would further decrease the Bi and Nb site BVS which already hold reasonable values.

3.5 Conclusions

Static disorder between the Bi and A sites and between the Nb and Ti sites was observed to occur in three-layer Aurivillius ceramics where an alkaline earth Ca^{2+} or Ba^{2+} was systematically substituted for Sr^{2+} in the base $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ lattice. The static disorder occurred in an effort to reduce interlayer strain between the $(\text{Bi}_2\text{O}_2)^{2+}$ layer and the perovskite blocks. Interlayer strain was shown to be predominantly determined by the average size of the A site cation. Interlayer strain was reduced with smaller average A site cation radii. Larger average A site cation radii increased A site strain and necessitated



(a)



(b)

Figure 3.17: BVS for the A (a) and Ti (b) sites being corrected for the O1 deficiency.

increased static disorder. The A site was the dominant factor in determining the a lattice parameter. Nb-Ti site static disorder did not appear to be affected by the average A site cation radius or A site strain.

3.6 Acknowledgements

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Chapter 4

Non-stoichiometric Structures

4.1 Introduction

The goal of this thesis was to create an oxygen deficient three layer Aurivillius ceramic for use as an electrolyte in a solid oxide fuel cell (SOFC), or similar ionic conducting device. It was possible to do this based on the synthesis and structural knowledge gained from Chapters 2 and 3. Generally, the introduction of oxygen vacancies into a host structure is achieved by aliovalent substitution. A cation of lesser charge, but similar size is substituted for a higher valence cation, such as Al^{3+} for Ti^{4+} with the end result, if the structure is to maintain charge neutrality, is that an oxygen anion must be removed from the structure. Aliovalent substitution can be performed with complete or partial substitution for the host cation. Some structures are naturally oxygen deficient, such as the BIMEVOX type phase $\text{Bi}_4\text{V}_2\text{O}_{10}$ and the brownmillerite phase $\text{Ba}_2\text{In}_2\text{O}_5$.^{81–85} In both of these phases, oxygen vacancies occur naturally without the need for aliovalent substitution. Aliovalent substitution has been used for many oxide structures, including perovskites, pyrochlores, spinels, fluorites, etc., to create oxygen vacancies.

Aliovalent substitution in the Aurivillius system has been performed in several different studies. Palanduz *et al.* substituted Ti^{4+} in place of Nb^{5+} on the B site of $\text{SrBi}_2\text{Nb}_2\text{O}_9$ to generate oxygen deficient samples with conductivities on the order of $10^{-3} \frac{\text{S}}{\text{cm}}$ at 800°C .⁸⁶ Yasuda *et al.* synthesized $\text{Bi}_2\text{K}_{1-x}\text{Nb}_2\text{O}_{8.5-x}$ with A site substitution of K^+ replacing Sr^{2+} to obtain ionic conductivities on the order of $10^{-4} \frac{\text{S}}{\text{cm}}$ at 800°C .³⁸ Voisard *et al.* substituted onto the B site of the four-layer Aurivillius structure $\text{Bi}_4\text{SrTi}_4\text{O}_{15}$ with Mn^{3+} in place of Ti^{4+} to achieve conductivities on the order of $10^{-2} \frac{\text{S}}{\text{cm}}$ at 800°C .⁸⁷ Most notably, Kendall, *et al.*

synthesized oxygen-deficient three and four layer Aurivillius ceramics with very high ionic conductivities.^{40,42,88–90} B-site substitution was employed in both instances by replacing Ti^{4+} with Al^{3+} or Ga^{3+} to obtain conductivities on the order of $10^{-2} \frac{\text{S}}{\text{cm}}$ at 800°C for the 3 and 4-layer phases. The highest conductivities were obtained by Shulman *et al.* in the three layer $\text{Bi}_{4-x}\text{A}_x\text{Ti}_3\text{O}_{12-x}$ ($\text{A}=\text{Ca},\text{Sr}$) system where Bi^{3+} was replaced with a small amount of Ca^{2+} or Sr^{2+} ($x=0.2$).⁴¹ They observed conductivities on the order of $10^{-1} \frac{\text{S}}{\text{cm}}$ at 800°C .

While the ionic conductivities of these systems are quite high and the results are promising, the question of sample purity is a real concern. Even though the Aurivillius structure is open to cation substitution, the solubility range is relatively small, therefore, the possibility of secondary phases existing simultaneously with the Aurivillius phase is high. For example, the diffraction pattern shown in the work of Yasuda *et al.* clearly shows diffraction peaks belonging to an impurity phase.³⁸ Shulman *et al.*, Voisard *et al.*, and Palanduz *et al.*, offer no SEM or diffraction evidence for phase purity in their papers.^{41,87,86}

Kendall *et al.* showed x-ray diffraction patterns for their phases which clearly show a large impurity peak, which matches that of cubic stabilized Bi_2O_3 .^{40,42,88–90} Bi_2O_3 is well known as an excellent ionic conductor, and it is quite likely that the majority of the conduction in those samples is through the Bi_2O_3 impurity. Snedden, *et al.* were the first to speculate that the Bi_2O_3 is the prime conducting species in the three and four layer phases of Kendall *et al.*'s work.⁹¹

4.2 Plan of Attack

It was decided to use the $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ composition as a base for aliovalent substitution simply because it had a range of cation sites that could be modified. For example, many 3+, 4+, and 2+ cations exist that could fit in the respective host lattice sites. The decision as to which specific site should be targeted was based on the availability of dopant cations and the ionic radius of the substituting cation. Previous work by Armstrong *et al.* had shown an empirical Equation 3.1 which related the size of the A site and B site cations to the ideal a lattice parameter of the Aurivillius structure.³ Even though some cations exist with suitable charge, they would not work for substitution because they were either too large or too small. For instance, Zr^{4+} generated an unrealistic a lattice

parameter of 4.18Å when used (ionic radius 0.72Å). When studying the list of ionic radii, two appeared to match closely with that of Ti^{4+} (0.605Å), Al^{3+} and Ga^{3+} with radii of 0.535Å and 0.62Å respectively. These two cations were readily available in the form of Al_2O_3 and Ga_2O_3 . Initially, full Al^{3+} or Ga^{3+} substitution for Ti^{4+} was attempted, but later, mixed substitution with Ti^{4+} was attempted.

During the course of the experiments, it was learned that cation site mixing was occurring between the Bi and A sites and between the Nb and Ti sites of the parent $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ structure. For reasons which will later be explained, an interesting alternative to aliovalent substitution (Al^{3+} or Ga^{3+} for Ti^{4+}) was to use site mixing to create oxygen vacancies. In other words, since it was known that Sr^{2+} mixed onto the Bi site, extra Sr^{2+} was forced to occupy the Bi site as in $\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_2\text{TiO}_{11.9875}$ as this would have an identical effect to aliovalent substitution. Similarly, additional Ti^{4+} could be forced onto the Nb site as in $\text{Bi}_2\text{Sr}_2\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.9875}$. Simultaneous A and B type substitution could also be performed to insert more oxygen vacancies. Lastly, the effects of modifying the A site radius on the formation of oxygen vacancies could be observed by substitution of an alkaline earth (Ca^{2+} or Ba^{2+}) for Sr^{2+} and using the site mixing to generate oxygen vacancies as in $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ba}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$ or $\text{Bi}_2\text{Sr}_{1.5}\text{Ca}_{0.5}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.9875}$.

4.3 What I Am Going to Show You

Aliovalent substitution for the creation of oxygen vacancies will be used in two sets of compounds: those with simple Ga^{3+} or Al^{3+} substitution for Ti^{4+} , and those involving use of the site mixing for creation of oxygen vacancies. The solid solubility ranges of each method will be investigated since little is known about the solubility of Al^{3+} or Ga^{3+} in the Aurivillius structure. Table 4.I shows the range of compounds synthesized for both compositional ranges.

4.4 Experimental Details

All samples were generated using conventional solid state synthesis after the procedure mentioned in Chapter 2. The resultant powder was divided into two sections, one for diffraction analysis and the other portion pressed into a pellet and sintered for density, SEM, and conductivity measurements. Pellets were pressed using a 1 cm steel die with

Table 4.I: Complete List of Oxygen Deficient Compositions Synthesized.

Composition	Phase Pure ?
$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	Yes
$\text{Bi}_{3.95}\text{Ca}_{0.05}\text{Ti}_3\text{O}_{12-x}$	Yes
$\text{Bi}_{3.9}\text{Ca}_{0.1}\text{Ti}_3\text{O}_{12-x}$	No
$\text{Bi}_{3.85}\text{Ca}_{0.15}\text{Ti}_3\text{O}_{12-x}$	No
$\text{Bi}_{3.8}\text{Ca}_{0.2}\text{Ti}_3\text{O}_{12-x}$	No
$\text{Bi}_{3.75}\text{Ca}_{0.25}\text{Ti}_3\text{O}_{12-x}$	No
$\text{Bi}_{3.95}\text{Sr}_{0.05}\text{Ti}_3\text{O}_{12-x}$	Yes
$\text{Bi}_{3.9}\text{Sr}_{0.1}\text{Ti}_3\text{O}_{12-x}$	No
$\text{Bi}_{3.95}\text{Ba}_{0.05}\text{Ti}_3\text{O}_{12-x}$	Yes
$\text{Bi}_{3.95}\text{Pb}_{0.05}\text{Ti}_3\text{O}_{12-x}$	No
$\text{Bi}_2\text{La}_2\text{Ti}_3\text{O}_{12}$	Yes
$\text{Bi}_2\text{LaSrTi}_3\text{O}_{12-x}$	No
$\text{Bi}_2\text{La}_2\text{Ti}_2\text{GaO}_{12-x}$	No
$\text{Bi}_2\text{Ca}_2\text{Nb}_2\text{TiO}_{12}$	No
$\text{Bi}_2\text{SrCaNb}_2\text{TiO}_{12}$	Yes
$\text{Bi}_2\text{Sr}_{1.5}\text{Ca}_{0.5}\text{Nb}_2\text{TiO}_{12}$	Yes
$\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$	Yes
$\text{Bi}_2\text{Sr}_{1.5}\text{Ba}_{0.5}\text{Nb}_2\text{TiO}_{12}$	Yes
$\text{Bi}_2\text{SrBaNb}_2\text{TiO}_{12}$	Yes
$\text{Bi}_2\text{Ba}_2\text{Nb}_2\text{TiO}_{12}$	No
$\text{Bi}_2\text{Sr}_2\text{Ta}_2\text{TiO}_{12}$	Yes
$\text{Bi}_2\text{Ca}_2\text{Ta}_2\text{TiO}_{12}$	No
$\text{Bi}_2\text{Ba}_2\text{Ta}_2\text{TiO}_{12}$	No
$\text{Bi}_2\text{Sr}_2\text{Ti}_2\text{NbO}_{12-x}$	No
$\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{GaO}_{12-x}$	No
$\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{AlO}_{12-x}$	No
$\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{Al}_{0.5}\text{Ti}_{0.5}\text{O}_{12-x}$	No
$\text{Bi}_2\text{Sr}_{1.5}\text{Ca}_{0.5}\text{Nb}_2\text{Al}_{0.5}\text{Ti}_{0.5}\text{O}_{12-x}$	No
$\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{Al}_{0.25}\text{Ti}_{0.75}\text{O}_{12-x}$	No
$\text{Bi}_2\text{Sr}_{1.5}\text{Ca}_{0.5}\text{Nb}_2\text{Al}_{0.25}\text{Ti}_{0.75}\text{O}_{12-x}$	No
$\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{Al}_{0.05}\text{Ti}_{0.95}\text{O}_{12-x}$	Maybe
$\text{Bi}_2\text{Sr}_{1.5}\text{Ca}_{0.5}\text{Nb}_2\text{Al}_{0.05}\text{Ti}_{0.95}\text{O}_{12-x}$	Maybe
$\text{Bi}_{1.85}\text{Sr}_{2.15}\text{Nb}_2\text{TiO}_{12-x}$	No
$\text{Bi}_{1.9}\text{Sr}_{2.1}\text{Nb}_2\text{TiO}_{12-x}$	No
$\text{Bi}_{1.95}\text{Sr}_{2.05}\text{Nb}_2\text{TiO}_{12-x}$	Maybe
$\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_2\text{TiO}_{12-x}$	Maybe
$\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ca}_{0.525}\text{Nb}_2\text{TiO}_{12-x}$	Yes
$\text{Bi}_{1.975}\text{Sr}_{1.75}\text{Ca}_{0.275}\text{Nb}_2\text{TiO}_{12-x}$	Yes
$\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ba}_{0.525}\text{Nb}_2\text{TiO}_{12-x}$	Yes
$\text{Bi}_2\text{Sr}_2\text{Nb}_{1.9}\text{Ti}_{1.1}\text{O}_{12-x}$	No
$\text{Bi}_2\text{Sr}_2\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{12-x}$	Yes
$\text{Bi}_2\text{Sr}_{1.5}\text{Ca}_{0.5}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{12-x}$	Yes
$\text{Bi}_2\text{Sr}_{1.5}\text{Ba}_{0.5}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{12-x}$	Yes
$\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{12-x}$	Yes
$\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ca}_{0.525}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{12-x}$	Yes
$\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ba}_{0.525}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{12-x}$	Yes

Table 4.II: Bulk Densities of Hot Pressed Non-stoichiometric Samples.

Sample	Bulk Density (g/cm^3)	Percent Theoretical
$\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ca}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$	4.48	67
$\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_2\text{TiO}_{11.9875}$	5.34	80
$\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ba}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$	5.46	81
$\text{Bi}_2\text{Sr}_{1.5}\text{Ca}_{0.5}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.9875}$	5.02	75
$\text{Bi}_2\text{Sr}_2\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.9875}$	5.70	85
$\text{Bi}_2\text{Sr}_{1.5}\text{Ba}_{0.5}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.9875}$	5.07	76
$\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ca}_{0.525}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.975}$	5.66	84
$\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.975}$	5.69	85
$\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ba}_{0.525}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.975}$	6.21	93

a Carver press at about 25-30MPa. Pellets were sintered at 1050°C for 30 hours under a powder bed.

A second set of samples was further reacted using hot pressing. A custom hot press previously constructed at Alfred University was used for these experiments. A vertical tube furnace mounted on rails that allowed it to be moved up and down surrounded the sample chamber. Two high density (98%) alumina rods were placed vertically inside the tube furnace and were mounted in steel dies. Pre-sintered pellets were used for the hot pressing experiments. Some initial experiments were performed using green pellets, but were unsuccessful as the pellets disintegrated under the weight of the rams. The pre-sintered pellet sample was placed between the two alumina rams and the furnace was moved up into position around the pellet. Figure 4.1 shows a picture of the hot press used. A cantilever design was used to apply weight to the rams. About 60lbs of weight was hung on the end of the cantilever only after the furnace had reached its operating temperature. Each experiment went to 1000°C for 15 hours. The pellet was removed and the density was measured. All samples, hot pressed or not, had densities measured using ASTM-C140. Table 4.II shows the measured bulk densities for the hot pressed samples.

Following synthesis, x-ray diffraction was used to verify phase purity for all samples. All x-ray diffraction experiments were performed using a Siemens D500 diffractometer in Bragg-Brentano geometry, with a graphite diffracted beam monochromator, using fixed 0.3° divergence slits. Powder diffraction measurements for phase identification were made at the power of 40kV and 30mA, from 4-40°2 θ with a 0.04°2 θ step size and a 3 second count time

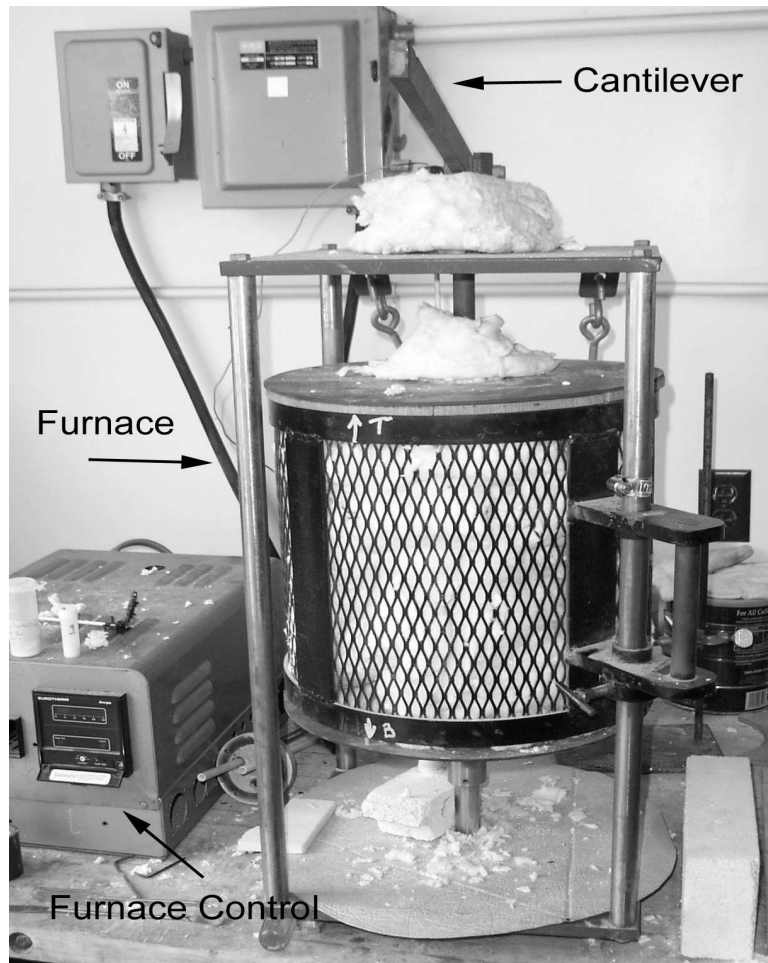


Figure 4.1: Photograph of the custom hot press used for the hot pressing experiments.

as this provided all the information necessary to determine phase purity without extended measurement times. The low two theta range was necessary to observe the (001) reflections of the Aurivillius structure. Samples were loaded in top-loaded sample holders using a Siemens sample changer sample/spinner and were spun at 50rpm during the diffraction measurement. Preferred orientation effects were minimized by careful sample loading.

In most cases, it was obvious from the diffraction pattern whether the material was pure or not based on the appearance of secondary diffraction lines, and in those cases where additional verification was required, the scanning electron microscope (SEM) was used for visual confirmation. SEM samples were either mounted as powder, or polished specimens. Powder samples were simply pressed onto the sample holder with the use of double-sided carbon tape. Polished specimens were prepared from portions of the pellets used for the density and conductivity measurements. A portion of the pellet was cut and polished by hand using 600 and ultimately 800 grit sand paper. The sample was pressed onto a sample holder using double sided carbon tape. Each sample was sputtered with a gold-palladium coating for an approximate 300Å coating thickness. A Phillips 515 SEM with LaB₆ filament was used to obtain secondary electron and backscattered electron images of the samples. A Kevex energy dispersive spectrometer (EDS) attachment was used to obtain elemental information.

Compositions that were deemed suitably pure were characterized using the Rietveld method. Powder diffraction measurements for Rietveld refinements were performed from 2-150°2 θ with a 0.02°2 θ step size and a 10 second count time.

A specific set of samples was sent to Argonne National Lab for measurement in the General Purpose Powder Diffractometer (GPPD). * Approximately 10 g of each powder was pressed into pellets and stacked in a vanadium sample holder. Room temperature time of flight (TOF) diffraction measurements were collected using four detector banks at 22°, 53°, 90°, and 145°.

Combined x-ray and neutron diffraction Rietveld refinements were performed on the data for each of the specimens using GSAS and the EXPGUI implementation.^{64,65} The 22° neutron data bank was not used because it did not contain much information. On samples where no neutron data was obtained, Rietveld refinements were performed using

*GPPD, General Purpose Powder Diffractometer, Intense Pulsed Neutron Source at Argonne National Laboratory.

x-ray diffraction data. The refinement procedure for both data sets was basically identical to that used in Chapter 3 with only small changes. Two small details will be mentioned however. The isotropic thermal parameters for the oxygen sites were only refined when neutron diffraction analysis had been performed. X-ray only refinements are insensitive to oxygen thermal parameters. The oxygen thermal parameters for the x-ray only data were set to a default value of $0.025(\text{\AA}^2)$ and unmodified for the duration of the refinement.

All samples were analyzed using both DC conductivity and AC impedance spectroscopy to determine the actual conductivity of the material. Full descriptions of these techniques as they applied to this thesis can be found in the appendix.

4.5 Phase Stability of Non-Stoichiometric Compositions

Initially, none of the phase stability boundaries were known for these materials, and as a result, a range of compositions were synthesized in order to determine the solid solution boundaries in $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$. It was quickly learned that the structure was intolerant to any amount of Ga^{3+} or Al^{3+} and caused the formation of a stable second phase of Bi_2O_3 . Mixed substitution attempts involving partial substitution of Ga^{3+} or Al^{3+} for Ti^{4+} resulted in removing the Bi_2O_3 impurity, but creating another stable second phase which was later determined to be a four layer Aurivillius phase. The reason for the formation of the second phases may lie in the structure's intolerance for large amounts of oxygen vacancies. Similarly, only limited amounts of site mixing substitution could be forced on the structure before secondary phases were formed. In some cases, the second phase formed even in very low doping level substitutions.

4.5.1 Phase Stability of Al^{3+} and Ga^{3+} Compositions

The Al^{3+} and Ga^{3+} substitution experiments were the very first compositions studied. It was thought that they would be the easiest to work with since they involved just the simple replacement of Al^{3+} or Ga^{3+} for Ti^{4+} in the $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ structure. Since the limit of Al^{3+} or Ga^{3+} solubility in the structure was unknown, it was decided to start with full replacement of Ti^{4+} with Al^{3+} or Ga^{3+} . At the same time that this work was performed, Kendall *et al.* published the work showing full substitution of Al^{3+} and Ga^{3+} for Ti^{4+} in $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$.^{40,88–90} The combined work of Kendall *et al.* showed convincingly

that $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{AlO}_{11.5}$ and $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{GaO}_{11.5}$ had formed with complete purity and they offered indexed diffraction patterns to support their claim. The ionic conductivities of these compositions were outstanding as they approached $10^{-1} \frac{\text{S}}{\text{cm}^2}$ at 800°C . The only difference between their diffraction patterns and the stoichiometric phase $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ was a large diffraction peak at approximately $27.9^\circ 2\theta$. While the difference between $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ and their $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{AlO}_{11.5}$ was very apparent, Kendall's group indexed this peak as a (106) reflection (PDF card 50-498).

