ROLE OF POINT DEFECTS IN PEROVSKITE MICROWAVE RESONATORS

BY

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THESIS

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ABSTRACT

Perovskite ceramics are used in a plethora of applications, including electroceramics, superconductors, semiconductors, refractories, catalysts, magnetoresistors, proton conductors, and substrates for semiconductor heteroepitaxy. Engineering defective structures in an attempt to modify properties is a long-established technique in materials chemistry; yet, no models exist which can predict the structure of perovskite compounds containing extrinsic point defects such as vacancies. An empirical approach is used here to develop a predictive model based solely on chemical composition and published ionic radii. Effective vacancy sizes were derived both empirically from an existing model for pseudocubic lattice-constants, as well as experimentally, from average bond lengths calculated from neutron diffraction data. Compounds of strontium-doped magnesium titanate were synthesized by the inorganic-organic steric-entrapment method with vacancies engineered on both the A- and B-sites. Effective vacancy sizes were then used in empirical models to predict changes in lattice constants. Interestingly, using experimentally refined bond lengths in the derivation of effective vacancy size seemed to overestimate the effect of these point defects. However, the use of calculated vacancy sizes, derived from previously reported prediction models, showed significant improvements in the prediction of the pseudocubic perovskite lattice.
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CHAPTER I

INTRODUCTION

The perovskite structure can be found in materials such as electroceramics, superconductors, refractories, catalysts, magnetoresistors, and proton conductors. Microwave resonators, in particular, are used extensively in the telecommunications industry. Recently the number of cell phone accounts passed the population of the United States [1] meaning that the average wireless customer owns more than a single device. Wireless technologies can only grow, requiring newer material systems to be developed. This diverse usage demands a profound understanding of relations between chemical composition and crystal structure.

Microwave resonators are used extensively in telecommunications equipment such as in cellular telephones and satellite links. They are vital to this multi-billion dollar market. Oxide ceramics are critical elements in these devices, and three properties are important in determining their usefulness as a dielectric resonator. First, the material must have a high dielectric constant ($\varepsilon_r$) to enable size reduction, the size of a microwave circuit being proportional to $\varepsilon_r^{3/2}$. Second, a high quality factor Q (low tan $\delta$) means fine frequency tunability and more channels within a given band. Third, these ceramic components play a crucial role in compensating for frequency drift because of their low temperature coefficients of resonant frequency ($\tau_f$). These properties are can tailored
through chemical doping. As doping normally causes crystal symmetry changes, understanding the crystal structure is paramount.
1.1 PROBLEM STATEMENT

To date there are two primary methods to aid in the prediction of perovskite materials: 1) Using empirically derived predictive models and 2) structure stability calculations through the minimization of bond valence sum deviations. However, the current predictive models for perovskite structures cannot account for defective structures such as ones which contain cation vacancies. In this study an empirically derived equation which can accept cation vacancies will be developed. To accomplish this, multiple defective perovskite compositions will be synthesized through chemical doping. Two types of defect composition families will be made: 1) compositions with only B-site vacancies and 2) compositions with simultaneous A- and B-site vacancies. Doping undefected $A^{2+}B^{4+}O_3$ perovskites like SrTiO$_3$ with trivalent species like La$^{3+}$ and Nd$^{3+}$ will create charge balancing vacancies on the A-site according to:

$$La_2O_3^{SrTiO_3} \rightarrow 2La_{Sr} + V_{Sr}'' + 3O_0^\gamma$$

Similarly, doping $A^{3+}B^{3+}O_3$ perovskites with tetravalent species like Ti$^{4+}$ will create these charge balancing vacancies on the B-site according to:

$$TiO_2^{La(Mg_{0.5}Ti_{0.5})O_3} \rightarrow Ti_{Mg} + V_{Mg}'' + 2O_0^\gamma$$

In both of these cases the defects created are positively charged therefore oxygen vacancies will have no tendency to charge compensate.
Using X-ray, electron, and neutron diffraction the structure of these compositions can be determined. Using measured bond lengths, between the cation and anions, an effective vacancy size can be calculated. This effective vacancy size, $r_{\text{V eff}}$, can then be used to adjust current predictive models to account for these point defects.
CHAPTER II