The synthesis of this phase in the present work proceeded very similarly to that of $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ as was described in Chapter 2. The sample required extended heating times to produce "phase pure" results. Figure 4.2 shows a set of experiments in $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{GaO}_{11.5}$ synthesis in which the sample was heated four separate times with intermittent regrindings. The final sample showed what looked to be an almost pure sample as it matched very well with PDF 50-498. However, when the phase identification was performed, potential PDF matches for Bi_2O_3 appeared and matched very well with the extra peak. At this point, we speculated that: 1. the $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{AlO}_{11.5}$ and $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{GaO}_{11.5}$ phases were pure, but of a lower crystal symmetry and thus the additional peak was the result of the decreased symmetry; or 2. the extra peak in fact belonged to Bi_2O_3 or a Bi_2O_3 -derivative and therefore the sample consisted of two phases, of which Bi_2O_3 likely was the dominant ionic conductor. In order to test this hypothesis, a sample of $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{GaO}_{11.5}$ was placed on the HTXRD for analysis. Figure 4.3 shows the HTXRD pattern for presynthesized $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{GaO}_{11.5}$ versus temperature. The sample was heated from 400°C to 1000°C then cooled and diffraction patterns were collected every 100°C . This figure clearly shows the extra peak disappearing at higher temperatures, then reappearing as the sample was cooled. This observation did not help to solve the problem. The peak disappearance and reappearance did fit with the symmetry explanation because as temperature increased, the symmetry might increase because of a phase transformation, therefore eliminating the peak. Another possibility was that the Bi_2O_3 phase could be simply melting and recrystallizing. SEM confirmed that a major second phase of Bi_2O_3 was present. Figure 4.4 shows an SEM micrograph of $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{GaO}_{11.5}$ in secondary and backscattered mode. Two regions of contrast appear, a grey phase which is the Aurivillius phase and a very bright phase. When EDS was performed on the bright region, Bi appeared as the dominant element as seen in Figure 4.5. Therefore, the additional peak in the diffraction patterns was reassigned

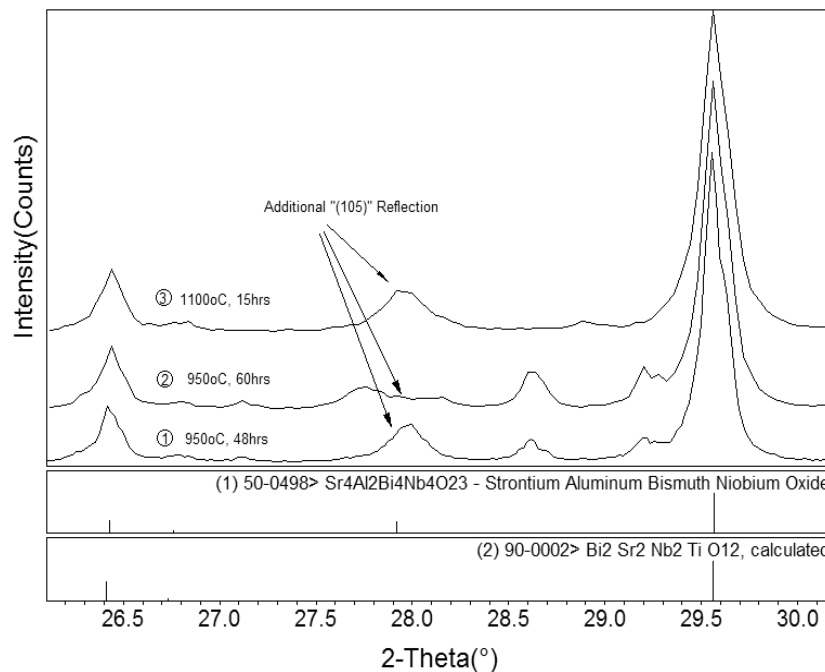


Figure 4.2: XRD patterns for $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{GaO}_{11.5}$ during solid state synthesis. Note additional (105) reflection. Calculated PDF card for $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ shown for comparison.

to that of Bi_2O_3 and it was realized that we had an impure material. It also explained the HTXRD patterns. The extra peak disappeared between 700-800°C, and seeing that Bi_2O_3 melts at about 819°C, the peak most likely belonged to Bi_2O_3 . What is interesting is that a number of clues were present all along that told the material's true identity. Each of the solid state samples had a strong yellow-orange color, similar to Bi_2O_3 whereas most pure $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ type phases were white. Likewise, the $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{GaO}_{11.5}$ samples always seemed to densify more than compositions such as $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$. The pressed pellets were always smaller than original, and, while not completely scientific, were much more difficult to crush into a powder. Basically, upon heating, the Bi_2O_3 impurity would melt, induce liquid phase sintering, then solidify upon cooling. It should be mentioned that samples synthesized with Al^{3+} showed exactly the same Bi_2O_3 impurity.

The question that was eventually asked was, "Why the Bi_2O_3 did not go into the crystal structure? And furthermore, if all this extra Bi_2O_3 formed, what happened to the remaining Sr, Nb, Ga, Al, Ti, etc?" Certainly, a third or fourth impurity phase must

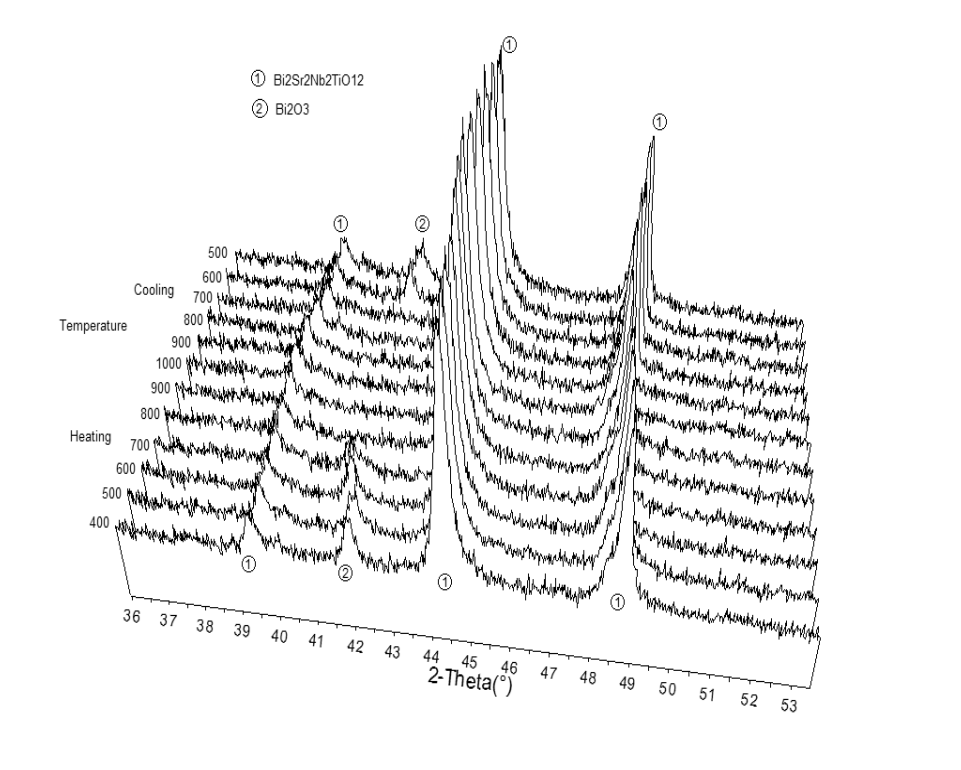


Figure 4.3: HTXRD patterns for a powder sample of $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{GaO}_{11.5}$ heated to 1000°C . Diffraction patterns collected every 100°C heating and cooling. Note the disappearance and reappearance of Bi_2O_3 as a result of melting.

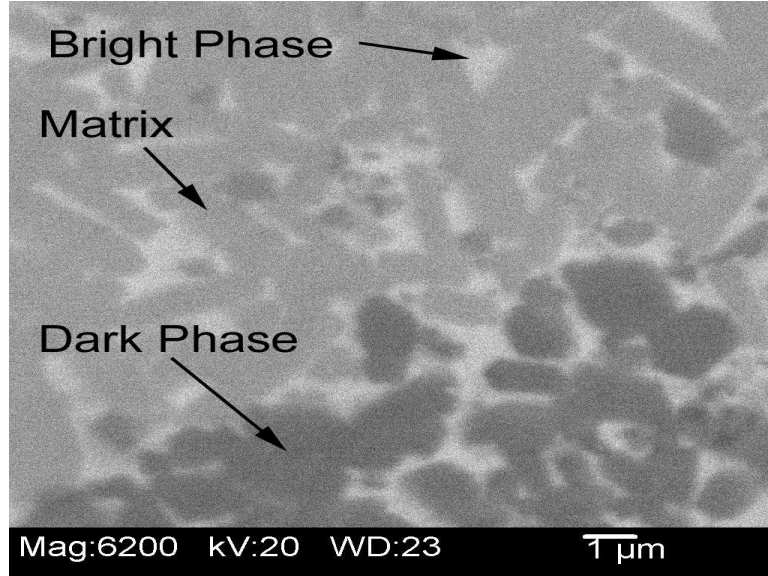
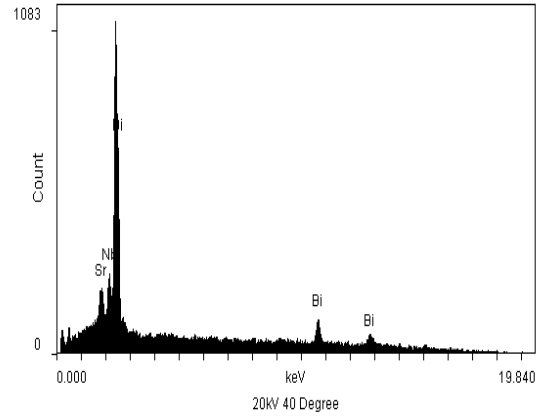


Figure 4.4: Backscattered electron SEM images of $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{GaO}_{11.5}$ highlighting the bright, dark, and matrix phases.

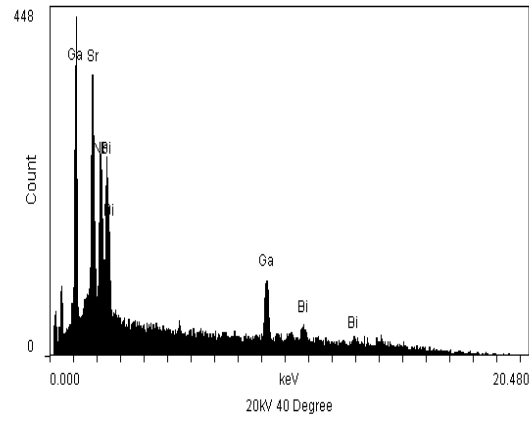
have also been present to account for the additional cations. Gallium, Ga^{3+} , has an ionic radius of $0.62\text{\AA}$ which is only slightly larger than Ti^{4+} ($0.605\text{\AA}$) and theoretically should have “fit” in the structure. Manganese, Mn^{3+} , has been fully substituted for Ti^{4+} in the $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ structure with no additional diffraction peaks, and Mn^{3+} is slightly larger than Ga^{3+} ($0.645\text{\AA}$).⁹² Therefore, the ionic radius of the substituting cation clearly was not the issue causing the Bi_2O_3 formation. It was reasoned that the structure may be intolerant to that many oxygen vacancies and as a result, on formation, the stable structure formed and diverted the remaining cations into Bi_2O_3 and whatever other phase formed. As a result of this observation, partial substitutions of Al^{3+} or Ga^{3+} for Ti^{4+} were attempted. Table 4.III shows the list of Al^{3+} - Ti^{4+} compositions attempted.

Table 4.III: Compositions Attempted Investigating the Ti-Al Solubility Boundary.

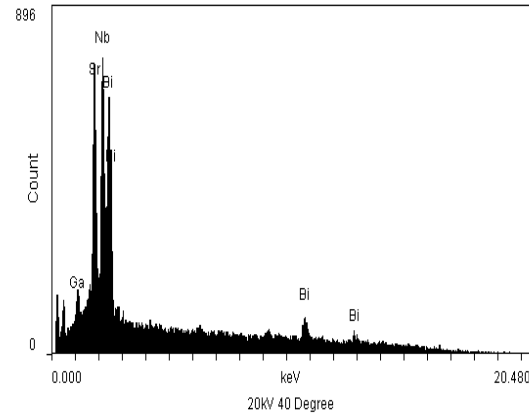
Composition	2nd Phase?
$\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{Ti}_{0.95}\text{Al}_{0.05}\text{O}_{11.975}$	Yes
$\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{Ti}_{0.75}\text{Al}_{0.25}\text{O}_{11.875}$	Yes
$\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{Ti}_{0.5}\text{Al}_{0.5}\text{O}_{11.75}$	Yes
$\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{Ti}_{0.25}\text{Al}_{0.75}\text{O}_{11.625}$	Yes



(a)



(b)

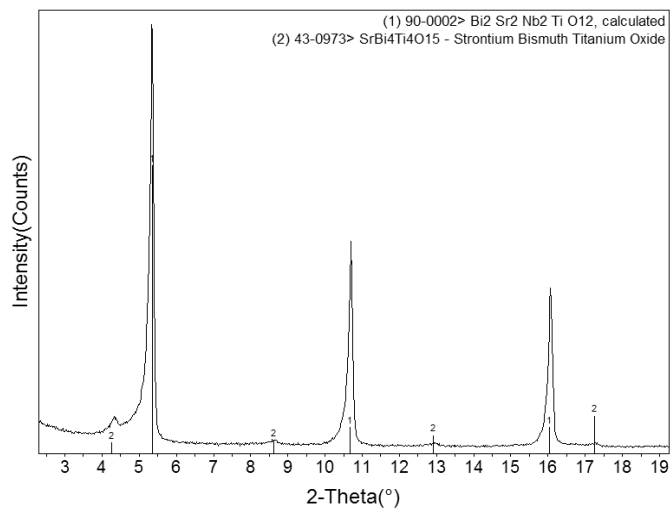


(c)

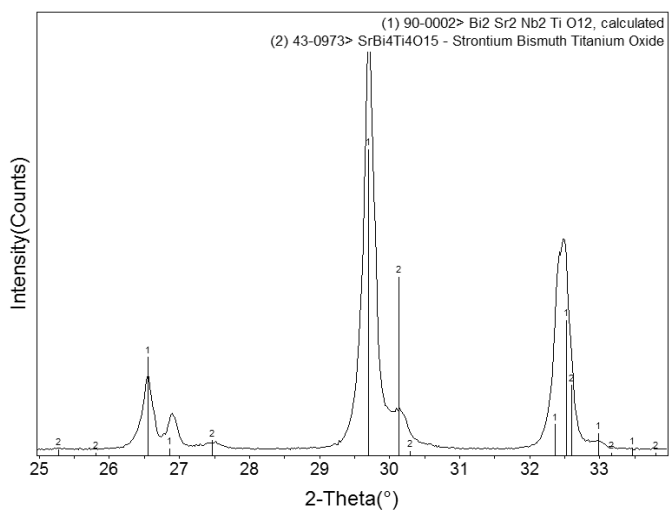
Figure 4.5: EDS spectra for “bright” Bi_2O_3 phase (a), the “dark” Ga-rich phase (b), and the “grey” matrix (c) of $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{GaO}_{11.5}$.

In this case, none of these phases formed a completely pure three layer Aurivillius phase. Figure 4.6 shows a low 2θ and high 2θ region of the x-ray diffraction pattern for one of the compositions listed in Table 4.III, $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{Ti}_{0.75}\text{Al}_{0.25}\text{O}_{11.875}$. Note, the large second phase peaks, especially those at low 2θ . The second phase was conclusively identified by the low angle reflections. The three-layer Aurivillius phases have three reflections below $20^\circ 2\theta$ whereas the four-layer structures have four peaks below $20^\circ 2\theta$. One phase $\text{Bi}_4\text{SrTi}_4\text{O}_{15}$, above all others appeared to make a good match, but it did not match up with all of the lines at the same time. $\text{Bi}_4\text{SrTi}_4\text{O}_{15}$ PDF 43-973 matched up well only with the higher angle lines when phase identification was initially performed. If the diffraction pattern was shifted to larger d-spacings, then the lower angle lines matched up with the PDF card. Figure 4.6 shows the PDF card 43-973 altered to fit the lower angle lines and higher angle lines. Since no PDF card exists for $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ or any similar composition, a PDF card was generated for $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ via a powder pattern calculated from the crystal structure refinements. The calculated PDF card for $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ is overlaid in Figure 4.6 for comparison. Rietveld refinements were performed on the data in an attempt to learn the second phase's true identity using the three layer phase $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ and the four layer phase. The lattice parameters and atomic positions of the four layer phase were modified in an attempt to get it to "fit" the observed data, but no good match was obtained. Higher symmetry forms of PDF 43-973 were attempted without success. The additional lines all appear to belong to one phase instead of having a third phase present. Therefore, it was decided that the second phase was probably a four layer Aurivillius phase, but somehow distorted. Peak shifting is often associated with changes in lattice parameters due to doping. However, for Aurivillius phases, one must also consider the formation of additional layered phases, eg. 3-layer vs. 4-layer. SEM was performed on this sample in order to determine whether the four layer phase could be observed under close inspection. However, no contrast difference was seen in the micrographs, whether it was in secondary (SE) or backscattered (BSE) mode.

Interestingly, no Bi_2O_3 was ever found to be present in any of these phases despite the fact that it was so prevalent in $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{GaO}_{11.5}$. There were two hypotheses considered as to why this would take place. One suggested that the Bi_2O_3 had simply evaporated from the sample and the remaining second phase consisted of the remnants of the other cations. This hypothesis had some merit because Bi_2O_3 is highly volatile at temperatures



(a)



(b)

Figure 4.6: X-ray diffraction pattern for $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{Ti}_{0.75}\text{Al}_{0.25}\text{O}_{11.875}$ highlighting a low 2θ (a) and high 2θ (b) regions. The PDF card 43-973 for the four layer Aurivillius phase is overlaid in each case.

above 700°C.⁹⁴ The second hypothesis suggested that the structure simply couldn't handle the excess oxygen vacancies and as a result, a base three layer structure would form and the remaining phases were diverted into Bi₂O₃. The second hypothesis ultimately made more sense because in all of the full substitution experiments (full Ga³⁺ or Al³⁺ for Ti⁴⁺), the samples were heated several times, at temperatures up to 1100°C, for periods of time up to 60 hours. If Bi₂O₃ was going to evaporate, it would surely have done so in the time span of a 60 hour heat treatment.

4.5.2 Phase Stability of Bi₂Sr₂Nb₂TiO₁₂ Site Mixing Compositions

Initial structure refinements led us to attempt to use site mixing to create oxygen vacancies. It was reasoned that if site mixing was occurring on the order of 15% Sr²⁺ substitution for Bi³⁺ in Bi₂Sr₂Nb₂TiO₁₂, then trying to put a little bit more Sr²⁺ into the structure in place of Bi³⁺, in a sense, aliovalently doping the structure with a 2+ charge for a 3+, seemed reasonable. Likewise, the idea was extended to substituting additional Ti⁴⁺ for Nb⁵⁺. Hervoches *et al.* had tried this approach in the Bi₂Sr₂Nb₂TiO₁₂ structure.⁴⁹ Using the Bi₂Sr₂Nb₂TiO₁₂ base structure, Hervoches *et al.* simultaneously investigated the solid solubility site mixing boundary of Sr²⁺ on the Bi site *and* Ti⁴⁺ on the Nb site while maintaining full oxygen stoichiometry. Bi_{1.6}Sr_{2.4}Nb_{1.6}Ti_{1.6}O₁₂ was one of the compositions they published, with combined x-ray and neutron diffraction Rietveld refinements. This structure was an end point representing the largest amount of Sr²⁺ able to be substituted for Bi³⁺. Based on the success of this work, it was deemed possible to generate oxygen vacancies by forced site mixing.

The three substitution methods that were eventually settled on were: 1. the A type, where additional alkaline earth was substituted for Bi³⁺, 2. the B type, where additional Ti⁴⁺ was substituted for Nb⁵⁺, and 3. the combination AB type, where both extra alkaline earth and Ti⁴⁺ was added. Since it was not known how much the Bi³⁺ could be successfully removed, a range of compositions were studied. The A type compositions were studied first. Table 4.IV shows the list of compositions attempted. Figure 4.7 shows x-ray diffraction patterns of the four A type compositions attempted. Note that Sr²⁺ addition is only possible up to Sr_{2.05} after which a second phase forms (PDF 43-973). This result was surprising since Hervoches *et al.* were able to put up to Sr_{2.4} into the structure. These four compositions were resynthesized three times in an attempt to make a phase pure compound,

Table 4.IV: A and B Type Non-stoichiometric Compositions Attempted.

Composition	Phase Pure ?
$\text{Bi}_{1.85}\text{Sr}_{2.15}\text{Nb}_2\text{TiO}_{11.925}$	No
$\text{Bi}_{1.9}\text{Sr}_{2.1}\text{Nb}_2\text{TiO}_{11.95}$	No
$\text{Bi}_{1.95}\text{Sr}_{2.05}\text{Nb}_2\text{TiO}_{11.975}$	No
$\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_2\text{TiO}_{11.9875}$	Maybe
$\text{Bi}_2\text{Sr}_2\text{Nb}_{1.9}\text{Ti}_{1.1}\text{O}_{11.95}$	No
$\text{Bi}_2\text{Sr}_2\text{Nb}_{1.95}\text{Ti}_{1.05}\text{O}_{11.975}$	No
$\text{Bi}_2\text{Sr}_2\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.9875}$	Yes

but unfortunately, the second phase peaks continued to appear. The B type compositions were very similar in that only a tiny amount (relatively speaking) of Ti^{4+} could be added to the structure. It was ultimately decided that the amount of alkaline earth or Ti^{4+} actually substituted in to the structure should be kept at $x = 0.025$ as this seemed to produce the best results. All of the samples listed in Table 4.V were synthesized again in larger quantities in order to use the final powder for structural, chemical, and electrical characterization.

Examination of the diffraction patterns following synthesis showed the same second phase peaks for several compositions. This was also the same (or similar) phase that appeared in the Ga-Al substitution studies. There did not seem to be any trends as to why the second phase peaks would appear, nor did it favor any specific cation substitution type. Some compositions had the secondary phase and some didn't. SEM was again used to try and identify the second phase with no success because the second phase had the same contrast as the main three-layer phase. It was ultimately decided to use the present samples for Rietveld analysis and electrical characterization. The second phase peaks had only a small fraction of the intensity of the major phase and would probably have little impact on the structural or electrical characterization.

4.6 Structural Analysis of Site Mixing Compositions

Nine compositions will be discussed in this section, as mentioned previously; three different types of forced site mixing, via the A site, B site and combined A and B sites, *and* alkaline earth substitution over the three compositions. Table 4.V shows the nine samples

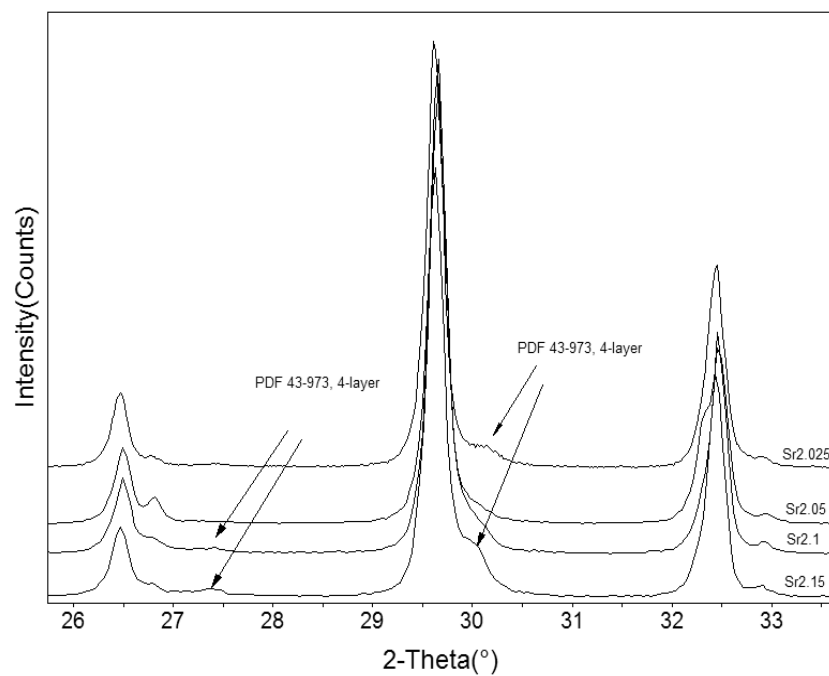
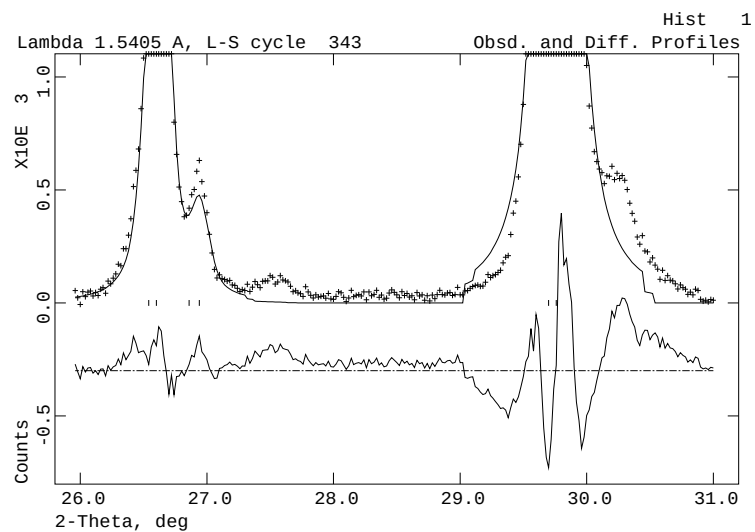


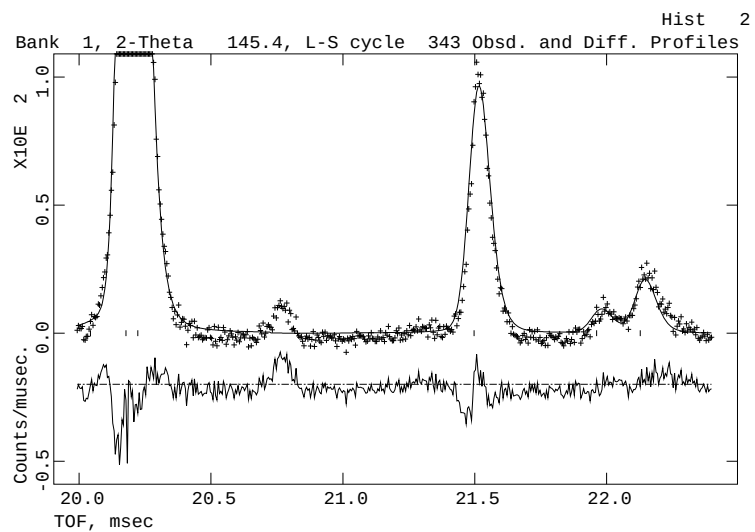
Figure 4.7: X-ray diffraction patterns for the four A-type compositions attempted showing the solubility limit for replacement of Bi^{3+} for Sr^{2+} .

used in this analysis as well as the method of substitution. Five of the compositions were analyzed using neutron powder diffraction because of limitations in neutron beam time. Structural refinements were performed on these five samples using combined neutron and x-ray diffraction Rietveld refinements. Rietveld refinements were performed on the other four samples using only the laboratory x-ray diffraction data. However, despite the fact that the x-ray refinements were of excellent quality, they lacked the sensitivity of the neutron results for the investigation of the oxygen anion sites. One of the greatest benefits of neutron diffraction is that it is highly sensitive to lighter elements such as oxygen. X-ray diffraction is relatively insensitive to the lighter elements because the x-ray electromagnetic wave primarily interacts with the electron cloud of the atom. Neutron diffraction on the other hand has direct interaction with the nucleus of the atom and as a result, neutron diffraction can be used to obtain precise atomic positions, thermal parameters, and occupancies of lighter elements; in the present case, oxygen. Ultimately, it allows more confident bond length calculations and ultimately higher quality BVS calculations. In fact, most of the crystal structure and BVS literature cited for this thesis were performed using neutron diffraction.^{43,46,47,49,53,60,77,78,83,95,96} Some portions of the x-ray only refinements were included for comparison, such as cation positions and lattice parameters since the x-ray data was more sensitive to these variables.

As mentioned in previously, not all of the samples were completely pure. A persistent second phase was present in several of the diffraction patterns which was most likely a four layer type Aurivillius phase. In the x-ray diffraction patterns, this took the form of a small shoulder on the high angle side of the 100% peak and a small peak appearing at approximately $27.2^{\circ}2\theta$. The intensity of these second phase peaks was extremely small, depending on the composition, but nonetheless noticeable. However, the secondary peaks had little effect on the refinement progress, nor did it effect the quality of the x-ray or neutron refinements. Figure 4.8 shows a comparison of typical second phase peaks in the x-ray and neutron diffraction patterns. The two regions in each figure which have no profile calculated for them pinpoint the location of the second phase peaks. Note, the scale on which the figures are plotted is only a small fraction of the actual intensity of each peak. The second phase peaks were included in the refinements as a disruption in the profile functions would have occurred by exclusion of those regions. The quality of the refinements was excellent as the weighted residual errors and χ -squared values were low for all compositions.



(a)



(b)

Figure 4.8: X-ray (a) and neutron (b) Rietveld refinement fits showing calculated, observed, and difference patterns for $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ca}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$. Note the second phase peaks with no calculated intensity.

The refinement of the nine phases proceeded exactly the same as the stoichiometric samples discussed in Chapter 3 with only slight modification. The initial cation fractions were adjusted to account for the additional alkaline earth (or Ti^{4+}) and retaining a total site occupancy of unity. For example, Sr^{2+} in $\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_2\text{TiO}_{11.9875}$ was 2.025, yet the total amount of Bi^{3+} and Sr^{2+} occupying the Bi site was still unity. Once all of the atomic coordinates were refined, they were “turned off” and the isotropic thermal parameters were refined. However, only the thermal parameters for the combined x-ray and neutron data were modelled. After convergence, any isotropic thermal parameter that was deemed unreasonably high was set to a default value of $0.025\text{\AA}^2$. Oxygen fractional occupancies were refined last. Initially, it was unknown which oxygen sites would become deficient, so all oxygen sites were refined at once. Oxygen sites that refined to occupancies greater than unity were “turned off” and their values reset to unity. It was understood from the data that certain oxygen sites were probably deficient because they had correspondingly large oxygen thermal parameters. It was not possible to simultaneously refine the oxygen thermal parameters and oxygen site occupancies, because these two parameters are known to correlate. The large oxygen thermal parameter, observed for several compositions indicates that the oxygen site was attempting to distribute its charge over a wide area, or in other words, that the site contained an oxygen vacancy or is disordered. While it would have been acceptable to leave the occupancies at unity and describe the oxygen defect by the large thermal parameter, an oxygen vacancy is easier to interpret, and so the oxygen thermal was set to a default value.

4.6.1 SEM Analysis of Non-Stoichiometric Compositions

Visual examination of the final compositions was performed by SEM analysis using the microscope described previously. Portions of the hot pressed pellets were broken away and polished using 600 grit sandpaper. The pellets were mounted on a sample holder using double sided carbon tape. The pellets were coated with Au/Pd to about $300\text{\AA}$ thickness using a sputtering unit. The surface appearance varied based on the density, but in general, it was difficult to make out individual grains except in cases where grains had pulled out due to polishing or a pore was present. However, in general, the surface density was much higher than samples that had not been hot pressed.

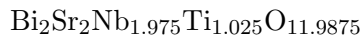


Figure 4.9 shows the SE and BSE electron micrographs, and the EDS spectrum for $\text{Bi}_2\text{Sr}_2\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.9875}$. The surface is fairly rough and individual rectangular shaped grains can be seen. Grain sizes range from about 1 to $5\mu\text{m}$. No contrast difference is seen in the BSE image, and the EDS spectra indicate all four cations expected for this sample.

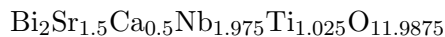


Figure 4.10 shows the SE and BSE micrographs, and the EDS spectra for $\text{Bi}_2\text{Sr}_{1.5}\text{Ca}_{0.5}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.9875}$. The sample surface appears to have the same density as $\text{Bi}_2\text{Sr}_2\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.9875}$ with the same type of rectangular blocky grains. The packing between individual grains appears to be random and brings up an important point. Pressing a sample with anisotropic grains to any degree of completion is difficult because it involves fracturing the individual grains in order to compact into a dense structure. Figure 4.10 gives a good picture of this process occurring. The BSE image shows some contrast in the center of the image concentrated around a pore. However, because the sample wasn't completely flat, the contrast difference could be just an artifact, or it could in fact be an indication of the presence of the secondary 4-layer phase.



Figure 4.11 shows the SE micrograph for $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ba}_{0.525}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.975}$. The sample surface for $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ba}_{0.525}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.975}$ was quite smooth with the absence of microstructural features. This sample had one of the highest densities at 93% theoretical. Another region of interest is shown in Figure 4.12. Here, the BSE image reveals a region of slightly darker contrast as compared to the SE image. EDS spectra taken for both the light and dark areas show a small degree of elemental difference is observed as the "darker" chunk has a slightly higher Nb content than the lighter matrix.

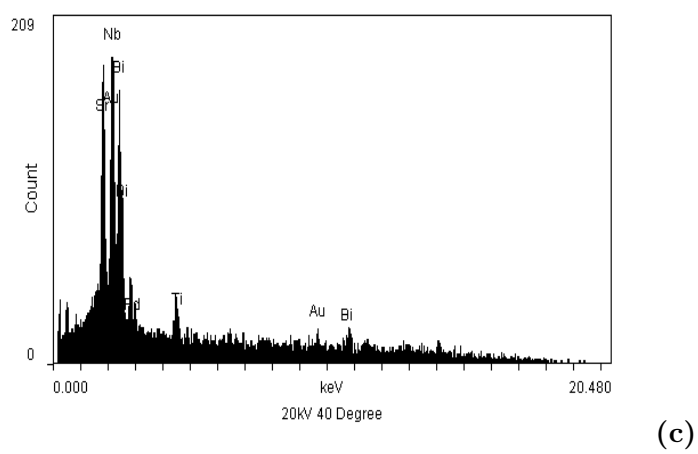
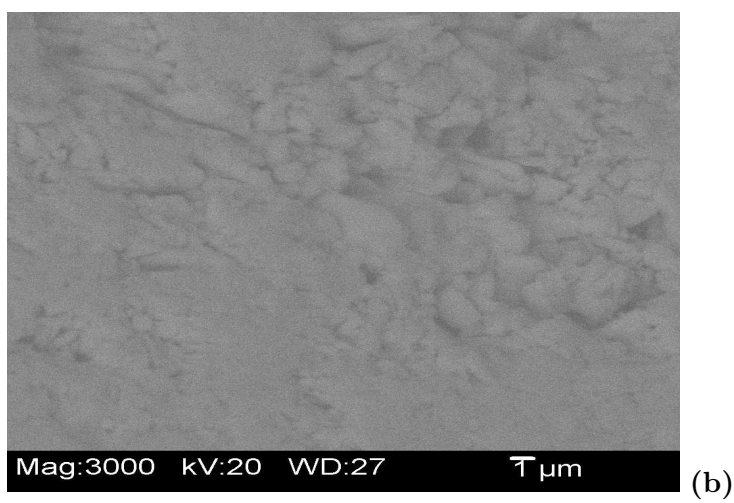
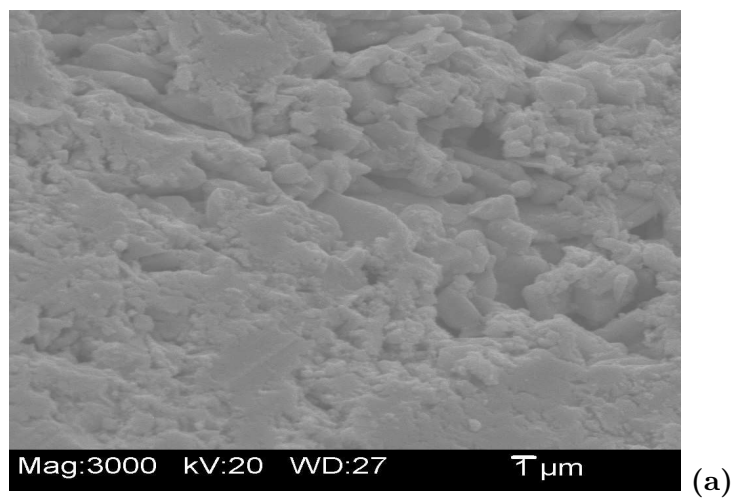


Figure 4.9: $\text{Bi}_2\text{Sr}_2\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.9875}$ SE (a) and BSE (b) micrographs, and EDS (c) spectrum.

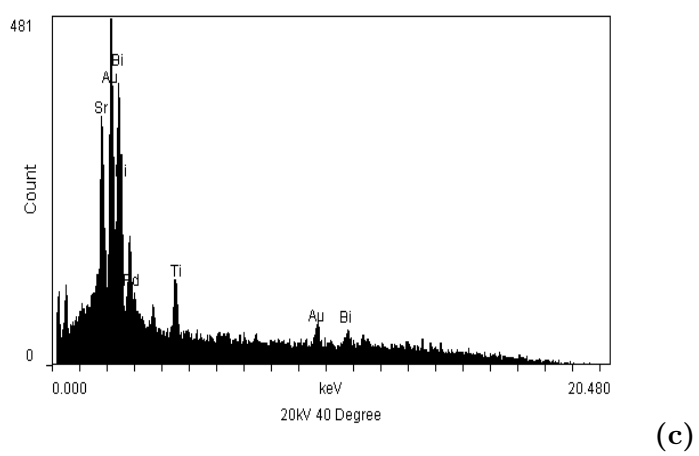
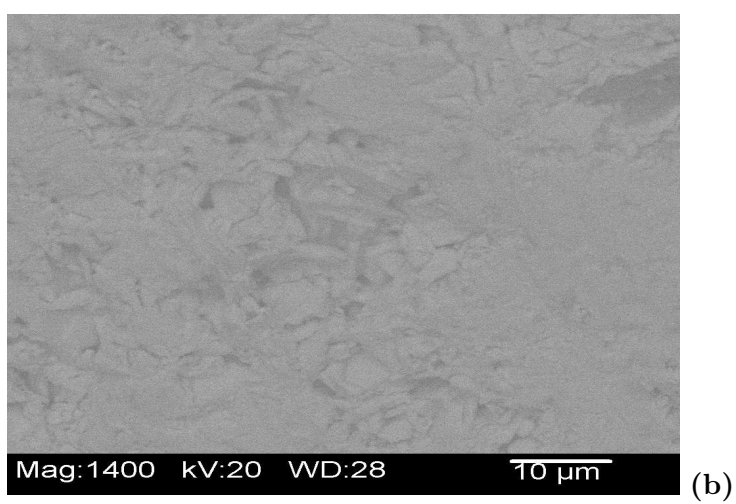
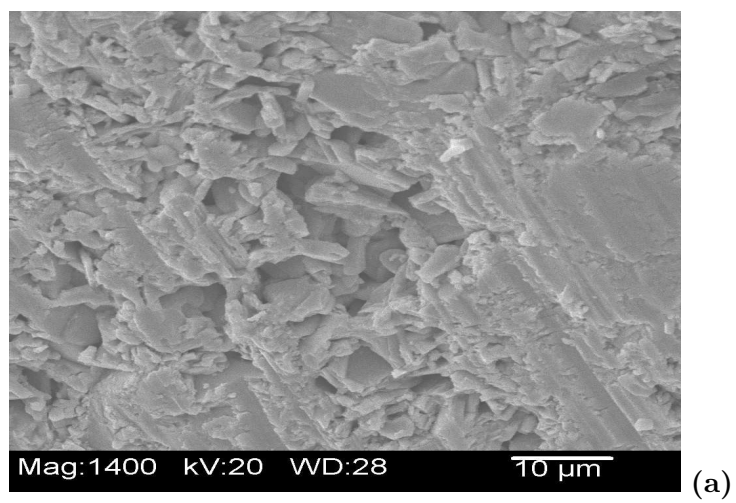


Figure 4.10: $\text{Bi}_2\text{Sr}_{1.5}\text{Ca}_{0.5}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.9875}$ SE (a) and BSE (b) micrographs, and EDS (c) spectrum.

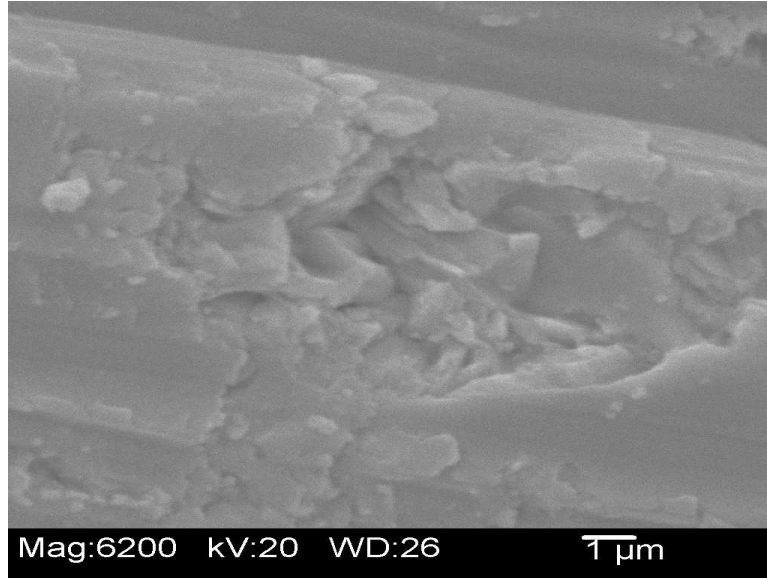


Figure 4.11: Secondary electron micrograph for $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ba}_{0.525}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.975}$.

Table 4.V: Nine Non-stoichiometric Site Mixing Compositions.