LITERATURE REVIEW

2.1 PEROVSKITE STRUCTURE

The perovskite structure, following the ABX$_3$ formula, is ubiquitous in functional materials. It is defined easily with reference to the aristo-type cubic $Pm\bar{3}m$ SrTiO$_3$, as seen in Figure 2.1. The structure has a larger 12 coordinated A-site cation (Sr$^{2+}$) sitting on the primitive cell corners with a six coordinated B-site cation (Ti$^{4+}$) sitting at the body center. The anions (O$^{2-}$) sit on the face centers of the primitive cell. As different chemistries are introduced to the structure by substitution on the A- and B-sites, this strain causes a distortion of the cubic cell which can result in a lowering of symmetry. Other phenomenon can drive a lowering of symmetry, such as, but not limited to, cation ordering, anti-parallel A-site cation displacements, and oxygen displacements. The characteristic feature of perovskites is the anion corner shared octahedra (BX$_6$). This is normally dominant cause of symmetry changes as oxygen displacements can easily occur through chemical doping and temperature change. These displacements are normally referred to as tilts of the octahedra.

Glazer pioneered the classification of these anion tilt systems [2, 3] by working with a model of four corner shared octahedra; 23 possible tilt systems and their corresponding space groups were reported. To aid in the classification of the tilt systems a
notation was developed. The notation of the tilt systems in perovskites assumes that the anion octahedral tilts are about the three cubic (or pseudocubic) axes, with letters $a$, $b$, and $c$ referring to tilt magnitudes about the [100], [010], and [001] directions. If two tilts are of the same magnitude then they will share the same letter, such that $aac$ refers to tilts about [100] and [010] having the same magnitude while the tilt about [001] is of a different magnitude. The major types of “tilting” of the anion octahera can be visualized in Figure 2.2 (a) and (b) looking down the primitive cubic cell. The two tilt types are anti-phase and in-phase given from their tilting (or rotating) either in opposite directions or in the same direction. Glazer also denoted the two types of tilting, in-phase and anti-phase tilting, with “+” and “-” superscripts, respectively. If there is no tilt about a particular axis a “0” superscript is used. As an example, $a^+b^-b^-$ would refer to in-phase tilting about the $[100]_{pc}$ and anti-phase tilts of equal magnitude about both $[010]_{pc}$ and $[001]_{pc}$. The anion tilting doubles the unit cell axes allowing for characteristic half reflections to be assigned to the two types of tilting. Anti-phase tilts produce half reflections of $\frac{1}{2}\{odd, odd, odd\}$ type while in-phase tilting will produce $\frac{1}{2}\{even, odd, odd\}$ type reflections [3].

To simplify much of the electron diffraction the three low indexed zone axes were simulated and indexed in the pseudocubic space group $Pm\bar{3}m$ [4] in order to visualize where the super lattice reflections occur in these patterns, which are reproduced in Figure 2.3. A symbol was given to the atomic displacements of $\alpha$, $\beta$ and $\gamma$ referring to anti-phase and in-phase anion octahedral tilting and anti-parallel A-site cation displacement, respectively [4]. The use of Glazer and Reaney’s [2-4] work allows for a simple analysis
for determining anion tilt systems. In the transmission electron microscope, ordering and double diffraction makes this analysis more difficult, but can aid in eliminating possible tilt systems, thereby making structural determination easier.

Howard and Stokes [5] expanded on Glazer’s original 23 proposed space groups by using group theory to find that out of those 23 space groups, 15 were uniquely possible or not symmetrically equivalent. This work was expanded upon by Howard et al. [6] for ordered doubled perovskites which then simplified the group theoretical relationships for perovskites to only 12 different possible space groups. Both of these group-subgroup relations are replicated in Figures 2.4 (a) and (b).

Electron diffraction is one of the more powerful techniques used for characterizing perovskites structures. The sensitivity of electrons to oxygen is far greater than both that of X-ray diffraction and neutron diffraction. Woodward and Reaney [7] used the previous group theory work to help determine the tilt systems of perovskites using only electron diffraction. Starting with the untilted $Pm\bar{3}m$ the space groups were systematically analyzed discussing which super lattice reflections would be present while looking down the $<100>_p$, $<110>_p$, and $<111>_p$ directions.

In all perovskites a pseudocubic cell can be defined. From this a pseudocubic lattice constant, $a_{pc}$, can then be calculated from the cube root of the cell volume normalized by the number of formula units:
Through simple geometric relationships, this pseudocubic lattice constant can then be defined in two more ways. In a cube, the face diagonal, or \( \langle 110 \rangle \) direction results in Equation 2.2 while the edge length or \( \langle 100 \rangle \) direction equals Equation 2.3. In both of these expressions, \( r_A \) is the radius of the A-site cation, \( r_B \) is the radius of the B-site cation and \( r_X \) is the radius of the anion. To simplify naming conventions while working with these two equations they are normally defined as \( a' \) and \( a'' \), respectively.

\[
a_{pc} = a' = 2/\sqrt{2}(r_A+r_X) \quad \text{(2.2)}
\]

\[
a_{pc} = a'' = 2(r_B+r_X) \quad \text{(2.3)}
\]

A perovskite tolerance factor, \( t \), was first suggested by Goldschmidt [8] and later refined by others such as Megaw [9]. Using these geometric relations in Equations 2.2 and 2.3 the tolerance factor was defined as:

\[
t = \frac{r_A+r_X}{\sqrt{2}(r_B+r_X)} \quad \text{(2.4)}
\]

This relation can give indications of the stretching and compressing of the A-O and B-O bonds and has been shown to help in indicating oxygen tilt trends in perovskites,
depending on the value of the tolerance factors [4]. The physical meaning behind this relationship is the stretching and compressing of the A-X and B-X bonds. At low values of t, a’ is underestimated while simultaneously a” is overestimated. This would imply a stretching of the r_A-r_X bond and a compression of the r_B-r_X bond. This relationship was demonstrated by Ubic [10] in bond valence (BV) calculations where the underestimated bonds were shown to be underbonded while the overestimated bonds were over bonded.

Bond valence theory was really used as an aid for understanding the “strengths” of bonds and the concept was solidified by Brown [11], but always was derived from Pauling [12]. The BV calculations related the bond distance and the valence charge of an ion in a given coordination. The BV can be simply calculated using the following equations

\[ s = \exp\left(\frac{r_0-r}{B}\right) \]  

(2.5)

where s is the bond valence, r_0 is the bond parameter (tabulated by Brown for a specific bond [13]), r is a single the bond length, and B is a numeric constant of 0.37 for most ionic compounds. By summing the values of s for each bond about an atom, a bond “strength” can be given to the site using the ideal valence of the ion as a reference. Normally the value of this bond valence sum is near the ideal valence, however below this value it is referred to be “underbonded” and if over the ideal value it is labeled as “overbonded”. This value can give insights into structural changes in some crystal structures.
2.1.1 PREDICTIVE MODELS

Reaney et al. looked at many strontium and barium based perovskite structures showing transitional values for $t$ corresponding to types of oxygen octahedral tilting (anti-phase and/or in-phase) [4]. It was found that for compounds with values from 1.0 to 0.985, no structural changes existed at room temperature. Compounds with a value of $t$ of 0.985 to 0.965 showed evidence of only anti-phase tilting. Finally a third boundary at $t$ equaling 0.965 was reported where the addition of in-phase tilting was found.

Lafaso and Woodward introduced the concept of a bond valence based tolerance factor [14]:

$$ t_{BV} = \frac{R_{0(A-X)} - B \ln(V_A/N_A)}{\sqrt{2}R_{0(B-X)} - B \ln(V_B/N_B)} $$

(2.6)

This equation relies solely on the bond valence parameters $R_{0(A-X)}$ and $R_{0(B-X)}$ and $B$ which is equal to 0.37. It also relies on the ideal valence states and coordination number of the A and B site cations. Unfortunately this does not accommodate all types of ion species or types of bonding that cannot be described as a bipartite system [15].

Slainas-Sanchez et al. [16] introduced the concept of the global instability index (GII) which allowed one to calculate the stability of the perovskite structure and the occurrence of anion octahedral tilting. GII is defined as:
\[
GII = \left[ \left( \sum_{i=1}^{N} \left( \sum_{j} s_{ij} - V_i \right) \right) / N \right]^{1/2}
\]

where the \( s_{ij} \) is the bond valence for a single bond, \( V_i \) is the formal charge unit for a particular atom in the asymmetric unit and \( N \) equals the number of atoms in the asymmetric unit (also known as \( Z \)). The inner sum can be completed for each atom in the crystal’s asymmetric unit, resulting in a root mean square for the structure. Normally if \( GII \) is >0.2 valence units (v.u.) then the structures are unstable, if <0.2 v.u. structures are tilted and when <0.1 v.u. it suggests an untilted perovskite structure. This was later developed into a computer algorithm, POTATO and subsequently the program SPuDS [14, 17]. However, these computer algorithms fall apart with simple structures such as SrTiO\(_3\) and CaTiO\(_3\) and cannot accommodate polyatomic anions.