Substitution Method	Alkaline Earth Content
	Ca
A	$\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ca}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$
B	$\text{Bi}_2\text{Sr}_{1.5}\text{Ca}_{0.5}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.9875}$
AB	$\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ca}_{0.525}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.975}$
	Sr
A	$\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_2\text{TiO}_{11.9875}$
B	$\text{Bi}_2\text{Sr}_2\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.9875}$
AB	$\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.975}$
	Ba
A	$\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ba}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$
B	$\text{Bi}_2\text{Sr}_{1.5}\text{Ba}_{0.5}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.9875}$
AB	$\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ba}_{0.525}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.975}$

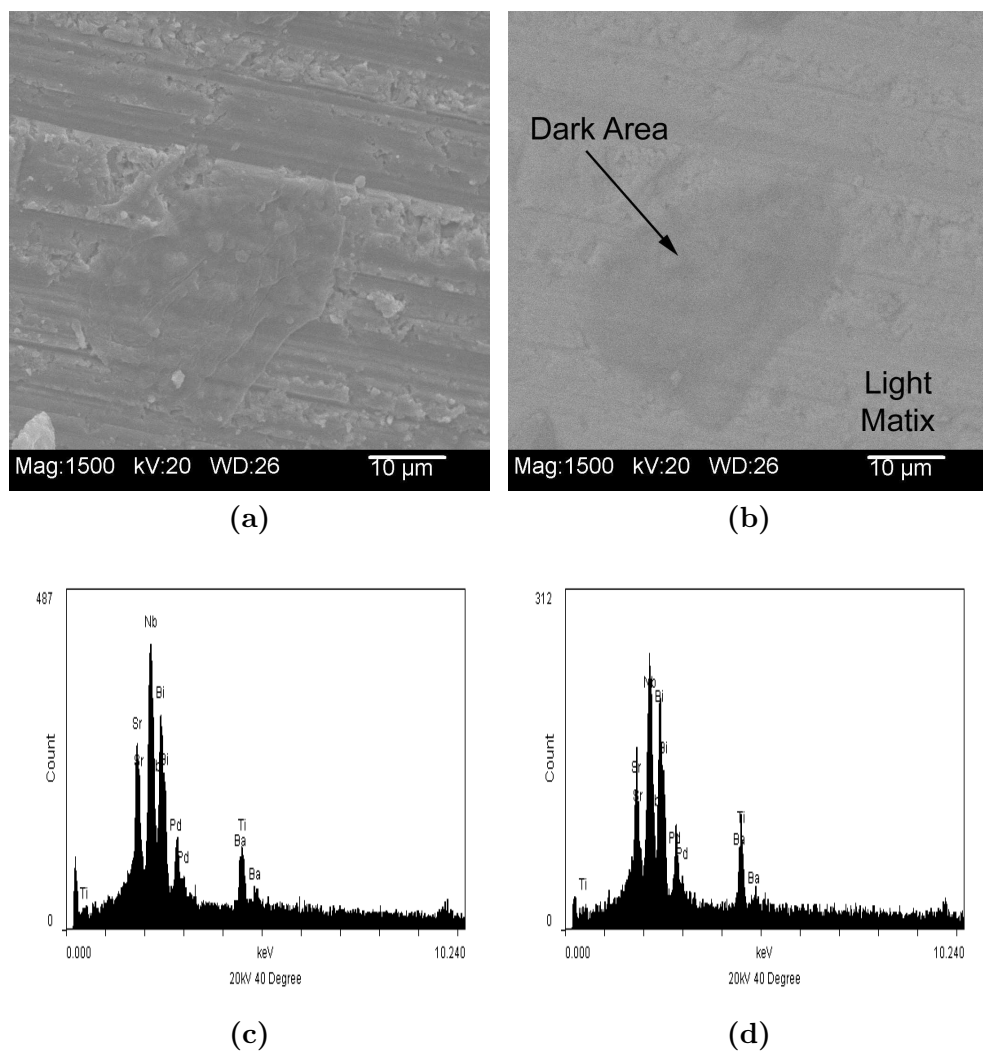


Figure 4.12: SE (a) and BSE (b) micrographs for $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ba}_{0.525}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.975}$, highlighting the “dark” chunk and lighter matrix and EDS spectra for the “dark” and light regions in (c) and (d).

4.7 Site Mixing Results, Crystal Structure Analysis

Crystal structure data for the nine synthesized phases can be found in the appendix. For reasons mentioned earlier, none of the compositions analyzed only with x-ray diffraction will be discussed in this section, except when discussing cation positions and lattice parameters. The samples that were synthesized had only the slightest compositional difference between themselves and their stoichiometric counterparts, so as a result, all of the compositions synthesized here will be compared directly to their stoichiometric equivalents. For example, only 0.025 additional Ca^{2+} was substituted for Bi^{3+} in $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ca}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$ and this would result in a theoretical oxygen stoichiometry of 11.9875 which is only slightly different than stoichiometric. However, the forced introduction of oxygen vacancies into the three layer Aurivillius structure did have a clear impact on specific areas of the structure. The analysis of this section will hinge upon a group of focused questions in an attempt to explain the effect of the cation substitution and ultimately oxygen vacancy creation on the crystal structure. These questions are:

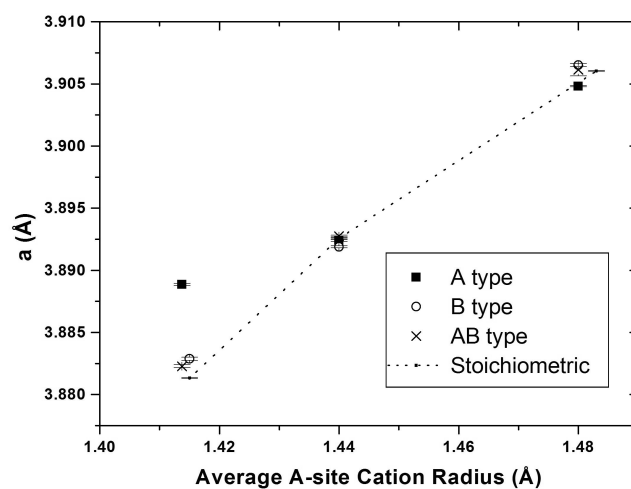
1. What is the effect of the additional alkaline earth or Ti^{4+} on the crystal structure?
2. How does the unit cell change?
3. Does the degree of Bi and A or Nb and Ti site mixing change?
4. How is the BVS of the various sites affected?
5. Where does the additional alkaline earth or Ti^{4+} reside?
6. Do the oxygen thermal parameters give an indication of the location of oxygen vacancies?
7. Which sites are oxygen deficient?
8. How does the oxygen stoichiometry change with unit cell size?
9. Are strain induced vacancies still created?

In general, the alkaline earth substitution into the non-stoichiometric crystal structure behaves exactly the same as the stoichiometric counterparts in terms of lattice parameter and site mixing variations. Increasing the size of the substituted alkaline earth increases

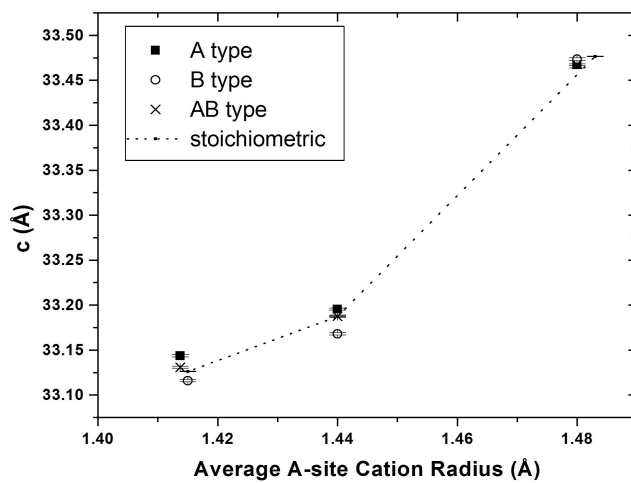
the size of the unit cell and the degree of site mixing. Figure 4.13 shows the a and c lattice parameters as a function of ACR. Almost no change is observed for the A type compositions versus stoichiometric except for the a lattice parameter for $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ca}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$ which is much larger than stoichiometric.

Site mixing between the Bi and A sites increases as larger alkaline earth is substituted on the A site. Figure 4.14 shows the total amount of alkaline earth occupying the Bi site. Compared to stoichiometric, a slight increase in mixing is observed. Possibly related to the change in a lattice parameter, the degree of site mixing for $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ca}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$ is noticeably larger than its stoichiometric counterpart, However, the error bars (all error bars are 3σ) indicate that the alkaline earth occupancy on the Bi site is not known with as much certainty. While Figure 4.14 highlights the total amount of alkaline earth occupying the Bi site, Figure 4.15 depicts the amount of Ca^{2+} or Ba^{2+} occupying the Bi site. The Ca^{2+} cation does not occupy the Bi site in any appreciable degree, but Ba^{2+} appears to favor Bi site occupation. This is the identical trend observed for the stoichiometric compositions. Notice that the overall degree of Ca^{2+} on the Bi site is significantly lower for $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ca}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$ than stoichiometric, whereas only a small difference is observed for the Ba compositions. This point is interesting because slightly more Ca^{2+} or Ba^{2+} has been added to the sample, yet it leads to an overall decrease in the amount of Ca^{2+} or Ba^{2+} presence on the Bi site. Because the overall degree of site mixing degree increases, the additional alkaline earth must come from Sr^{2+} .

The analysis of the stoichiometric compositions revealed that some Nb-Ti mixing occurred, but was unaffected by changes in ACR. Figure 4.16 shows the degree of Nb-Ti site mixing in the non-stoichiometric compositions. The pattern of site mixing is different than stoichiometric in that the trend shows a high point at $\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_2\text{TiO}_{11.9875}$ instead of a constant, invariant, Nb-Ti ratio, $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ca}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$ shows more Nb-Ti mixing than stoichiometric, $\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_2\text{TiO}_{11.9875}$ shows less, and no change is observed for $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ba}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$. Increased Nb-Ti mixing is observed for $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ca}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$, decreased mixing for $\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_2\text{TiO}_{11.9875}$, and no change for $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ba}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$. The B and AB types show increased mixing over stoichiometric. The increased mixing in $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ca}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$ may be related to the increased Bi A mixing and the larger lattice parameter.



(a)



(b)

Figure 4.13: a (a) and c (b) lattice parameters for the non-stoichiometric samples. Error bars are three sigma.

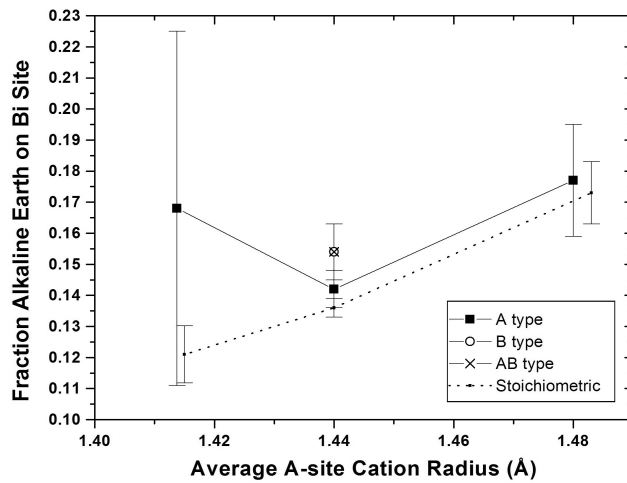


Figure 4.14: Total fraction of alkaline earth occupying the Bi site for the non-stoichiometric compositions. Error bars are three sigma.

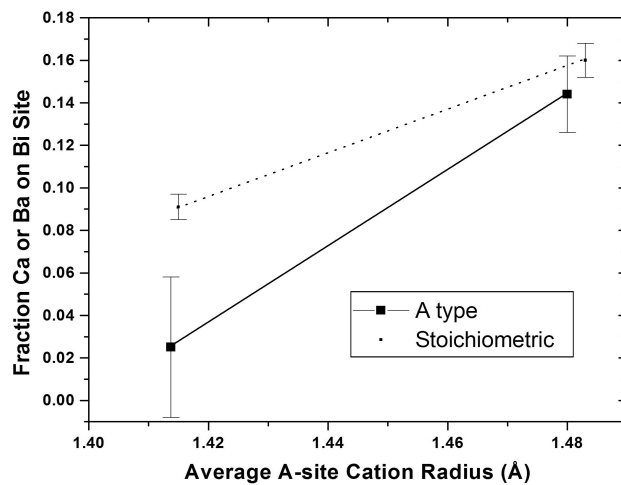


Figure 4.15: Fraction of Ca^{2+} or Ba^{2+} occupying the Bi site for the non-stoichiometric compositions. Error bars are three sigma.

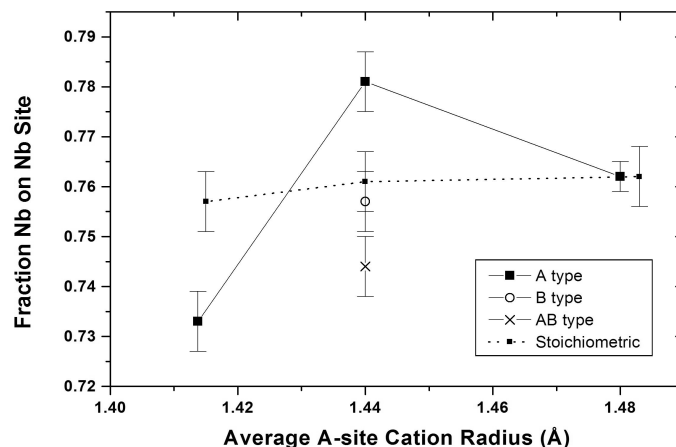


Figure 4.16: Fraction Nb^{5+} on the Nb site for the non-stoichiometric compositions. Error bars are three sigma.

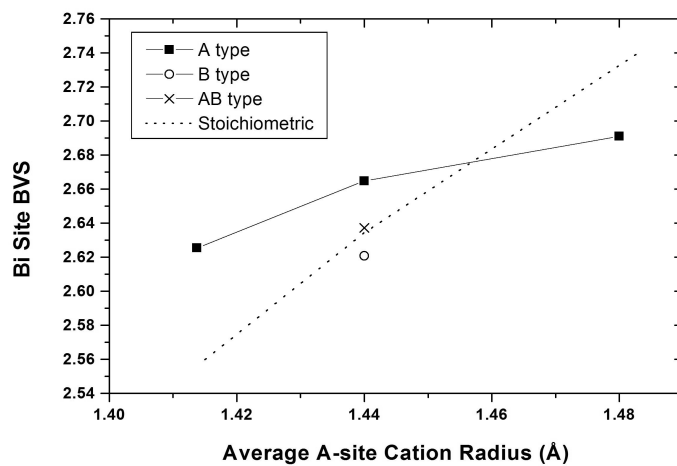
Bond valence sum (BVS) calculations for the non-stoichiometric compositions show the large differences compared to stoichiometric. Figures 4.17 and 4.18 show the BVS calculations for the Bi, A, Nb and Ti sites respectively. Overall, the trends displayed by the Bi and A sites are the same as stoichiometric.

As mentioned previously in Chapter 3, the Bi site BVS did not appear to correlate with other structural features, but it did increase with ACR, and this is similar to what is observed in the present compositions. The A site was found to have the greatest impact on the unit cell. For example, the A site BVS was found to increase linearly with a lattice parameter. Furthermore, the A site BVS was directly related with the degree of site mixing between the Bi and A sites. The A site BVS was shown to increase with ACR as larger alkaline earths were substituted into the lattice. Ba^{2+} substitution had a greater impact than Ca^{2+} substitution on increasing the A site BVS due to its large size. All of the A site BVS for stoichiometric compositions were overbonded, meaning that the formal cation charge was greater than the ideal cation valence for that cation. Another way of describing overbonding is that the bonds surrounding the atom in question are in a state of compression.

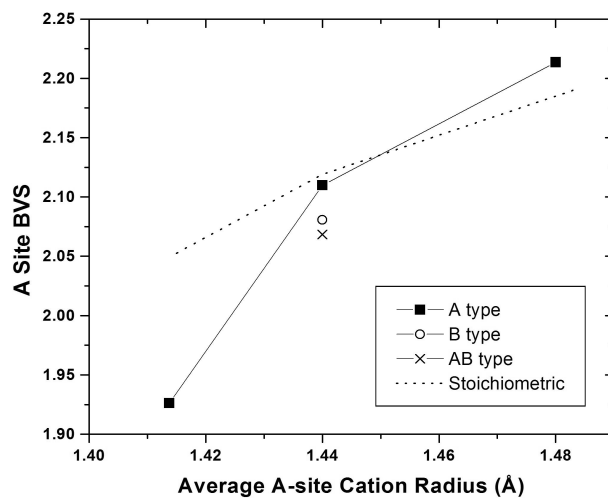
In the present case, the A site BVS were almost identical to stoichiometric except for $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ca}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$. $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ca}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$ shows an underbonded A site with a BVS of 1.93. In other words the A-oxygen bonds were in a state of tension. The Nb and Ti site BVS show the largest departure from stoichiometric. $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ca}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$ and $\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_2\text{TiO}_{11.9875}$ show significantly lower Nb site BVS's than stoichiometric while the $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ba}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$ BVS is unchanged. The Nb site BVS was previously shown to be directly related with the degree of Nb-Ti site mixing. If we analyze the variables related to the Nb site, we can find justifications for the BVS behavior. $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ca}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$ showed increased Ti^{4+} on the Nb site. The additional 4+ charge reduces the overall BVS on that site. However, Figure 4.16 showed even less Ti^{4+} substituting for Nb^{5+} in $\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_2\text{TiO}_{11.9875}$, yet its Nb site BVS was still low. Thus, some other factor besides the Nb site occupancy must be affecting the BVS.

The Ti BVS is markedly different than stoichiometric. Whereas the stoichiometric compounds had an increasing Ti BVS, the non-stoichiometric compositions show a relatively flat trend. While probably no real difference between $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ca}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$ and stoichiometric occurs, $\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_2\text{TiO}_{11.9875}$ and $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ba}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$ have lower Ti BVS than stoichiometric. Thus, while the Bi and A sites show moderate changes from stoichiometric, the Nb and Ti sites show large differences. Since it was shown that the Ti site plays a role in determining residual structural strain, it would be interesting to note the effect of the low Ti BVS on the present compositions.

The changes in BVS were directly related to bond length changes between the respective cations and oxygen anions. As a bond length increases, generally, the corresponding BVS decreases, etc, as per Equation 3.2. Previously when analyzing the stoichiometric compositions, it was found that all A-O bond lengths increased as a function of ACR. Figure 4.19 shows a similar relationship for the A-O1, A-O3, and A-O5 bond lengths in the non-stoichiometric compositions. While the A-O1 bonds show little difference from stoichiometric for any composition, the A-O3 and A-O5 show significant differences. The A-O3 was much larger for $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ca}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$ compared to stoichiometric, whereas it was unchanged from stoichiometric for the other compositions. The larger A-O3 and A-O5 bonds for $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ca}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$ explain the smaller observed A site BVS. The A-O5 bond lengths showed an interesting trend in that

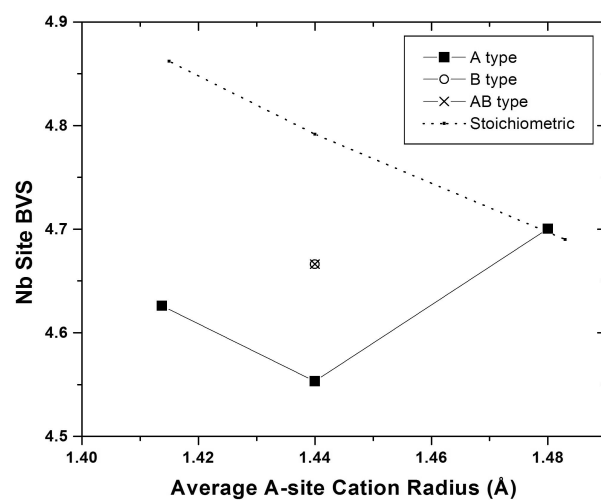


(a)

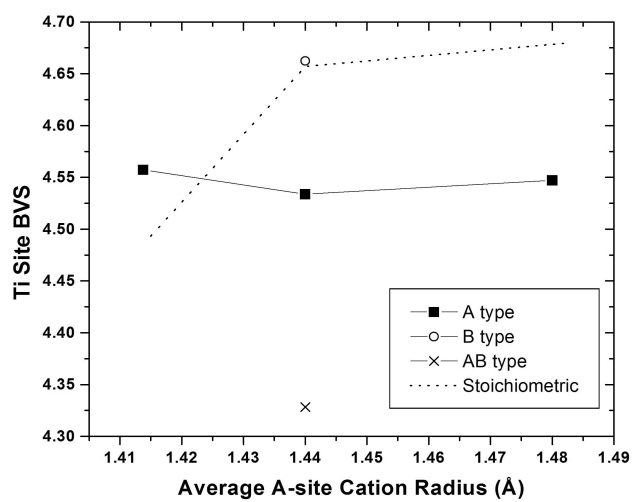


(b)

Figure 4.17: Bond Valence Sum versus ACR for the Bi (a) and A (b) sites for the non stoichiometric samples.



(a)



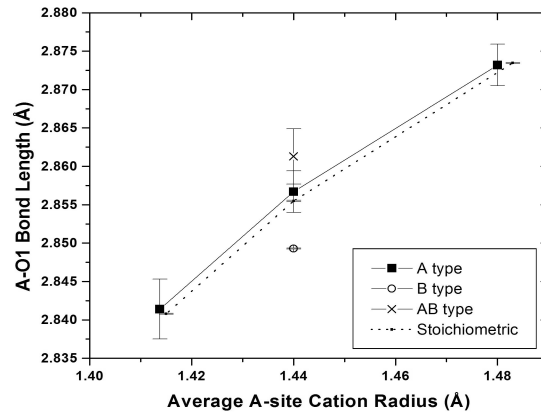
(b)

Figure 4.18: Bond Valence Sum versus ACR for the Nb (a) and Ti (b) sites for the non stoichiometric samples.

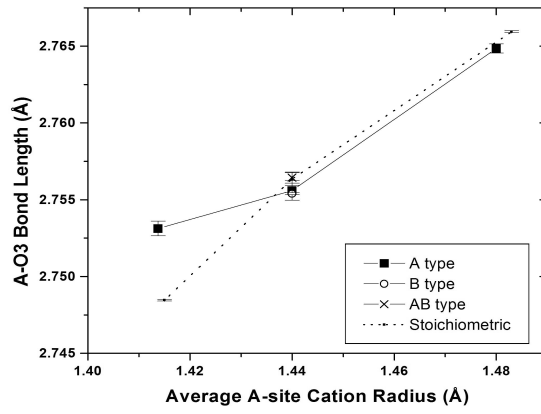
the A-O5 for $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ca}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$ was approximately the same size as that of $\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_2\text{TiO}_{11.9875}$ however it was not immediately apparent why this would occur. $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ba}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$ shows no A-O bond length difference from stoichiometric.

The Nb-O bond lengths as seen in Figure 4.20, showed clear differences over stoichiometric. All Nb-O3 were smaller, all Nb-O4 were larger, and all Nb-O5 were lower than stoichiometric. As with the stoichiometric, in general, all Nb-O bond lengths increased with ACR. The changes in A-O and Nb-O bond lengths over stoichiometric could be due to the unit cell expanding in the a or c direction. In other words, if a bond length increases, this could cause the unit cell to increase. The Nb-O3 and Nb-O4 bonds lie in the c direction whereas the Nb-O5 bond lies in the a direction. Therefore, an Nb-O3 or Nb-O4 bond length increase or decrease would directly effect the c lattice parameter and the Nb-O5 would effect the a lattice parameter. Despite the fact that the Nb-O3 and Nb-O4 bonds change in opposite directions, the overall change is an increase in the Nb-O bond length in the c direction and thus an increase in that lattice parameter. Furthermore, the increase in Nb-O5 bond length for $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ca}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$ and $\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_2\text{TiO}_{11.9875}$ help explain the slightly larger a lattice parameter over stoichiometric compositions. Similarly, the A-O3 bond length lies in the plane of the a axis, and the corresponding A-O3 increase for $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ca}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$ explains the larger a lattice parameter. The A-O5 on the other hand would effect both a and c .

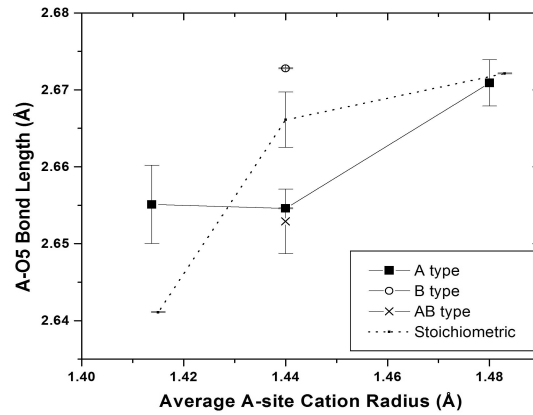
The differences in Nb-O bond lengths and for that matter, the A-O bond lengths, must be associated with changes in the atomic coordinate of the Nb (and A) site. The a lattice parameter does not change appreciably between the corresponding stoichiometric and non-stoichiometric compositions (excluding $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ca}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$), yet the c lattice parameters are slightly larger for all of the non-stoichiometric compositions. Thus, the Nb atomic position would have to be positioned farther away from the unit cell center than stoichiometric because this would cause an overall expansion of the cell at least in the c direction. Figure 4.21 shows the atomic coordinate of the Nb site with respect to ACR. As expected, the Nb position is slightly displaced farther away from the unit cell center and closer to the O4 oxygen position. Despite the Nb displacement the Nb-O4 bond length still increases ($\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ca}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$ and $\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_2\text{TiO}_{11.9875}$). Therefore, the O4 oxygen position must also move farther from the unit cell center. Figure 4.22 shows this to be the case as the O4 oxygen position is significantly farther from the unit cell



(a)

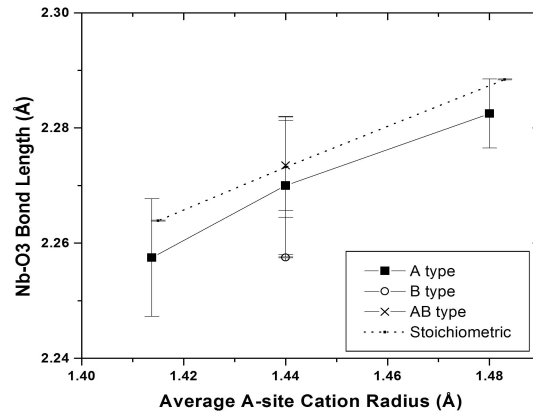


(b)

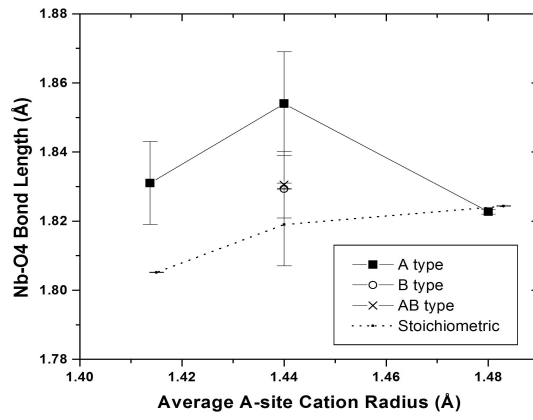


(c)

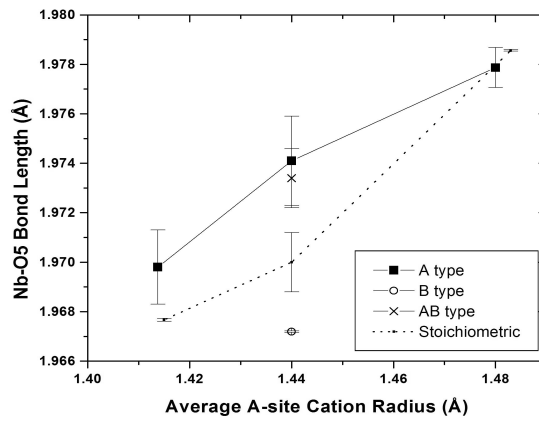
Figure 4.19: Bond lengths for A-O1 (a), A-O3 (b), and A-O5 (c) for the non-stoichiometric samples.



(a)



(b)



(c)

Figure 4.20: Bond lengths for Nb-O3 (a), Nb-O4 (b), and Nb-O5 (c) for the non-stoichiometric samples.

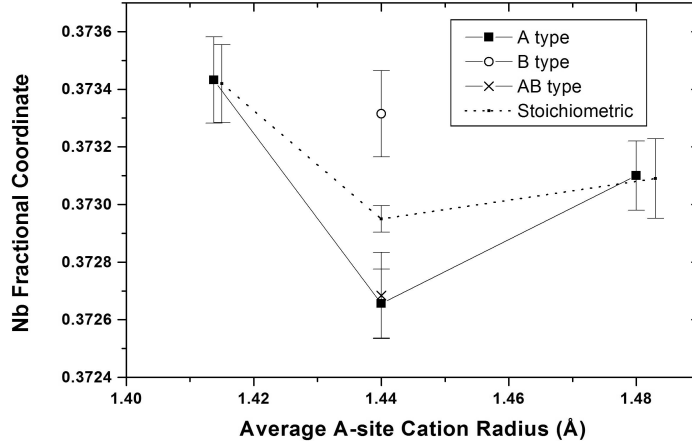


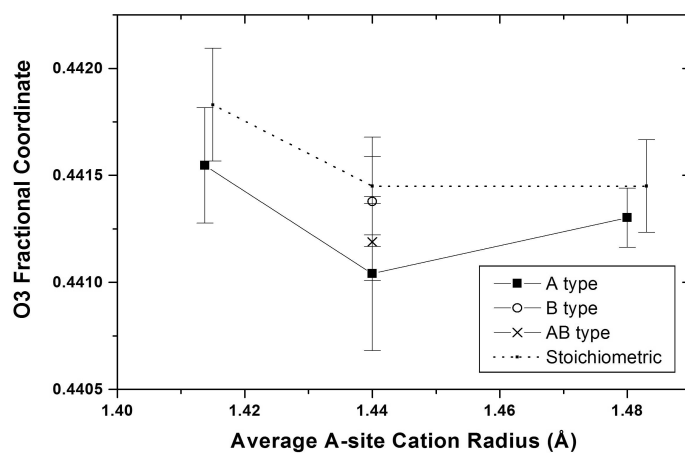
Figure 4.21: Fractional coordinate of the Nb site in the non-stoichiometric compositions.

center than stoichiometric. The O3 site has also been displaced from the unit cell center as seen in Figure 4.22 and explains the slightly shorter Nb-O3 bonds. The O5 oxygen position also changed slightly from stoichiometric, but due to the proximity of the error bars, the change is probably minimal. Interestingly, the A site coordinate did not appear to change as compared to stoichiometric.

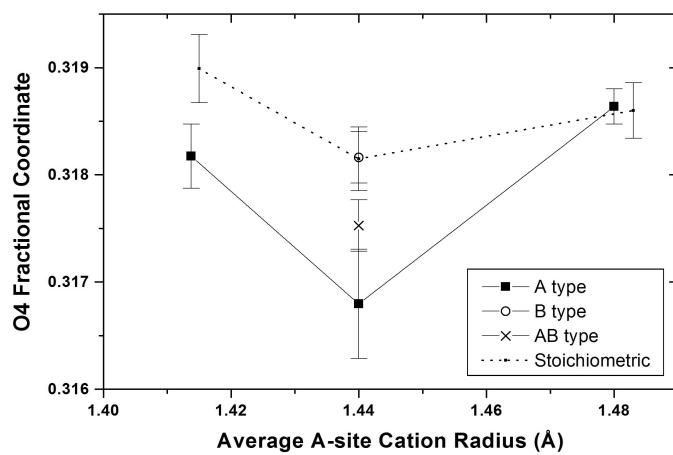
The compositions studied in the present work all have either additional alkaline earth and/or Ti^{4+} . It is clear that the additional alkaline earth resides on the A site from observation of Figure 4.15 and 4.14. Because the overall degree of site mixing increases, yet less Ca^{2+} or Ba^{2+} resides on the Bi site, the additional alkaline earth must stay on the A site. $\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_2\text{TiO}_{11.9875}$ on the other hand is not subject to this limitation, and it is clear that the additional Sr^{2+} moves to the Bi site.

Calculation of ACR involved a bit of thought, because these samples had an additional amount of Ca, Sr or Ba and it had to be decided where to put the additional cation since the occupancy of the A site could not stay at 2.025. Normally, ACR was calculated via the following Equation 4.1

$$ACR = \frac{(1.5 * r_{\text{Sr}^{2+}}) + (0.5 * r_{\text{A}^{2+}})}{2} \quad (4.1)$$



(a)



(b)

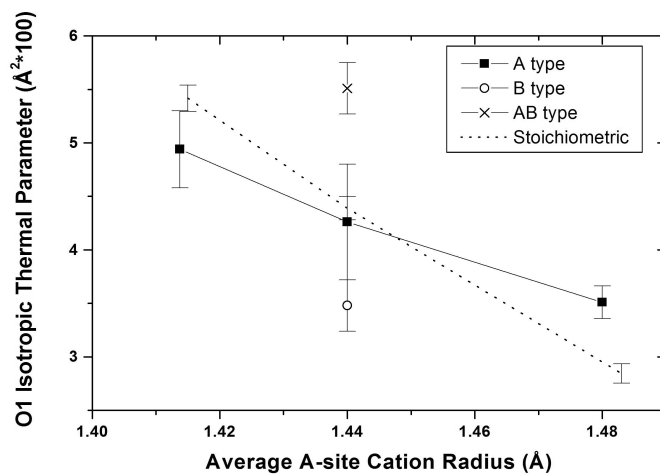
Figure 4.22: Fractional coordinate for the O3 (a) and O4 (b) sites for the non-stoichiometric samples.

Here, $r_{Sr^{2+}}$ represents the ionic radius of Sr^{2+} and $r_{A^{2+}}$ is the ionic radius of the substituting alkaline earth cation. Note that the total occupancy of the A site is two. In Chapter 3 it was observed that Ca^{2+} had a strong preference for remaining on the A site whereas Ba^{2+} preferred to mix to the Bi site. As a result, in the calculation of ACR for the Ca samples, the additional Ca^{2+} was left on the A site, and 0.025 Sr^{2+} was moved to the Bi site in order to maintain an occupancy of 2. The new ACR equation for the Ca samples is seen in Equation 4.2. The ACR for the Ba substituted compositions still used Equation 4.1. The same two equations were used for the B and AB type compositions.

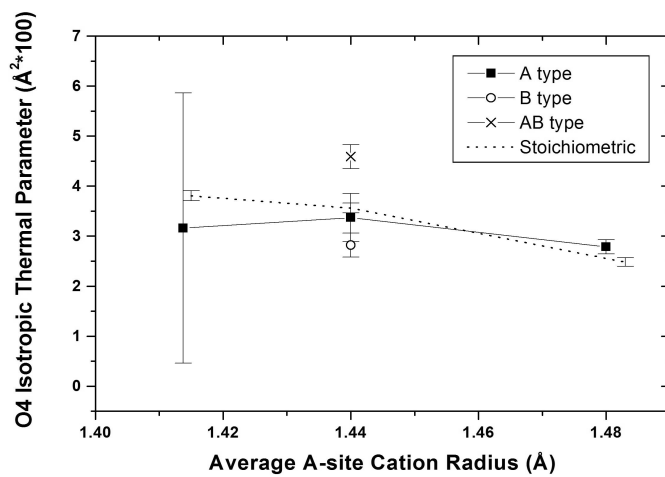
$$ACR = \frac{(1.475 * r_{Sr^{2+}}) + (0.525 * r_{A^{2+}})}{2} \quad (4.2)$$

The beauty of the neutron diffraction measurements is that they allowed for the oxygen thermal parameters to be refined. Since these compounds all had oxygen vacancies present, a high oxygen thermal parameter would be the first good indication of the oxygen vacancy location. Remembering back to the stoichiometric compounds, the O1 thermal parameters were found to be unusually high, especially the Ca substituted compositions (see Figure 3.16). It would be interesting to see if a similar effect was observed in the non-stoichiometric compositions. Figure 4.23 shows the oxygen thermal parameters for the O1 and O4 sites. Only the O1 and O4 thermal parameters showed larger than normal values. Similar to the stoichiometric, the O1 thermal parameter value was much larger than normal for an oxygen site. The O1 thermal decreased with ACR similar to stoichiometric.

Once a suitable thermal parameters were obtained and recorded, the O1 and O4 thermals were reset to the default value of $0.025 \text{ \AA}^2$ and then the oxygen occupancies were refined. As mentioned previously, oxygen deficient sites were directly related to sites with large thermal parameters. Figures 4.24 and 4.25 show the oxygen fractional occupancies for the O1, O3, O4 and O5 sites respectively. Interestingly, oxygen sites such as the O3 and O5 were found to be deficient despite the fact that the respective thermal parameters were normal. The O1 site showed the largest degree of oxygen deficiency, followed next in order of overall oxygen deficiency by the O3, O5, and O4 sites. The O1 and O3 occupancies increased towards unity with ACR with, $Bi_{1.975}Sr_{1.5}Ba_{0.525}Nb_2TiO_{11.9875}$ being fully occupied on the O3 site. While an oxygen deficiency existed for the O4 and O5 site, no overall pattern was observed as a function of ACR.

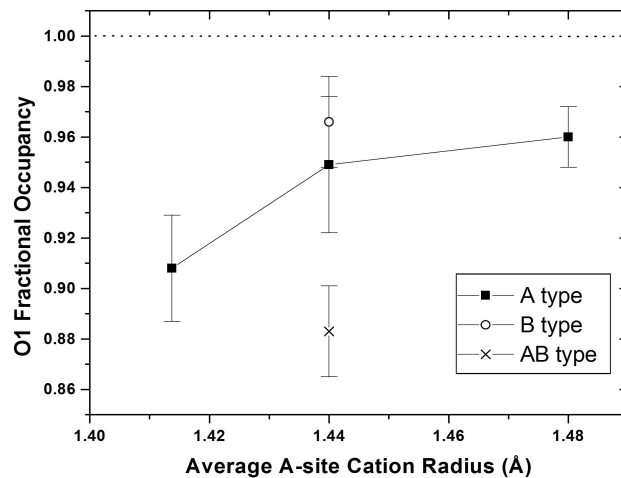


(a)

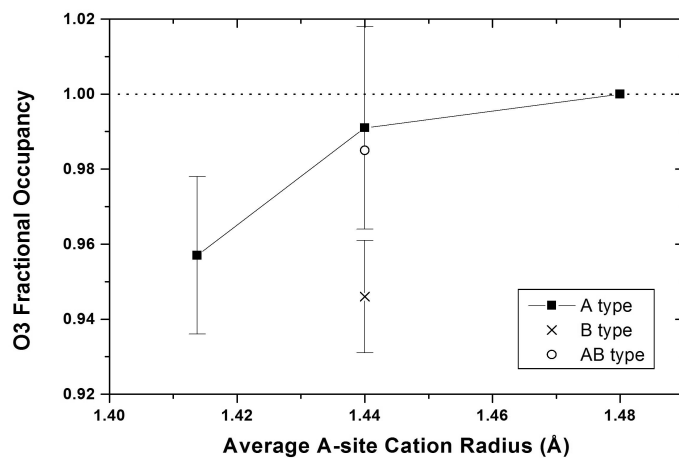


(b)

Figure 4.23: Isotropic thermal parameters for the O1 (a) and O4 (b) oxygen sites for the non-stoichiometric samples.

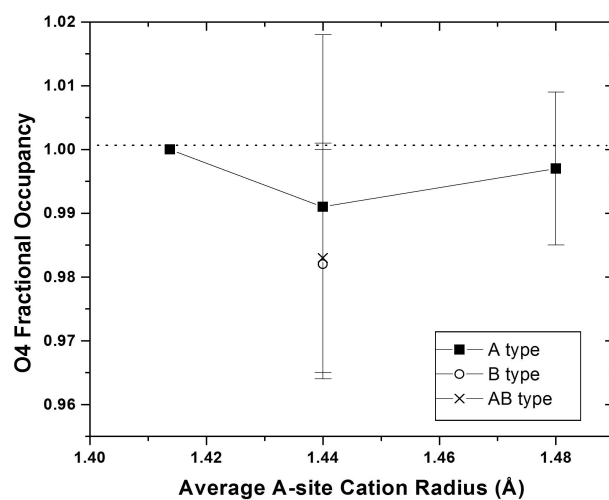


(a)

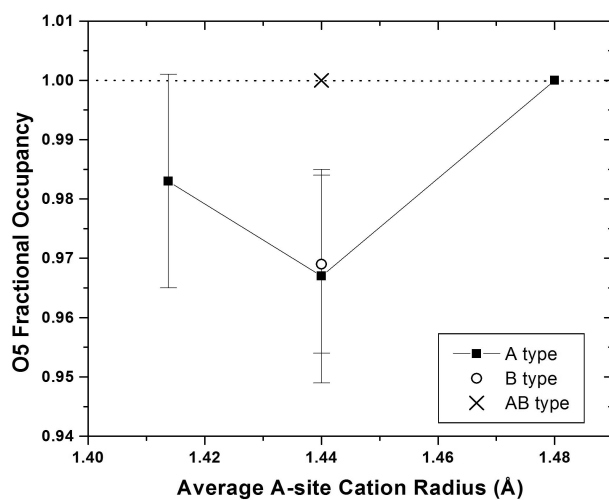


(b)

Figure 4.24: Oxygen fractional occupancies for the O1 (a) and O3 (b) sites for the non-stoichiometric samples.



(a)



(b)

Figure 4.25: Oxygen fractional occupancies for the O4 (a) and O5 (b) sites for the non-stoichiometric samples.

The O1 oxygen deficiency in the stoichiometric compositions was thought to be directly the result of unrelieved strain between the A and Ti sites. In other words, the vacancies that were created were strain induced. The Ca substituted compositions showed the largest O1 deficiencies. This was explained by the observation that because the A site now contained a significant amount of smaller Ca^{2+} , it decreased the A site BVS and the a lattice parameter for the cell. The shrinking a forced the A-O1,O3,O5 bonds to shrink as a consequence. The Ti site was directly affected by the A-O bond length decrease because the Ti site shares the O1 and O3 oxygens with the A site. As a result, an A-O bond length decrease directly causes a Ti-O bond length decrease. Because the Nb-Ti site mixing ratio did not vary extensively with ACR, the Ti site BVS increased dramatically as a result of the Ti-O bond length decrease. The link between the structure and the large O1 thermal parameters became clear as an O1 vacancy would factor in to lower the Ti BVS back to reasonable values for its level of Nb substitution.

The non-stoichiometric samples showed increased oxygen deficiency compared to stoichiometric. The relationship between the two sets of compositions was not clear and as a result the oxygen stoichiometries of all compositions were analyzed. Since aliovalent substitution was *not* performed on the stoichiometric compositions, any oxygen deficit was assumed to be strain induced. The oxygen stoichiometry for the non-stoichiometric compositions was calculated for each oxygen site, and the results tallied. Then, the amount of oxygen vacancies actually designed into the structure was subtracted from this total giving the amount of strain induced vacancies in the non-stoichiometric compositions. Table 4.VI shows the oxygen deficiency per site, along with the total strain induced vacancies, compared directly with those obtained from the stoichiometric compositions.

It was very interesting to note that the amount of vacancies left over after subtraction roughly equals the amount found in the stoichiometric compositions. The only real differences that occur show up in $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ba}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$ and $\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.975}$ as these show much larger strain induced vacancies than stoichiometric. However, if error bars were applied to the $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ba}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$ data, it is quite likely, especially due to the very small oxygen deficiency, that the result would be the same as the other non-stoichiometric samples. Furthermore, under this light, the result for $\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.975}$ does not appear to be that bad either. The fact that about the same amount of strain induced vacancies were created in the non-

Table 4.VI: Oxygen Stoichiometry for each Oxygen Site.

The total amount of oxygen deficiency per site is listed as well as the amount of strain induced deficiency. The strain induced deficiency for stoichiometric compositions are listed for comparison. A ratio of non-stoichiometric to stoichiometric strain induced oxygen vacancies is listed for comparison.

Oxygen Site	Sample				
	A Ca	A Sr	A Ba	B Sr	AB Sr
O1	0.180	0.096	0.074	0.064	0.225
O3	0.082	0	0	0.027	0.101
O4	0	0	0	0.032	0.026
O5	0.065	0.127	0	0.121	0
total strain induced	0.327	0.223	0.073	0.244	0.353
total from stoich.	0.339	0.211	0.027	0.211	0.211
ratio of NS to Stoich	0.97	1.06	2.68	1.16	1.67

stoichiometric compositions compared to stoichiometric further supports the notion that the oxygen deficiency was indeed strain induced.

4.8 B and AB Type Composition Structural Results

Up to this point, the B and AB type compositions have not been discussed due to the overall complexity of the relationships of all the compositions. The B and AB types will be discussed separately, but will be compared to stoichiometric and A type compositions when appropriate. Furthermore, only $\text{Bi}_2\text{Sr}_2\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.9875}$ and $\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.975}$ will be discussed because they were the only two of the B and AB compositions that have neutron diffraction data.

4.8.1 B Type Structural Analysis

The B type compositions involved the substitution of additional Ti^{4+} for Nb^{5+} in an effort to create oxygen vacancies. Only a small amount of the substitution occurred, so in general, the major structural trends remained the same as stoichiometric compositions. However, some features were markedly different. $\text{Bi}_2\text{Sr}_2\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.9875}$ was oxygen deficient on all oxygen sites (excluding the O2) however because of the variance in standard

deviation, it was difficult to say that they were significantly different than the A type compositions. Thermal parameters likewise were on par with stoichiometric. The A-O1, A-O5, and all Nb-O bond lengths were significantly different than stoichiometric or the A type compositions. The A-O1 was smaller and the A-O5 was longer than stoichiometric or A type. The Nb-O3 and Nb-O5 were shorter than stoichiometric or A type, but the Nb-O4 was only shorter than the A type (Nb-O4 longer than stoichiometric). The Ti-O and Bi-O bonds lengths were all unremarkable. As we learned previously, the bond length variations were a direct result of cation and oxygen displacements. The A and Nb site cation positions were significantly further displaced towards the center of the unit cell compared to stoichiometric or A type. However, the oxygen positions did not show any significant change over stoichiometric. No remarkable differences are observed in the site mixing trends as the B types follow closely to the stoichiometric trends. B type BVS values are slightly lower for the Bi and A sites, the Nb site BVS is moderately lower, and the Ti site BVS is unchanged from stoichiometric. $\text{Bi}_2\text{Sr}_2\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.9875}$ had an average oxygen stoichiometry compared to the other composition types. $\text{Bi}_2\text{Sr}_2\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.9875}$ shows slightly smaller a and much smaller c lattice parameters compared to stoichiometric.