Ubic derived an empirical model by analyzing over 132 different perovskites to predict lattice constants, and yielding a model with an average absolute error of 0.806% [18]:

\[
a_{pc} = 0.0544 + 0.47016(r_A + r_X) + 1.29212(r_B + r_X)
\]

where \( r_A \), \( r_B \) and \( r_X \) are the ionic radii assuming a twelve-fold, six-fold and two-fold coordination, respectively. Ubic later reported that using six-fold coordination for all species gave a better result with an average absolute error of just 0.60% [10], yielding:

\[
a_{pc} = 0.06741 + 0.49052(r_A + r_X) + 1.29212(r_B + r_X).
\]
a reason for the improvement was contributed to the inaccuracy of some atomic radii in higher coordination numbers. In the end, this above predictive model improved upon SPuDS and was even able to handle second-order Jahn-Teller distortions [10]. Ubic and Subodh later use similar approaches to look at orthorhombic perovskites. Again, the equations derived assumed six-fold coordination for all atomic species, yielding:

\[
\begin{align*}
    a &= -0.86631 + 1.514921 \,(r_A + r_X) + 1.310215 \,(r_B + r_X) \\
    b &= 1.114993 + 0.082623 \,(r_A + r_X) + 2.101275 \,(r_B + r_X) \\
    c &= -1.20754 + 1.625883 \,(r_A + r_X) + 2.470594 \,(r_B + r_X)
\end{align*}
\]

(2.10) (2.11) (2.12)

with absolute relative errors of 0.616%, 1.089% and 0.714% for the lattice constants a, b, and c, respectively. Many of these models help in prediction of lattice constants, yet, none of them can accommodate point defects. An early investigation in this was reported in a single system by Ubic, where the effective size of a cation vacancy was measured using the experimental data [18]. It was shown that even though a vacancy does not have any physical size, it does take up space in a crystal.
2.1.2 DEFECTIVE PEROVSKITES

Early investigations of defective perovskite systems were completed on lead based systems as much of the analysis could be completed gravimetrically (Knudsen effusion) [19, 20] by utilizing the high vapor pressure of PbO. It was found that vacancies would distribute on the A- and B-sites depending not only on composition, but the partial pressure of oxygen [19-23]. Much of this work relied on the relative low temperature volatility of PbO versus the comparable components of the ceramics (ZrO$_2$, La$_2$O$_3$ etc.). In particular there was much interest in the lanthanum doped lead titanate series. It was found that the lanthanum would exclusively sit on the A-site in defective structures, even in the presence of B-site vacancies [23]. However, this work did not investigate the upper solubility limit of A-site vacancies. Suriyayothin and Eror proposed the creation of some A-site cation vacancies in Sr$_{1.3x/2}$La$_x$ZrO$_3$ [24]. Through X-ray diffraction they investigated the solubility of La in SrZrO$_3$ finding a 7 % solubility limit of lanthanum.

As interest in these defective materials expanded, the structure and properties of the highly defective materials following Ln$_{2/3}$TiO$_3$ (Ln = Ce, La) and Ln$_{1/3}$NbO$_3$ (Ln = Nd, Pr) were reported [25-27]. In all of these systems the vacancies ordered with the A-site cation forming a layered structure.
Guo et al. investigated the dielectric properties of La\((1-x)\)/3Ag\(x\)NbO\(_3\) [28], in particular looking at its order-disorder transitions. The cation ordering was confirmed to decrease as the dopant level of the silver increased (less vacancies) and the dielectric constant was reported to increase due to the NbO\(_6\) tilt angle decreasing [28].

Kawakami et al. looked at the thermoelectric properties of A-site defective neodymium doped Ca-Mn-O system [29]. He concluded that the addition of A-site vacancies provided major contributions to a decrease in thermal conductivity and an increase in the electrical conductivity in these compositional series.

Very recently, theoretical models have shown that ferromagnetism in SrTiO\(_3\) and BaTiO\(_3\) is possible through B-site vacancies [30, 31]. This property has become of great interest and it was found that by using aliovalent species the B-site in La\(_{0.75}\)Sr\(_{0.25}\)Mn\(_{1-x}\)O\(_3\) could accommodate up to a 8% vacancy concentration [32].