4.8.2 AB Type Structural Analysis

The AB type compositions involved the simultaneous substitution of additional alkaline earth *and* Ti^{4+} into the crystal structure. This compound should give double the oxygen vacancies of the A or B types. Just like the A and B types, the major structural trends with ACR were the same for the AB type compositions. But, some of the minor features were different. For example, the AB type showed O1, O3 and O4 deficiencies, but no O5 deficiency. Furthermore, the AB type O1 and O3 sites were the most highly oxygen deficient for any composition. Correspondingly, the O1 thermal parameter was the highest of any composition. The O4 thermal parameter was also large for this composition. The A-O1 and A-O3 bond lengths were similar to stoichiometric, yet the A-O5 was smaller than stoichiometric and had the same length as the A type composition. Similarly, the Nb-O3 and Nb-O5 were unchanged from stoichiometric, while the Nb-O5 was larger, but the same size as the A type composition. Unlike the B type composition, the A and Nb cation position showed no displacement compared to stoichiometric. The oxygen positions did show some variation. The O3 and O4 moved away from the unit cell center whereas the O5 moved

towards the center. Most of the site mixing trends were unchanged from stoichiometric. However Figure 4.16 showed increased Nb-Ti mixing for $\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.975}$ compared to stoichiometric, B, or A type. BVS variation in general had the same pattern as the B type composition, except for the Ti site BVS which had the lowest value of any composition. Interestingly, $\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.975}$ was the most highly oxygen deficient composition. The lattice parameters for $\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.975}$ are unchanged from stoichiometric.

4.9 Non-Stoichiometric Crystal Structure Discussion

Analysis of the non-stoichiometric compositions revealed that a small modification to the crystal chemistry resulted in a significant change in the crystal structure. Some trends were identical however, such as the lattice parameter variation with ACR, the degree of site mixing with ACR, and the Bi and A site BVS variation with ACR. From previous discussion, it was observed that BVS's decreased upon allowing the oxygen vacancies to be included in the BVS calculations. This observation should not be surprising because if an atom is not present, then it can't form a bond, and thus, the bond can not contribute to the BVS. Obviously, the lack of an oxygen atom resulted in the BVS decrease in each cation site in the crystal structure. However, the missing fraction of oxygen wasn't the only factor which contributed to the BVS decrease. Bond lengths heavily influence the BVS calculations, and as was observed, several key bond lengths increased or decreased as a result of the crystal chemistry change. The factor initiating the bond length change was twofold, presence and effect of the oxygen vacancy on the surrounding oxygen anions. Figure 4.26 shows a schematic of the O1 and O3 oxygen environment in the three layer structure. Note that the O3 oxygens are in the plane of the O1 oxygen, and form the apical bonds to the Ti^{4+} cation (the O1 form the four in-plane bonds of the Ti octahedra). It is easier to understand the effect of cation vacancies on a crystal structure. A vacant cation site leaves several oxygen anions without a terminus, and as a result, they are pulled in closer towards the other cation they are bound to. This in effect increases the apparent radius of the cation vacancy. The structural change imposed on the oxygen anions is directly related to the loss of the cation. When an oxygen vacancy occurs, the effect on the structure is indirect, but the behavior is similar. The loss of an oxygen will reduce the charge shielding

between near neighbor cations and as a result, the cations will want to distance themselves from each other. If displacement is not an option, then increasing the cell volume may accomplish this goal. In the present situation, it was not clear what effect the oxygen vacancies had on the cation positions as no discernable pattern was found. On the other hand, oxygen anions in proximity to an oxygen vacancy, in general, moved away from the vacancy. These details were first highlighted in Figure 4.22. One of the difficulties that appeared in this analysis was the fact that more than one oxygen site was vacant. For example it was difficult to say with certainty that oxygen A moved away from vacancy B, when in fact oxygen A and B both had some amount of oxygen deficiency. The ideal way to observe this would be to find a structure with only one oxygen deficient site and observe how the surrounding oxygen anions responded. Fortunately, $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ba}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$ provided an excellent example to follow because it was primarily deficient on the O1 site. From Figure 4.22, we see that the O3 oxygen moves away from the O1 site. The O3 actually moves away from the O1 in all A type compositions, including the B and AB types. Similarly, samples that had O5 deficiencies, the O4 site moved away from the vacancy. But, these same compositions also had the O1 deficiency and therefore the O3 which we previously stated as moving away from the O1 is now found to move *closer* to the deficient O5 site. If we take a look at the overall oxygen deficiency, the O1 site is more deficient than any other and it is possible that the O3 is actually being influenced more by the O1 vacancy. Therefore, we can state that in general, when a site is vacant, the surrounding oxygen anions will move away from the vacancy unless they are acted on by a more dominant vacancy.

While the oxygen trend is clear, the reason for it is not well understood. The oxygen displacement follows the opposite trend of a cation vacancy. The oxygen anions that undergo displacement are not bound to the vacant oxygen site, but, every time a vacancy occurs, it affects two different cations. In the case of the O1 vacancy, the A and Ti sites are directly affected. The loss of one of the cation-anion bonds might trigger the cation to pull the remaining oxygen anions closer to itself, but this does not occur, rather, the A-O and Ti-O bonds all increase in length.

Ultimately, it should now be understood that the repositioning of the oxygen anions leads to a corresponding increase or decrease in the cation-oxygen bond length and thus decreases or increase the BVS for that site.

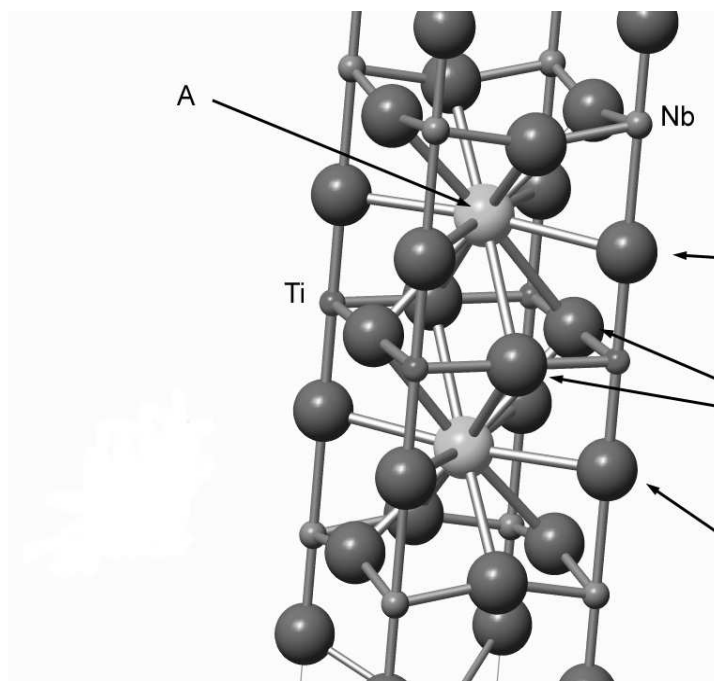


Figure 4.26: Schematic of the cation-oxygen environment for an O1 vacancy in the three layer Aurivillius structure.

The non-stoichiometric structure contained more oxygen vacancies than the stoichiometric compositions and more vacancies than were actually added to the structure. In Chapter 3, the assumption was made that a portion of these vacancies were the result of residual lattice strain between the A and Ti layers of the structure. Furthermore, once the total vacancy fraction was decomposed, it was learned that roughly the same amount of strain induced vacancies were created in the non-stoichiometric compositions as were created in the stoichiometric compositions. We also know from Chapter 3 that the oxygen position and cation-oxygen bond length changes acted to change the a and c lattice parameters. While we can make the assumption concerning the strain induced vacancies, nothing has been discussed concerning the degree of oxygen vacancy concentration as a function of crystal structure. If we plot the oxygen stoichiometry as a function of a lattice parameter as seen in Figure 4.27, we see an interesting relationship. Oxygen stoichiometry appears to be linearly related to the a lattice parameter. In other words, increasing the a lattice parameter decreases the number of oxygen vacancies and vice versa. While not linear, the relationship between oxygen stoichiometry and c lattice parameter is similar.

The stoichiometric compositions also show a linear relationship with respect to the a lattice parameter.

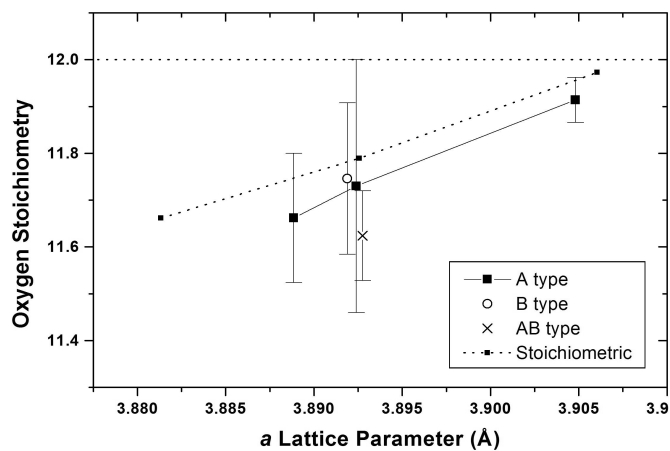
We learned in Chapter 3 that A site lattice strain was linearly related to the a lattice parameter (see Figure 3.5) and as a result, the oxygen stoichiometry may also be related to the A site strain. Figure 4.28 plots oxygen stoichiometry as a function of the A site BVS. While not linear for the A type compositions, the trend shows decreased oxygen stoichiometry as the A site BVS increases. Interestingly, the stoichiometric compositions show a nearly linear trend. Because the actual amount of oxygen vacancies added to the structure is small compared to what were actually present, essentially what Figure 4.27 plots is the number of strain induced oxygen vacancies as a function of lattice parameter. The difference therefore, between the stoichiometric and non-stoichiometric samples is simply the additional amount of oxygen vacancies added to the structure. Oxygen stoichiometry was also plotted versus the other three cation site BVS values in order to find a relationship. Figure 4.28 shows that the Bi site has a similar trend as the A site BVS in that larger Bi site BVS show increased oxygen stoichiometry for the non-stoichiometric and stoichiometric compositions. In fact, the oxygen stoichiometry appears to be linearly related to the Bi site BVS. Until this point, the Bi site has not given any clear indication that it affects the crystal structure. This is not to say that it *does not* have an effect, but rather that the relationships haven't been obvious. The Nb and Ti site BVS's showed no relationship with oxygen stoichiometry. Therefore, it now appears that strain induced vacancies are influence by more than just the Ti and A site strain, but also the unit cell size. It is difficult to make this type of statement because why should the unit cell size influence the oxygen stoichiometry of a sample? However, the Aurivillius crystal structure is quite complex and is based on several competing interrelationships. An interlayer strain between the $(\text{Bi}_2\text{O}_2)^{2+}$ layer and perovskite blocks initiates site mixing to mediate the strain. Increasing the size of the A site leads to more site mixing. Secondly, a strain exists within the perovskite block between the A and Ti sites. A strain which leads to the creation of oxygen vacancies and which can be relieved by increasing the A site size. A certain number of oxygen vacancies will be created regardless of the original composition solely as a result of the perovskite block strain. What is still not understood is how the three of these observations are related, although the degree of importance is easily understood. Clearly, the most dominant factor is the $(\text{Bi}_2\text{O}_2)^{2+}$ and perovskite block interlayer strain as this forces the Bi and A site

mixing. This would be followed by the A-site BVS and lastly the perovskite block strain. What the careful user can take from this analysis is that it is possible to manipulate the oxygen stoichiometry of the three-layer Aurivillius structure by changing the unit cell size.

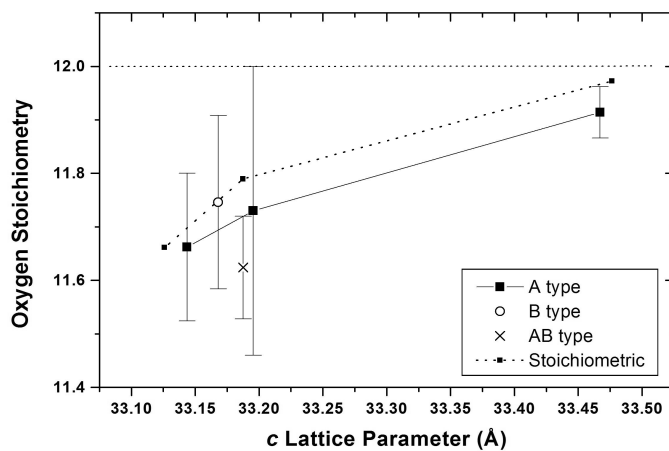
The ionic conductivity of the stoichiometric compositions gave the proof necessary to suggest that oxygen vacancies were present in the crystal structure and focused on the O1 site. In the present situation, oxygen vacancies are still found on the O1 site, but the O3, O4 and O5 have also been found to be deficient. It would be interesting to see the effect of these additional vacancies on the ionic conductivity of the material. Note, while even though the term ionic conductivity is used here, no experiments were performed using ion-blocking electrodes or in reduced pO_2 atmospheres to verify the presence of electronic conduction. However, the large number of oxygen vacancies leads us to suspect that the mechanism of conduction is probably ionic. The electrical properties of these materials will be discussed in Chapter 4.

4.9.1 B and AB Type Composition Discussion

It is interesting that the AB composition follows the same trend as the A type in terms of cation displacement. The “A type” substitution in $Bi_{1.975}Sr_{2.025}Nb_{1.975}Ti_{1.025}O_{11.975}$ apparently dominates the cation displacement. The B type composition $Bi_2Sr_2Nb_{1.975}Ti_{1.025}O_{11.9875}$ favors cation displacement instead of oxygen displacement to account for the oxygen vacancy presence. However, this is interesting seeing that $Bi_2Sr_2Nb_{1.975}Ti_{1.025}O_{11.9875}$ shows about the same amount of strain induced vacancies as $Bi_{1.975}Sr_{2.025}Nb_2TiO_{11.9875}$ and stoichiometric. The presence of the additional Sr^{2+} in $Bi_{1.975}Sr_{2.025}Nb_2TiO_{11.9875}$ must dominate the atomic displacements as modification to the A site must have a stronger effect on the structure than that of the B site. It is not surprising that $Bi_{1.975}Sr_{2.025}Nb_{1.975}Ti_{1.025}O_{11.975}$ has the lowest Ti site BVS because Table 4.VI indicates that it has the largest O1 and O3 deficiencies, which direct factor into the BVS decrease. Thus it is clear from the analysis that B site substitution will introduce roughly the same amount of oxygen vacancies as A or stoichiometric, but it appears to have less impact overall on the structure. The AB type is also successful at introducing oxygen vacancies, but has a larger impact on the crystal structure.

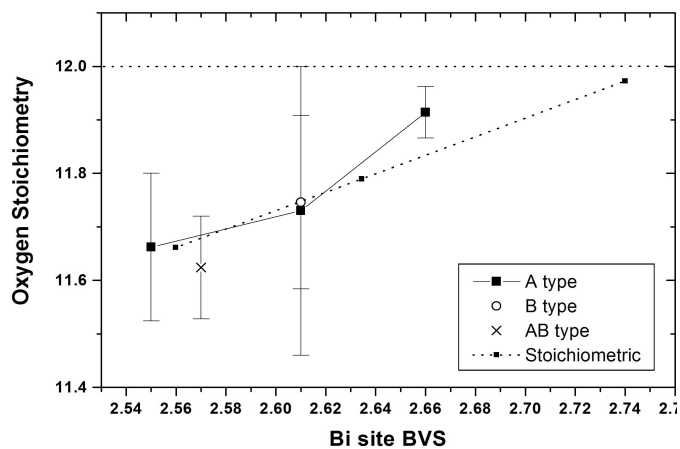


(a)

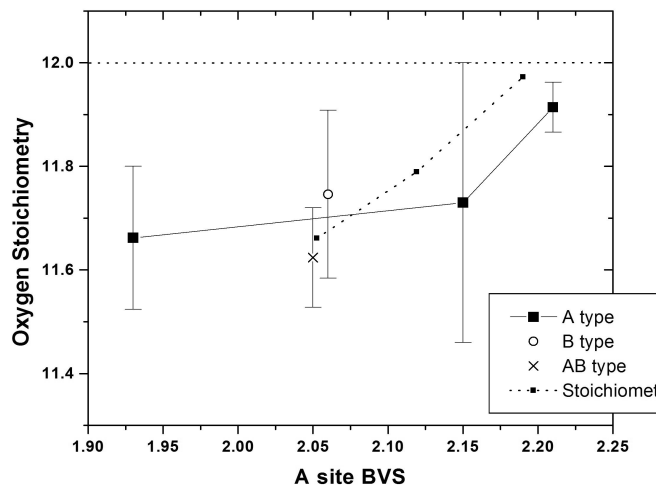


(b)

Figure 4.27: Oxygen stoichiometry as a function of a (a) and c (b) lattice parameter for the non-stoichiometric samples.



(a)



(b)

Figure 4.28: Oxygen stoichiometry as a function of Bi (a) and A (b) site bond valence sum for the non-stoichiometric samples.

4.10 Conductivity Results for the Non-stoichiometric Compositions

The ionic conductivities of all nine compositions (A, B, AB) were obtained from the two point DC measurements. A complete description of the DC conductivity experimental setup can be found the Appendix. Figure 4.29 shows Arrhenius plots for all A, B, and AB compositions respectively. No conductivity plot was obtained for $\text{Bi}_2\text{Sr}_{1.5}\text{Ba}_{0.5}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.9875}$ because the pellet disintegrated in the hot press. A second sample also decomposed when repressed. A complete description of the DC conductivity apparatus and experimental conditions can be found in the appendix. Figure 4.30 shows Arrhenius plots for those A, B, and AB compositions which had neutron diffraction data, for easier comparison to previous discussion.

All samples show ionic conductivities on the order of $10^{-4} \frac{\text{S}}{\text{cm}}$ at 800°C . The B type compositions appear to have slightly higher conductivities at 800°C , than the A or AB, but the degree of difference is very small. Activation energies were calculated from the data by fitting straight lines to the data. Only $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ba}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$ showed what would appear to be two conduction regions. The activation energies as seen in Table 4.VII range from 1 to 1.6eV. The activation energies appear to be similar to those observed by other oxygen vacancy conductors such as $\text{Zr}_{0.81}\text{Y}_{0.19}\text{O}_2$ (1.0eV) and $\text{Ce}_{0.9}\text{Ca}_{0.15}\text{O}_2$ (0.9eV) respectively.⁹⁷

Table 4.VII: Activation Energies of the Non-stoichiometric Compositions.

Composition	Activation Energy (E_a , eV)
$\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ca}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$	1.51
$\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_2\text{TiO}_{11.9875}$	1.47
$\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ba}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$	1.00
$\text{Bi}_2\text{Sr}_{1.5}\text{Ca}_{0.5}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.9875}$	1.62
$\text{Bi}_2\text{Sr}_2\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.9875}$	1.57
$\text{Bi}_2\text{Sr}_{1.5}\text{Ba}_{0.5}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.9875}$	NA
$\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ca}_{0.525}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.975}$	1.45
$\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.975}$	1.57
$\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.975}$	1.04

If the number of charge carriers were to be calculated, then along with the conductivity

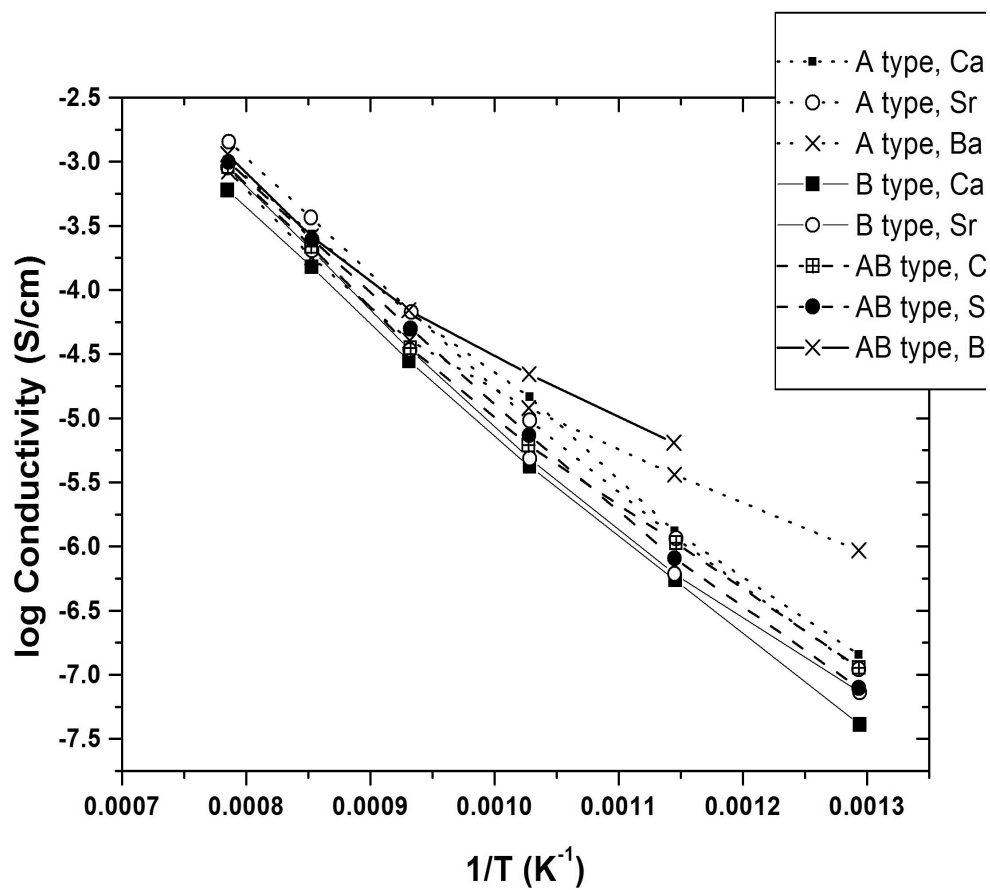


Figure 4.29: Arrhenius plots of log conductivity versus $1/T$ for all non-stoichiometric compositions from DC conductivity measurements.

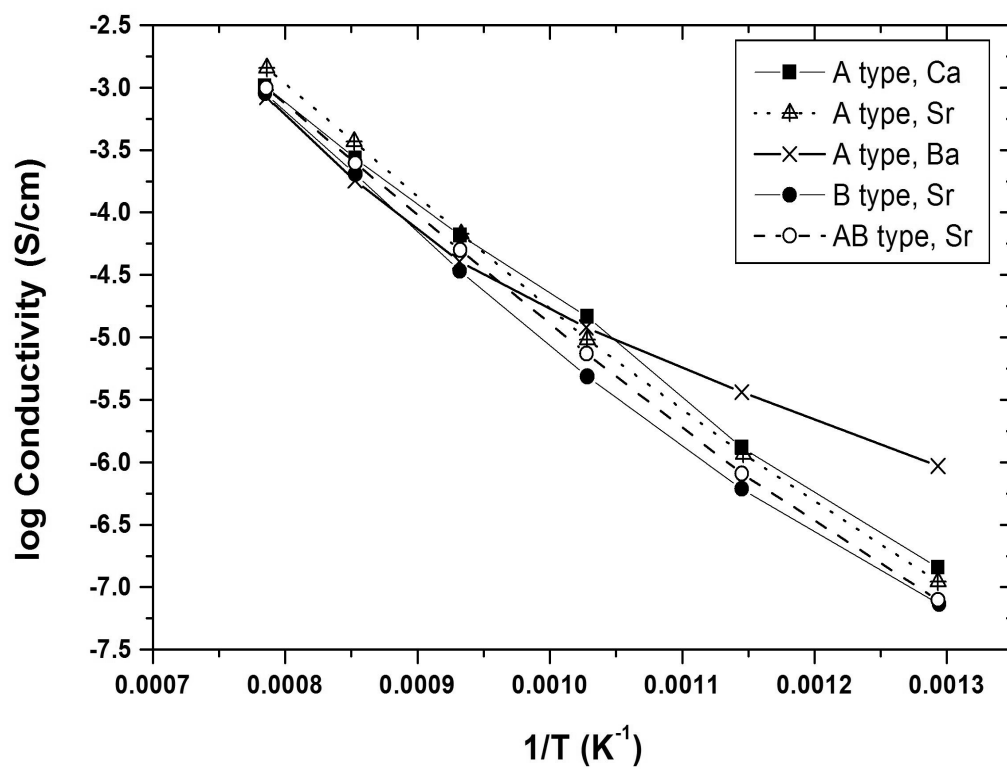


Figure 4.30: Arrhenius plots of log conductivity versus $1/T$ for the non-stoichiometric compositions with neutron data only, obtained from DC conductivity measurements.

values already known, the mobility of the charge carrier could be calculated according to Equation 4.3.

$$\sigma = ne\mu \quad (4.3)$$

Where σ is the conductivity $\frac{1}{ohmcm}$, n is the number of charge carriers per unit volume $\frac{\#}{cm^3}$, e is the charge of the carrier, and μ is the carrier mobility $\frac{cm^2}{Vsec}$. The equation can be rearranged to solve for μ . Table 4.VIII shows the calculated number of carriers for each compound assuming a tetragonal unit cell of volume $2.58 \times 10^{-24} cm^3$ (a 3.90Å and c 33.12Å) along with the mobilities calculated for each temperature. The mobility ranges from 10^{-12} to $10^{-10} \frac{cm^2}{Vsec}$ at low temperature and increases with temperature to 10^{-10} to $10^{-7} \frac{cm^2}{Vsec}$ at 1000°C.

Table 4.VIII: Ionic Mobilities of the Non-stoichiometric Compositions.

Composition	Mobility ($\frac{cm^2}{Vsec}$)					
Temperature	500	600	700	800	900	1000
Bi _{1.975} Sr _{1.5} Ca _{0.525} Nb ₂ TiO _{11.9875}	8.25E-11	7.53E-10	8.41E-09	3.76E-08	1.56E-07	5.87E-07
Bi _{1.975} Sr _{2.025} Nb ₂ TiO _{11.9875}	1.55E-11	1.55E-11	1.51E-11	9.12E-12	9.16E-11	9.63E-10
Bi _{1.975} Sr _{1.5} Ba _{0.525} Nb ₂ TiO _{11.9875}	3.04E-11	3.60E-11	2.00E-11	4.25E-10	2.12E-09	8.26E-09
Bi ₂ Sr _{1.5} Ca _{0.5} Nb _{1.975} Ti _{1.025} O _{11.9875}	4.92E-12	3.99E-12	4.70E-12	3.91E-12	1.14E-11	1.53E-10
Bi ₂ Sr ₂ Nb _{1.975} Ti _{1.025} O _{11.9875}	7.34E-12	8.10E-12	7.12E-12	1.57E-12	5.56E-11	4.65E-10
Bi ₂ Sr _{1.5} Ba _{0.5} Nb _{1.975} Ti _{1.025} O _{11.9875}	na	na	na	na	na	na
Bi _{1.975} Sr _{1.5} Ca _{0.525} Nb _{1.975} Ti _{1.025} O _{11.975}	4.41E-12	4.47E-12	5.02E-12	1.78E-12	3.29E-11	3.09E-10
Bi _{1.975} Sr _{2.025} Nb _{1.975} Ti _{1.025} O _{11.975}	4.63E-12	4.76E-12	4.35E-12	1.38E-12	4.07E-11	4.18E-10
Bi _{1.975} Sr _{1.5} Ba _{0.525} Nb _{1.975} Ti _{1.025} O _{11.975}	5.04E-11	3.42E-11	1.34E-10	1.12E-09	5.15E-09	1.76E-08

About an order of magnitude more carriers ($10^{22} cm^{-3}$) are produced than other well known oxygen conductors. However, the calculated mobilities are four to five orders of magnitude lower than those for the same oxygen conductors.⁹⁷ Thus, the low mobilities explain the low observed ionic conductivities, however, the question to be asked now is why the mobilities are so low.

Many theories exist to explain the low conductivities observed in the present samples, however only a few pertain to this specific material. Several researchers have suggested a relationship between a perovskite tolerance factor and the free volume of the unit cell as factors that affect conductivity.^{98–103} Neither of these apply in this case because the conductivities are low for all samples. It is possible however that defect associations are restricting the available carriers from moving.^{104,105} Defect association occurs when the

positively charged defect shares a coulombic attraction to the negatively charged cation (*i.e.* A^{2+} on a B^{4+} site). The defect pair is a stable entity and requires some amount of energy to break the pair and allow the defect to move. The defect pair idea does not fit well with the present compositions because no highly negative cation sites are being created during the site mixing. In other words, the hypothetical A^{2+} on a B^{4+} site to create A_B'' does not occur. The only way a A_B'' could form is if Sr^{2+} or equivalent occupied a Ti^{4+} site. However, if a defect pair were to form on the O1 site, the positively charged vacancy would be able to bind with *two* Bi^{3+} cations occupying the A site; on either side of the O1 site. Furthermore, it is also possible that the oxygen vacancies order over long range and form a superlattice.^{104,106–108} The long range ordering prohibits long range conductivity because the oxygen vacancy is faced with another vacancy of like charge and thus, its progress is impeded. Superlattice structures are generally discovered by the presence of additional superlattice reflections in the diffraction patterns. The present compositions did show additional reflections, but these were thought to be the result of a small quantity of a second phase. Oxygen vacancy ordering has been observed for several compounds including brownmillerites ($Ba_2In_2O_5$) and the BIMEVOX compounds ($Bi_4V_2O_{11}$).^{85,107} Specifically in these two compounds, the low temperature structure had relatively immobile, ordered oxygen vacancies, whereas as temperature increased, a discontinuity was observed in Arrhenius plots of conductivity, relating the transformation to the high temperature phase which had high conductivity and disordered oxygen vacancies. However, not all oxygen vacancy superlattice structures have order-disorder transformations. In fact, no conductivity discontinuity was observed in the present work.

It is very difficult to come up with a solid reason for why the oxygen mobilities are so low in these compounds. Basically, the oxygen vacancy needs to have an oxygen anion want to jump into its spot. In the present compositions, this action does not appear to be energetically favorable. The three layer Aurivillius structure has complex relationships as described previously. It is possible that a mobile oxygen ion will cause a disruption in the bonding which will ultimately destabilize the balance between interlayer strain, the A site and the perovskite blocks. In theory, the ideal three layer Aurivillius structure would have no interlayer strain, a low A site BVS, and no strain induced oxygen vacancies. This might increase the mobility of the available oxygen ions to the point where if vacancies were added to the structure, they might become mobile. What is clear from this analysis is

despite the fact that the non-stoichiometric structure contains more oxygen vacancies, they are relatively immobile. It is difficult to speculate on the actual conduction mechanism in these structures. While it is clear that oxygen vacancies exist, it is not clear whether it is the oxygen vacancy is the charge carrier. One possibility that has been overlooked until now is the existence of a small polaron type conduction mechanism. The small polaron mechanism works by having a cation trapping an extra electron.^{105,109,110} As a result of the charge of the electron, the cation radius increases, and introduces a polarization on the surrounding lattice. The electron at this point is no longer free to move conduct as a free electron or even in a band, but rather the polaron conducts by hopping from site to site. Essentially, if an oxygen anion leaves the structure and forms a vacancy, a charge balance must occur in order to neutralize the positively charged vacancy. This can occur by the reduction of a surrounding cation. Since in general polarons occur in transition elements, it is likely that either Nb^{5+} or Ti^{4+} reduces in the presence of the oxygen vacancy. However, since we know that the O1 site with the large oxygen deficiency lies in the equatorial plane of the TiO_6 octahedra, it is more likely that Ti^{4+} reduces to Ti^{3+} . Ti^{4+} reduction and small polaron generation have been observed in literature before, however, because Ti^{4+} already has a full electron configuration with the four plus state, the addition of an electron would leave an unpaired electron in the 4s orbital, a condition which some have said to be unlikely for polaron creation.^{111,112} The polaron hopping mechanism is a likely candidate due to the fact that the mechanism is known for its small mobilities.¹¹⁰ Polaron hopping would indicate an electronic rather than ionic conduction mechanism.

Returning to the oxygen vacancies; it is known that oxygen vacancies exist throughout the structure, including in the $(\text{Bi}_2\text{O}_2)^{2+}$ plane, but it is not known whether the oxygen vacancies conduct anisotropically through a specific plane or whether they conduct isotropically through the entire structure. The Bi_2O_3 structure is well known as an excellent ionic conductor. Bi_2O_3 can exist in several stable crystal structures, most are reasonable conductors, but the high symmetry, high temperature, cubic fluorite crystal structure has the highest ionic conductivity.²⁶ The oxygen vacancies are disordered in the cubic symmetry and promote the high conductivity. Because of the excellent conductivity of oxygen vacancies in Bi_2O_3 , it is possible in the Aurivillius materials that any conduction that does occur will do so in the Bi_2O_3 layer. For several reasons, this speculation makes sense. Bismuth is a highly polarizable cation, and as a result, could “move” out of the way easier

as an oxygen vacancy moved by. Furthermore, the $(\text{Bi}_2\text{O}_2)^{2+}$ layer has a lone pair of electrons which project stereochemical repulsion on the O4 and O5 oxygen sites. The lone pair is also easily polarizable compared to a cation, and therefore it is possible that an oxygen vacancy could travel along the O4 plane in the $(\text{Bi}_2\text{O}_2)^{2+}$ layer. The only similar materials to the Aurivillius structure that demonstrate ionic conductivity are the BIMEVOX type materials. The BIMEVOX materials are very similar to the Aurivillius structure, and some even say that they belong to the same family of structures. For the most part, oxygen vacancy conduction in the BIMEVOX materials is between the $(\text{Bi}_2\text{O}_2)^{2+}$ layers, but generally not *in* or *through* the $(\text{Bi}_2\text{O}_2)^{2+}$ layers.¹¹³ Furthermore, this anisotropic conduction pathway has been verified through the use of single crystal AC impedance spectroscopy measurements.¹¹⁴ While it is clear that the BIMEVOX type structure favors conduction between the layers, it should be pointed out that it is a naturally oxygen deficient structure with intrinsic oxygen vacancies lying in the V^{5+} octahedra. Thus, in conclusion, it is more likely that ionic conduction in the Aurivillius system occurs in the $(\text{Bi}_2\text{O}_2)^{2+}$ layer rather than the perovskite blocks.

Chapter 5

Future Work

In order to bring this work to a close, I would like to make a few observations, then summarize what type of future work should be done in this system. We really don't have to go farther than $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$, as all other compositions studied in this thesis were subtle variations of this phase. While the synthesis effort put forth in this thesis was large, most likely, the process should be optimized. The polymerized complex method, despite its failures here, should still be given heavy consideration when investigating future synthesis attempts because when it was done correctly, it produced phase pure materials at low temperatures, in fast times. One of the main problems with its use in this thesis was on the materials side. We simply did not have adequate tools to handle the materials correctly. NbCl_5 was one of the most difficult reactants to use as it would immediately start reacting to form oxalates when exposed to atmosphere. Furthermore, because the HCl had some residual water, it would form a gel if it were not mixed into solution quickly. Ideally, the entire polymerized complex process, from taking the chemicals out of the jar to final ashing should be done in one self contained glovebox, running under an inert atmosphere. In this way, we would not have to worry about the NbCl_5 reaction, or be concerned with inhaling any of the vapors produced from the processing or the ashing.

As far as the crystal structure refinements go, we really need to obtain higher quality conductivity measurements to determine confidently, whether the three layer structure $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$ and its derivatives are oxygen deficient, and furthermore to determine whether the conductivity observed is ionic or electronic in nature. I would propose that new materials be synthesized, this time to near full density by incorporating the hot press

into the process. Clearly, the densities obtained in this work from the hot press were not optimal. If fully dense samples can be obtained which are free of the defects associated with the hot press, then the conductivity measurements could take place knowing that the material is ready to provide good data.

The structural data obtained from the combined x-ray and neutron Rietveld refinements was very interesting and allowed us to look at the material in a new way. While the site mixing between the Bi and A sites and the strain induced oxygen vacancies did not appear to be related, they were both related to the size of the unit cell. The degree of site mixing and the degree of strain induced vacancies both increased as the a lattice parameter decreased. It would be interesting to take these observations to their extremes and observe their effects on the structure. If a were decreased to the point where no Bi-A site mixing was observed, what would happen to the degree of strain induced vacancies? Similarly, if the strain induced vacancies were decreased to zero by increasing the a dimension (Ba^{2+} substitution), what would happen to the degree of Bi-A site mixing? We think that on the lower end, a boundary would be reached where the lattice parameter could not be decreased any further without destabilizing the structure. On the high end, it is already known that a solubility limit exists and thus, phase formation would not proceed past that point.

The Ba^{2+} containing compositions showed the lowest Ti BVS *and* the smallest amount of strain induced oxygen vacancies. The degree of Bi-A site mixing was at its highest, but this did not appear to be a problem. As a result, the Ba^{2+} compositions may be classified as more likely to produce good ionic conductors and should then be the focus point of a new investigation into aliovalent substitution in these materials. As it was already learned from the non-stoichiometric analysis, substitution of Ga^{3+} or Al^{3+} was unsuccessful in the synthesis of phase pure materials. For that matter, the site mixing based compositions were barely successful in this aim. However, it is possible that we were looking at the problem incorrectly. What if we were to take a crystal structure such as $\text{Bi}_2\text{Sr}_{1.5}\text{Ba}_{0.5}\text{Nb}_2\text{TiO}_{12}$ and then perform aliovalent doping of a 3+ charge for Ti^{4+} . This type of experiment could work. It is possible that all of the oxygen vacancies created by the unresolved strain (be it stoichiometric or non-stoichiometric), formed some type of defect association with one of the cation sites and as a result were not available for transport. If a structure were created with unassociated oxygen vacancies, such as the ones proposed, then the three layer prototype structure $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$, could have potential as an ionic conductor.

As far as other topics are concerned, it would be interesting to know the identity of the persistent second phase that appeared in the non-stoichiometric compositions. All of the phase identification showed it to be a distorted four layer Aurivillius phase, however, Rietveld refinements were unable to determine its identity. Seeing that most of the non-stoichiometric compositions had a small amount of this compound, it would be nice to know what it was and what type of impact it might have on the electrical properties of the material. Furthermore, why was it created in the first place? Was it the result of incomplete solid state synthesis or the result of the structure rejecting some part which did not fit? TEM analysis should be able to determine the phase's identity.

The identity of the charge carriers still remains unknown. Further experiments need to be performed in order to identify the true charge carriers and design future compositions for improved ionic conductivity. Furthermore, the electrical conductivities of the stoichiometric and non-stoichiometric compositions were on the same order of magnitude over the entire temperature range. This tells us that the site mixing in the non-stoichiometric compositions did little to introduce mobile oxygen vacancies in the structure. Furthermore, it tells us that the conduction mechanism is probably the same for both sets of compositions. It does little however to reveal which mechanism, be it oxygen vacancies, small polarons, etc., is dominating the conductivity. Further electrical characterization needs to be performed in low oxygen partial pressures to reveal the conduction mechanism.

Furthermore, the problems with the AC impedance measurement instrument need to be rectified in order to produce high quality, publication quality data. The current design is a good first attempt, but I believe that it has certain limitations besides those mentioned previously which hinder its intelligent use. One of the main problems I had was that it was never known until the entire measurement was performed whether the leads were making complete contact with the lead wires. If it were possible to make a set of standard samples, ie samples that were ionic conductors, electronic conductors, fully dense, partially dense, etc. and then compare your impedance data to the data obtained from the standards in order to get an idea whether the instrument performed correctly or whether your sample was faulty. Often, AC impedance measurements had to be performed up to 10 times per sample in order to obtain *one* seemingly good data set.

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Appendix A, Structural Data

This section contains the crystal structure data for the stoichiometric and non-stoichiometric compositions synthesized in this thesis.

Table A.I: Refined Atomic Data for $\text{Bi}_2\text{SrCaNb}_2\text{TiO}_{12}$.

I4/mmm		a=3.871(1)Å			c=33.05(1)Å	
Atom	Site	Fraction	x	y	z	U (100*Å ²)
Bi ³⁺	Bi	0.46(2)	0	0	0.2134(1)	1.3(1)
Sr ²⁺	Bi	0.08(2)	0	0	0.196(1)	1.3(1)
Bi ³⁺	Bi	0.39(2)	0	0	0.2134(1)	1.3(1)
Ca ²⁺	Bi	0.06(2)	0	0	0.196(1)	1.3(1)
Bi ³⁺	A	0.03(2)	0	0	0.0629(2)	2.1(2)
Sr ²⁺	A	0.41(2)	0	0	0.0629(2)	2.1(2)
Bi ³⁺	A	0.10(2)	0	0	0.0629(2)	2.1(2)
Ca ²⁺	A	0.44(2)	0	0	0.0629(2)	2.1(2)
Nb ⁵⁺	Nb	0.745(6)	0	0	0.3739(2)	0.4(1)
Ti ⁴⁺	Nb	0.255(6)	0	0	0.3739(2)	0.4(1)
Ti ⁴⁺	Ti	0.49(1)	0	0	0.5	0.0(3)
Nb ⁵⁺	Ti	0.51(1)	0	0	0.5	0.0(3)
O	O1	1	0	0.5	0	7.2(5)
O	O2	1	0	0.5	0.25	1.1(2)
O	O3	1	0	0	0.4421(3)	3.4(4)
O	O4	1	0	0	0.3198(4)	4.3(4)
O	O5	1	0	0.5	0.1159(2)	2.4(2)
wRp = 10.1%			$\chi^2 = 3.82$			

Table A.II: Refined Atomic Data for $\text{Bi}_2\text{Sr}_{1.5}\text{Ca}_{0.5}\text{Nb}_2\text{TiO}_{12}$.

I4/mmm		a=3.88132(9)Å			c=33.12(1)Å	
Atom	Site	Fraction	x	y	z	U (100*Å ²)
Bi ³⁺	Bi	0.47(2)	0	0	0.2134(1)	1.7(1)
Sr ²⁺	Bi	0.03(2)	0	0	0.197(2)	1.7(1)
Bi ³⁺	Bi	0.41(2)	0	0	0.2134(1)	1.7(1)
Ca ²⁺	Bi	0.09(2)	0	0	0.197(2)	1.7(1)
Bi ³⁺	A	0.03(2)	0	0	0.06263(1)	2.5(2)
Sr ²⁺	A	0.72(2)	0	0	0.06263(1)	2.5(2)
Bi ³⁺	A	0.09(2)	0	0	0.06263(1)	2.5(2)
Ca ²⁺	A	0.16(2)	0	0	0.06263(1)	2.5(2)
Nb ⁵⁺	Nb	0.757(6)	0	0	0.3734(1)	0.6(1)
Ti ⁴⁺	Nb	0.243(6)	0	0	0.3734(1)	0.6(1)
Ti ⁴⁺	Ti	0.513(9)	0	0	0.5	0.3(4)
Nb ⁵⁺	Ti	0.486(9)	0	0	0.5	0.3(4)
O	O1	1	0	0.5	0	5.4(4)
O	O2	1	0	0.5	0.25	1.5(2)
O	O3	1	0	0	0.4418(3)	2.9(3)
O	O4	1	0	0	0.3190(3)	3.8(3)
O	O5	1	0	0.5	0.1167(2)	2.3(2)
wRp = 8.26%				$\chi^2 = 3.24$		

Table A.III: Refined Atomic Data for $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{TiO}_{12}$.