Lanthanum modified lead zirconium titanate (PLZT) can be tailored to have both A and B site vacancies. Using the charge differences of Pb\(^{2+}\) and La\(^{3+}\), vacancies can be created on the A-site, while difference ratios of Zr\(^{4+}\) and T\(^{4+}\), lanthanum content and partial pressure of PbO have large influences on the B-site vacancy concentration [33]. Because of the complexity of this system the properties are still under great investigation, but it has been suggested that the A-site modification does affect dielectric properties [34].
Much of the work investigating these defective structures was driven by their material properties. However, many investigations said little about how the crystal structure changed as a function of vacancy concentration. More recently there has been some evidence of an increase in the A-O bond length from the addition of A-site vacancies which was attributed to the coulombic charges [35, 36]. These observations were secondary, as the main focus of these studies was to measure the vacancy effects on dielectric properties.

Positron lifetime spectra have been used [37] to investigate these defect structures after modeling of positron dynamics in solids [38]. This technique utilizes the difference annihilation characteristic depending on where the annihilation occurs (defects, surface or crystal bulk). This positron lifetime can then be related to a concentration of relevant defects [37].

2.2 PROCESSING

Ceramic processing for most bulk ceramics in laboratories has been accomplished using the “shake and bake” method. Normally the most common precursors used are oxides and carbonates primarily because of their availability and low cost. The process relies on diffusion of the starting materials which, depending on the desired product, maybe impossible to produce if second phases form readily. Various sol-gel methods have been reported [39] and produced highly desirable products (nano-particles, formability, and amorphous powders) for their applications. The sol-gel method is a process which
includes creating a “sol”, or a stable suspension of fine particles, normally through hydrolysis or condensation. All sol-gel processes have a drying step which is the most critical step, but also constitutes its typical weakness. This step is carried out with extreme care because as the sol is dried and becomes a gel it is the capillary forces that can destroy the network of particles. This is not the only hurdle that must be dealt with, even if the solvent is taken out with great care. Removal of solvent becomes harder and harder as the overall solvent content decreases.

In 1967 Pechini patented a sol-gel process [40] which successfully fabricated ceramics for capacitors. This stabilization of the starting metals, normally alkoxides, was accomplished using alpha-hydroxycarboxylic acids (i.e. citric and lactic acids) with the addition of polyhydroxyl alcohols (i.e. ethylene glycol) to form a resin through condensation reactions. The chelation hinders precipitation resulting in ceramic powders with improved homogeneity and smaller particle size. This method has been used to produce ferroelectrics [41] which are isomorphous with the materials in this study.

More recently Kriven et al. patented a simpler process [42, 43] where polyvinyl alcohol (PVA) was used as a mechanism to mechanically entrap precursor cations by combining aqueous salts in a 5-10 % w/w PVA solution. Polyvinyl alcohol is a polar hydrocarbon featuring a single hydroxyl group per repeat unit. This negative charge was found to aid in the entrapment of positively charge cations, without chelation [44], via weak hydrogen bonding [45]. Using the total cation charge of the final product desired, an ideal amount of organic can easily be found. Examples of how the amount of organic was
determined for the compositions under investigation here are found in Figure 2.5. The ratios of 6:1, 4:1 and 3:1 (not all were used, but shown for as examples) of cation charge to organic functional groups is shown with the resulting molar ratios which can then be used to calculate the proper amount of organic to use in synthesis. Further studies were done to investigate the contributions from just the steric interactions of the polymer itself. Polyethylene glycol (PEG), which is a non-polar molecule without function groups, was put through the same scrutiny of the PVA and found to stabilize the solutions for powder synthesis [44]. This added contribution allowed for the tailoring of the processing route so that there was no need for a 1:1 ratio of cation charge to polymer function groups. Lee et al. investigated multiple silicates looking at changing this charge based ratio, as well looking to see what the affect the degree of polymerization has on the synthesis [46]. This has been successful in the synthesis of BaTiO$_3$ [43] and has been able to accommodate up to 3 types of precursors for producing perovskites [45].