I4/mmm		a=3.8925(12)Å			c=33.18(15)Å	
Atom	Site	Fraction	x	y	z	U (100*Å ²)
Bi ³⁺	Bi	0.864(9)	0	0	0.2142(1)	1.7(1)
Sr ²⁺	Bi	0.1316(9)	0	0	0.197(1)	1.7(1)
Bi ³⁺	A	0.864(9)	0	0	0.06296(1)	2.5(2)
Sr ²⁺	A	0.136(9)	0	0	0.06296(1)	2.5(2)
Nb ⁵⁺	Nb	0.761(6)	0	0	0.3729(1)	0.6(1)
Ti ⁴⁺	Nb	0.239(6)	0	0	0.3729(1)	0.6(1)
Ti ⁴⁺	Ti	0.522(9)	0	0	0.5	0.9(3)
Nb ⁵⁺	Ti	0.477(9)	0	0	0.5	0.9(3)
O	O1	1	0	0.5	0	4.4(3)
O	O2	1	0	0.5	0.25	2.0(2)
O	O3	1	0	0	0.4414(2)	2.0(2)
O	O4	1	0	0	0.3181(3)	3.6(3)
O	O5	1	0	0.5	0.1179(2)	1.5(2)
wRp = 8.65%				$\chi^2 = 3.12$		

Table A.IV: Refined Atomic Data for $\text{Bi}_2\text{Sr}_{1.5}\text{Ba}_{0.5}\text{Nb}_2\text{TiO}_{12}$.

I4/mmm		a=3.9060(8)Å			c=33.47(11)Å	
Atom	Site	Fraction	x	y	z	U (100*Å ²)
Bi ³⁺	Bi	0.49(2)	0	0	0.2150(1)	1.4(1)
Sr ²⁺	Bi	0.01(2)	0	0	0.199(1)	1.4(1)
Bi ³⁺	Bi	0.34(2)	0	0	0.2150(1)	1.4(1)
Ba ²⁺	Bi	0.16(2)	0	0	0.199(1)	1.4(1)
Bi ³⁺	A	0.01(2)	0	0	0.0629(1)	2.1(1)
Sr ²⁺	A	0.74(2)	0	0	0.0629(1)	2.1(1)
Bi ³⁺	A	0.16(2)	0	0	0.0629(1)	2.1(1)
Ba ²⁺	A	0.09(2)	0	0	0.06229(1)	2.1(1)
Nb ⁵⁺	Nb	0.762(6)	0	0	0.3731(1)	0.1(1)
Ti ⁴⁺	Nb	0.238(6)	0	0	0.3731(1)	0.1(1)
Ti ⁴⁺	Nb	0.524(9)	0	0	0.5	0.0(3)
Nb ⁵⁺	Nb	0.476(9)	0	0	0.5	0.0(3)
O	O1	1	0	0.5	0	2.8(3)
O	O2	1	0	0.5	0.25	1.2(2)
O	O3	1	0	0	0.4415(2)	2.0(3)
O	O4	1	0	0	0.3186(2)	2.53(1)
O	O5	1	0	0.5	0.1174(1)	1.0(2)
wRp = 8.07%				$\chi^2 = 2.65$		

Table A.V: Refined Atomic Data for Bi₂SrBaNb₂TiO₁₂.

I4/mmm		a=3.9222(8)Å			c=33.65(11)Å	
Atom	Site	Fraction	x	y	z	U (100*Å ²)
Bi ³⁺	Bi	0.49(2)	0	0	0.2154(1)	1.8(1)
Sr ²⁺	Bi	0.01(2)	0	0	0.198(1)	1.8(1)
Bi ³⁺	Bi	0.32(2)	0	0	0.2154(1)	1.8(1)
Ba ²⁺	Bi	0.18(2)	0	0	.198(1)	1.8(1)
Bi ³⁺	A	0.01(2)	0	0	0.0633(1)	2.8(1)
Sr ²⁺	A	0.49(2)	0	0	0.0633(1)	2.8(1)
Bi ³⁺	A	0.18(2)	0	0	0.0633(1)	2.8(1)
Ba ²⁺	A	0.32(2)	0	0	0.0633(1)	2.8(1)
Nb ⁵⁺	Nb	0.757(6)	0	0	0.3728(1)	0.5(1)
Ti ⁴⁺	Nb	0.242(6)	0	0	0.3728(1)	0.5(1)
Ti ⁴⁺	Nb	0.514(9)	0	0	0.5	0.3(3)
Nb ⁵⁺	Nb	0.485(9)	0	0	0.5	0.3(3)
O	O1	1	0	0.5	0	2.1(2)
O	O2	1	0	0.5	0.25	1.9(2)
O	O3	1	0	0	0.4416(2)	2.3(2)
O	O4	1	0	0	0.3188(2)	2.7(2)
O	O5	1	0	0.5	0.1180(1)	1.5(1)
wRp = 7.63%			$\chi^2 = 2.44$			

Table A.VI: Refined Atomic Data for $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ca}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$.

I4/mmm		a=3.8888(9)Å			c=33.143(2)Å	
Atom	Site	Fraction	x	y	z	U (100*Å ²)
Bi ³⁺	Bi	0.33(5)	0	0	0.2143(2)	1.32(9)
Sr ²⁺	Bi	0.17(5)	0	0	0.202(1)	1.32(9)
Bi ³⁺	Bi	0.48(4)	0	0	0.2143(2)	1.32(9)
Ca ²⁺	Bi	0.03(4)	0	0	0.202(1)	1.32(9)
Bi ³⁺	A	0.16(5)	0	0	0.0625(2)	2.3(1)
Sr ²⁺	A	0.58(5)	0	0	0.0625(2)	2.3(1)
Bi ³⁺	A	0.02(3)	0	0	0.0625(2)	2.3(1)
Ca ²⁺	A	0.24(4)	0	0	0.0625(2)	2.3(1)
Nb ⁵⁺	Nb	0.733(6)	0	0	0.3734(2)	0.4(1)
Ti ⁴⁺	Nb	0.267(6)	0	0	0.3734(2))	0.4(1)
Ti ⁴⁺	Ti	0.47(1)	0	0	0.5	0.2(3)
Nb ⁵⁺	Ti	0.53(1)	0	0	0.5	0.2(3)
O	O1	1	0	0.5	0	4.9(4)
O	O2	1	0	0.5	0.25	2(2)
O	O3	1	0	0	0.4415(3)	2(2)
O	O4	1	0	0	0.3182(3)	3(3)
O	O5	1	0	0.5	0.1171(2)	2(2)
wRp = 9.62%				$\chi^2 = 3.47$		

Table A.VII: Refined Atomic Data for $\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_2\text{TiO}_{11.9875}$.

I4/mmm		a=3.89239(8)Å			c=33.195(1)Å	
Atom	Site	Fraction	x	y	z	U (100*Å ²)
Bi ³⁺	Bi	0.858(6)	0	0	0.21417(6)	1.75(8)
Sr ²⁺	Bi	0.142(6)	0	0	0.201(1)	1.75(8)
Bi ³⁺	A	0.870(6)	0	0	0.0630(1)	2.2(2)
Sr ²⁺	A	0.130(6)	0	0	0.0630(1)	2.2(2)
Nb ⁵⁺	Nb	0.781(6)	0	0	0.3729(1)	0.6(1)
Ti ⁴⁺	Nb	0.219(6)	0	0	0.3729(1)	0.6(1)
Ti ⁴⁺	Ti	0.56(1)	0	0	0.5	0.4(2)
Nb ⁵⁺	Ti	0.44(1)	0	0	0.5	0.4(2)
O	O1	1	0	0.5	0	4.3(5)
O	O2	1	0	0.5	0.25	3.0(4)
O	O3	1	0	0	0.4410(3)	1.6(4)
O	O4	1	0	0	0.3168(5)	3.4(5)
O	O5	1	0	0.5	0.1174(2)	1.6(3)
wRp = 8.39%				$\chi^2 = 1.78$		

Table A.VIII: Refined Atomic Data for $\text{Bi}_{1.975}\text{Sr}_{1.5}\text{Ba}_{0.525}\text{Nb}_2\text{TiO}_{11.9875}$.

I4/mmm		a=3.9048(6)Å			33.467(1)Å	
Atom	Site	Fraction	x	y	z	U (100*Å ²)
Bi ³⁺	Bi	0.47(2)	0	0	0.2151(1)	1.60(8)
Sr ²⁺	Bi	0.03(2)	0	0	0.1976(9)	1.60(8)
Bi ³⁺	Bi	0.36(2)	0	0	0.2151(1)	1.60(8)
Ba ²⁺	Bi	0.03(2)	0	0	0.1976(9)	1.60(8)
Bi ³⁺	A	0.14(2)	0	0	0.0623(1)	2.79(9)
Sr ²⁺	A	0.58(5)	0	0	0.0623(1)	2.79(9)
Bi ³⁺	A	0.02(3)	0	0	0.0623(1)	2.79(9)
Ba ²⁺	A	0.24(4)	0	0	0.0623(1)	2.79(9)
Nb ⁵⁺	Nb	0.733(6)	0	0	0.373(1)	0.84(9)
Ti ⁴⁺	Nb	0.267(6)	0	0	0.373(1))	0.84(9)
Ti ⁴⁺	Ti	0.47(1)	0	0	0.5	0.5(3)
Nb ⁵⁺	Ti	0.53(1)	0	0	0.5	0.5(3)
O	O1	1	0	0.5	0	3.5(2)
O	O2	1	0	0.5	0.25	1.9(1)
O	O3	1	0	0	0.4413(2)	2.2(1)
O	O4	1	0	0	0.3186(2)	2.8(1)
O	O5	1	0	0.5	0.11745(9)	1.55(8)
wRp = 7.51%				$\chi^2 = 3.83$		

Table A.IX: Refined Atomic Data for $\text{Bi}_2\text{Sr}_2\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.9875}$.

I4/mmm		a=3.89189(9)Å			33.168(1)Å	
Atom	Site	Fraction	x	y	z	U (100*Å ²)
Bi ³⁺	Bi	0.843(3)	0	0	0.21405(9)	1.18(9)
Sr ²⁺	Bi	0.157(3)	0	0	0.1998(9)	1.18(9)
Bi ³⁺	A	0.843(3)	0	0	0.0628(1)	1.83(2)
Sr ²⁺	A	0.157(3)	0	0	0.0628(1)	1.83(2)
Nb ⁵⁺	Nb	0.757(2)	0	0	0.3734(2)	0.4(2)
Ti ⁴⁺	Nb	0.230(2)	0	0	0.3734(2)	0.4(2)
Ti ⁴⁺	Ti	0.564(3)	0	0	0.5	0.3(1)
Nb ⁵⁺	Ti	0.461(3)	0	0	0.5	0.3(1)
O	O1	1	0	0.5	0	3.5(2)
O	O2	1	0	0.5	0.25	1.2(2)
O	O3	1	0	0	0.4415(2)	1.3(2)
O	O4	1	0	0	0.3184(2)	2.8(2)
O	O5	1	0	0.5	0.1182(2)	0.9(1)
wRp = 9.34%				$\chi^2 = 4.31$		

Table A.X: Refined Atomic Data for $\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_{1.975}\text{Ti}_{1.025}\text{O}_{11.975}$.

I4/mmm		a=3.89276(8)Å			c=33.188(1)Å	
Atom	Site	Fraction	x	y	z	U (100*Å ²)
Bi ³⁺	Bi	0.846(9)	0	0	0.214(1)	1.71(8)
Sr ²⁺	Bi	0.154(9)	0	0	0.200(1)	1.71(8)
Bi ³⁺	A	0.858(9)	0	0	0.0632(2)	2.7(1)
Sr ²⁺	A	0.142(9)	0	0	0.0632(2)	2.7(1)
Nb ⁵⁺	Nb	0.744(6)	0	0	0.3727(2)	0.9(1)
Ti ⁴⁺	Nb	0.256(6)	0	0	0.3727(2)	0.9(1)
Ti ⁴⁺	Ti	0.514(9)	0	0	0.5	0.8(3)
Nb ⁵⁺	Ti	0.486(9)	0	0	0.5	0.8(3)
O	O1	1	0	0.5	0	5.5(2)
O	O2	1	0	0.5	0.25	3.0(2)
O	O3	1	0	0	0.4412(2)	1.7(2)
O	O4	1	0	0	0.3175(2)	4.6(2)
O	O5	1	0	0.5	0.1175(2)	2.0(1)
wRp = 9.67%			$\chi^2 = 5.34$			

Appendix B, Electrical Characterization

Electrical characterization was performed on all samples via either two point DC conductivity or two point AC impedance spectroscopy via the equipment listed previously. An applied discussion of these two techniques, using actual data obtained from the author’s own catalog of data, will be discussed prior to examination of the results. Specific aspects of each technique, *i.e.* things to look out for, potential problems will be discussed. However, the theory behind both techniques will not be discussed here. Excellent discussions of the theory behind AC impedance spectroscopy can be found in literature.^{1–9}

B.1 DC Conductivity Experiments

The DC conductivity experiments were performed using equipment and controls that allow easy and rapid data measurements. The actual heating profiles and measurement steps are set by a PC, using Labview. The term “point” represents the total number of different points that a lead terminal will make contact with a sample. In a two point measurement, there are only two total spots on the sample which are electroded. Four point measurements on the other hand, have four different electroded points on the sample. To eliminate a point of confusion, a two point measurement, *may* have four terminals actually making contact with the sample; two terminals come from the signal, and another two for measuring the response. However, two of those terminals will contact the same electroded portion of the sample. The two point measurement may not be ideal for all samples, especially those that suffer from polarization effects. In some ceramic materials, especially those that are dielectrics, the electric field applied to the sample can cause an

ionic flow of material through the sample. Since the field only moves in one direction, the ions will diffuse to one end of the sample and “pile up”. Thus, if one were to plot ionic current versus time, it would have an exponentially decreasing slope because once the ions “piled up”, they are no longer free to move, and since there are a limited number of mobile species in the sample, even a normally conducting sample will show a non conducting behavior. Furthermore, the act of ions moving from one side to another sets up a space charge polarization inside the material with an electric field opposing the applied field. The four point measurement will be of benefit because the measurement terminals are no longer located in the same spot as the load terminals.

B.2 AC Impedance Spectroscopy

AC impedance spectroscopy experiments were performed using a similar computer-furnace arrangement as the DC measurements, but instead of a DC power supply, voltmeter and ammeter, a Solartron 1260 Impedance Gain-Phase Analyzer was used. Five point measurements were employed on pellet samples using platinum wire leads. Two leads supplied the AC signal, two separate leads took the readings. All four leads were shielded and grounded together. Compensation files were created by taking short circuit and open circuit readings over the entire temperature range. Impedance measurements were taken over a 10Hz to 10MHz range from high to low frequency. The compensation files were automatically applied to the data using the method described in the HP impedance measurement handbook (Method I).¹ Compensation files were also manipulated using the method described by Edwards *et al.*, which involves developing temperature dependent circuit parameters to account for lead contributions (Method II).² Figure B.2 shows a Cole-Cole (Z'' vs Z' , or imaginary versus real impedance) plot for a $\text{Bi}_{3.95}\text{Ca}_{0.05}\text{Ti}_3\text{O}_{11.95}$ sample at 500°C, and highlights the raw and corrected data at high frequency. Little difference was noted between the two correction methods and as a result, Method I was used. Data was collected every 100°C at a heating rate of 10° per minute with measurements collected after 10 minutes hold, from room temperature to 1000°C. Cooling measurements were performed, but no difference was observed between the heating and cooling cycles. Figure B.1 shows a picture of the actual AC impedance unit used for these experiments. Note, the placement of the Solartron, the lead wires and the furnace. The length of the lead



Figure B.1: Picture of the AC impedance unit used for these experiments.

wires actually limits the range of frequency measurement. Longer lead wires will decrease the high frequency range measurable. The lead wires are standard coaxial cables until they reach a point under the furnace, at this point, platinum wires extend the remainder of the distance inside the furnace. The four lead wires travel through a ceramic honeycomb support to where they make contact with the sample.

The Z'' vs Z' plots were used to obtain resistances of the respective microstructural elements. In all compositions, only one impedance arc was obtained with a small secondary electrode arc. The arc was assumed to be that of the bulk or grain interior. Resistances were obtained from the impedance spectra in one of two ways, either by estimating the resistance from the Z'' vs Z' plot via the low frequency intercept with the Z' axis, or by fitting the impedance arc with the equivalent circuit modelling program Zview. The estimated resistance was obtained from Z'' vs Z' plots whose axes were set to identical resistance values in that this would give a true representation of the arc semicircle. On most occasions, an electrode arc overlapped with the bulk arc, and as a result, the approximate intercept was estimated.

Impedance arcs were also fitted using the program Zview in order to obtain resistances. In general, a simple parallel RC circuit was adequate to model the bulk arc. A range of data which appeared to be of the same arc was selected, then a circle fit to that portion.

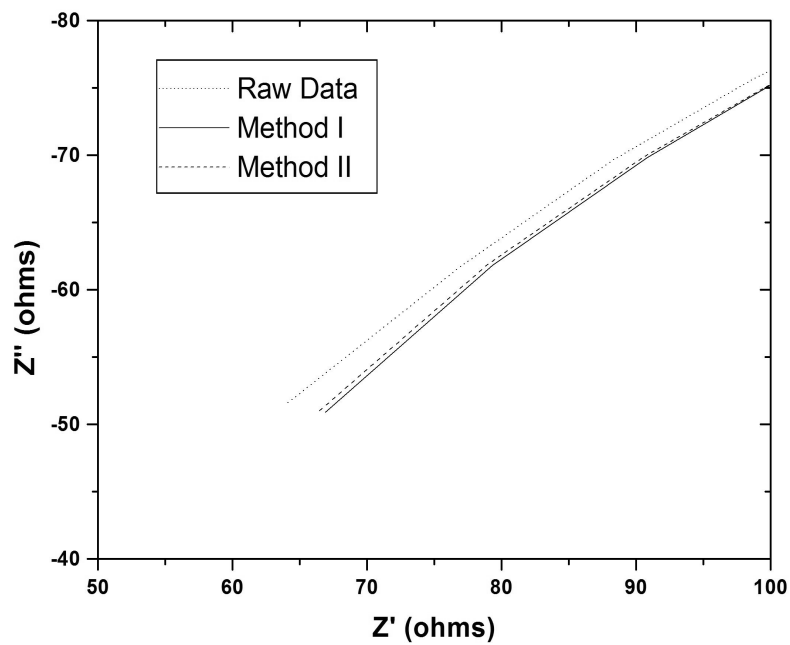
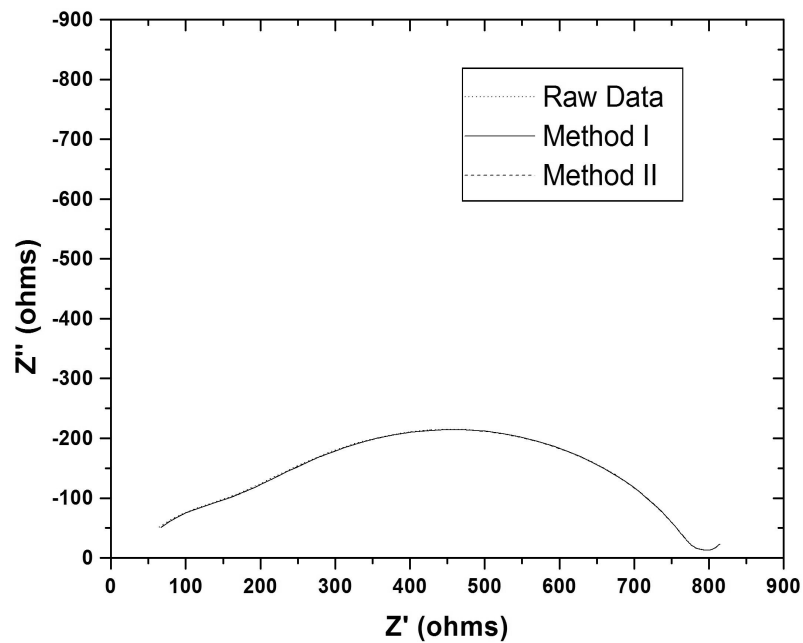


Figure B.2: Imaginary versus real impedance plot for $\text{Bi}_{3.95}\text{Ca}_{0.05}\text{Ti}_3\text{O}_{11.95}$ at 500°C showing the uncompensated data, and the data compensated using Method I and Method II.

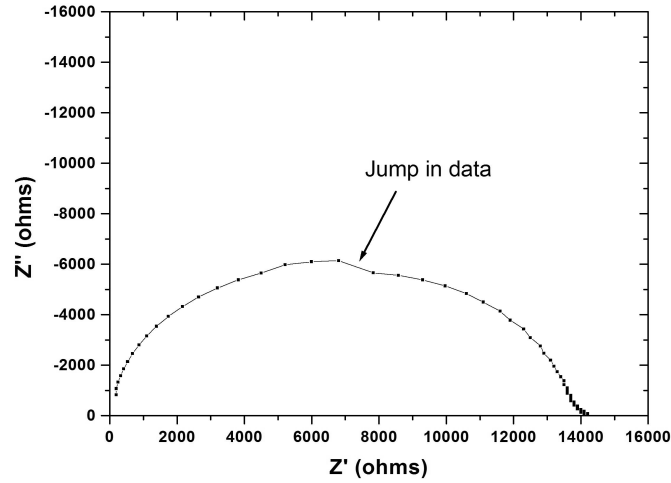


Figure B.3: Experimental artifact observed in each AC impedance data set.

Starting resistances and capacitances were then estimated by using Zview's "Instant Fit" routine, and these values were inserted into the model. Constant phase elements (CPE) were used instead of capacitors because all of the arcs were depressed semicircles. However, successful fitting was obtained only a fraction of the time because the main arc was actually a combination of smaller arcs. It was not possible to simultaneously model the portions which appeared to be separate arcs. Because of the existence of the multiple arcs, it was not possible to fit the data. Furthermore, an error appeared in each data set which was probably the result of some kind of instrumental error. Figure B.3 shows an example of this error in a Z'' vs Z' plot for $\text{Bi}_{1.975}\text{Sr}_{2.025}\text{Nb}_2\text{TiO}_{11.9875}$ at 800°C . The error moved to lower resistances as temperature increased, but remained at about the same frequency. The error did not affect the lower temperature fitting, but it made fitting impossible at higher temperatures.

Because of the existence of multiple overlapping arcs and the impedance error, none of the AC data was used in the calculation of conductivity.

B.3 References

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