One of the advantages of this route is the flexibility of the process to accommodating nano-particles into the powder synthesis. It has been shown that because of the nano-particles, diffusion distances are small enough to easily obtain single phase products as the other precursor cations are atomically mixed [47, 48]. This advantage is useful when attempting to make compositions where the starting materials have solubility issues. In particular titanium based compounds have been shown to work well with this process [45].
By changing the types of organic, this simple synthesis route can be tailored for cation and anion precursors which are incompatible or not soluble with water. In this process the organic is the small monomer ethylene glycol. As this is a non-polar molecule, lacking any functional groups, as a polymer it more useful as a monomer and has been found to aid in the stabilization of the cations and precursor for powder synthesis [49]. In particular this again has been shown to aid in the stabilization of titanium isopropoxide (TISO). The use of TISO over the previously described nano-particle route as the Ti$^{4+}$ ion, allows for the cation to become interatomicly mixed [43, 45]. One large drawback to using TISO is it is highly reactive with water. When used with some hydrated salts, the TISO will decompose to an oxide making it difficult to obtain a single phase product.
2.3 FIGURES

Figure 2.1. Computer model of the perovskite SrTiO$_3$. Strontium atoms are on the corners while the titanium is at the center of the octahedron. Oxygens are at the face centers of the cube (corners of the octahedron).
Figure 2.2. Simulations of a general perovskite structure showing four corner shared anion octahedra. Two types of tilting is normally seen: (a) anti-phase anion octahedral tilting and (b) in-phase anion octahedral tilting.
Figure 2.3. Simulations of electron diffraction patterns showing the location of where half reflections for the three main symmetry lowering atom displacements will occur in relation to the fundamental spots. The patterns are looking down the three directions of the cubic lattice of the perovskite <100> (a), <110> (b), and <111> (c). A key for the different types are labeled in (d).
Howard and Stokes generated group-sub group relationships using the program ISOTROPY for general perovskite structures (a) [5] and or ordered perovskites (b) [6]. In both figures the dashed lines indicate a first order transition by Landau theory.
Figure 2.5. A simple schematic of how the cation to organic (representation of PVA showing the functional group) charges are used to calculate molar amounts for synthesis. $A' = $ Sr, $A'' = $ (Nd, La), $B' = $ Mg and $B'' = $ Ti.
CHAPTER III

EXPERIMENTAL PROCEDURES

3.1 COMPOSITIONS

Compositions of the NdMg$_{1/2-2y}$Ti$_{9/4+y}$O$_3$ (NMT, \(y = 0, 0.01, 0.015, 0.02, 0.03, 0.04, 0.05\)) and eight compositions in the Sr$_{27/20-81x/20}$(La,Nd)$_{27x/10}$Mg$_{13/30(1/2-2y)}$Ti$_{1/15(73/8-13y)}$O$_3$ (SLMT and SNMT \(x = 7/27, 71/270, 4/15, 37/135; y = 5/104, 7/130, 4/15, 31/520\)) family were synthesized using the organic-inorganic steric entrapment method [42]. High-purity ionic salts, Sr(NO$_3$)$_2$ (99.0% Alfa Aesar), La(NO$_3$)$_3$·6H$_2$O (99.9% Alfa Aesar), Nd(NO$_3$)$_3$·6H$_2$O (99.9% Alfa Aesar), Mg(NO$_3$)$_2$·6H$_2$O (99.0% Fluka Analytic) were used in conjunction with TiO$_2$ nano-powder (99.5% Sigma Aldrich) or titanium IV isopropoxide Ti[OCH(CH$_3$)$_2$]$_4$ (TISO) (99.995% Alfa Aesar) for powder synthesis.

For the rest of this study the compositions will be referred to by their vacancy concentrations, [V]. Even though the naming convention is unneeded for the NMT compositions as \(y = [V]\), the simultaneous A- and B-site vacant compositions SNMT and SLMT are a function of \(x\) and \(y\) and cannot be correlated directly to a vacancy concentration. Therefore, for NMT = [V] = 0B, 0.5B, 1.0B, 1.5B, S(N,L)MT = [V] = 0, 0.5 AB, 1.0 AB, 2.0A 1.0B.
3.2 NON-AQUEOUS SYNTHESIS ROUTE

For the compositions NdMg$_{1/2-2y}$Ti$_{y+3/2}$O$_3$ (NMT) a nonaqueous route was used. This process utilized the organic monomer ethylene glycol (EG) (Fisher Scientific) aiding in the stabilization of titanium isopropoxide (TISO) and other cation salts. To deal with the hygroscopic nature of the neodymium and magnesium nitrate, standardized solutions were made with DI water. Prior to synthesis stoichiometric amounts were measured from the standard solutions and the nitrates were dried at 110 °C to remove excess water. A process diagram for this route is seen in Figure 3.1(a). The neodymium and magnesium nitrate salts were dissolved into approximately 200 mL of isopropanol. A stoichiometric amount of TISO was dissolved in isopropanol and mixed until clear. The amount of EG used was determined by a molar ratio which was 2:3, [moles of predicted final product]:[EG]. The EG was first dissolved in isopropanol and then combined with the TISO, mixed until clear, and then slowly added to the solution of neodymium and magnesium nitrate salts. As the TISO solution was added the mixture slowly turned from clear to cloudy blue. The mixture was heated on a hot plate (set to ~175 °C) until a minimal amount of solvent was left. The mixture was then put into a vented furnace at 250 °C to finish drying. The dried gel was then crushed and calcined at 600 °C for 1 h resulting in a very porous and X-ray amorphous powder.
3.3 AQUEOUS SYNTHESIS ROUTE

For the compositions with strontium doping the minimal solubility $\text{Sr(NO}_3\text{)}_2$ in isopropanol called for the modification of the synthesis route. Standardized solutions were again used for the rare earth cations sources. A process flow diagram is seen in Figure 3.1(b). The strontium, lanthanum, neodymium and magnesium nitrate salts were dissolved in approximately 200 mL of DI water. Next polyvinyl alcohol (PVA) with molecular weight 9,000-10,000 (Fisher Scientific) was added to the solution. Using a 1:1 molar ratio NMT to PVA solution the proper amount was added utilizing a 5% w/w solution of polyvinyl alcohol in deionized water (DI) prepared the day before. Increasing the organic amount yielded a very exothermic reaction. After the PVA was added, the pH of the solution was adjusted to approximately 3 by the addition of nitric acid. A standardized dispersion of TiO$_2$ nanoparticles (DI and TiO$_2$ nanoparticles at a pH of approximately 2) was measured then added. The entire mixture was allowed to mix for 1-2 hours using a stir bar. The water was evaporated on a hot plate at 200-250$^\circ$C then the beaker was placed in a vented oven, loosely covered, and dried at 250$^\circ$C. Again, the dried gel was crushed and then calcined at 600$^\circ$C for 1 h producing an X-ray amorphous powder.
3.4 TEST PELLETS AND CHARACTERIZATION TECHNIQUES

Specific surface area analysis was performed on post calcined powders (600°C for 1 h) using an ASAP 2020 (Micromeritics). 11 points were used to calculate BET isotherm.

The amorphous powders were crystallized at 1200°C and checked for phase purity using an X-ray diffractometer (Siemens D5000). The powders were milled using a planetary ball mill (Fritsch Pulverisette 7) at 500 RPM for 30 minutes. Yttria stabilized zirconia jars, media and DI water were used. The powders were dried, sieved (100 μm) and consolidated into cylindrical pellets at 100 MPa. The pellets were then put in a cold isostatic press (American Isostatic Presses, Inc) held at 275 MPa for 5 minutes. Pellets of the NMT compositions were sintered at 1400°C for 3 h, whereas SLMT and SNMT pellets were sintered at 1250°C for 3 h.

Synchrotron X-ray radiation was used to investigate the [V] saturation limits utilizing X-14 powder diffractometer at Brookhaven National Laboratory at the National Synchrotron Light Source (NSLS). Samples for the transmission electron microscope (TEM) were made via conventional methods and imaged at 200KeV (2100 HR and 2010, JEOL). Neutron diffraction data of sintered powders were obtained at Oak Ridge National Laboratory on the POWGEN diffractometer (instrument BL-11A) at the Spallation Neutron Source (SNS). Analysis of time-of-flight diffraction data was completed using the programs GSAS [50] and EXPGUI [51]. Parameters that were refined included scale...
factors, background coefficients, cell parameters, atomic positions, isotropic temperature factors for all atoms, zero-point correction and absorption.
3.5 FIGURES

Figure 3.1. The inorganic-organic steric entrapment process for the both the non-aqueous (a) and aqueous route (b) is shown here.
CHAPTER IV

RESULTS AND DISCUSSION

4.1 CERAMIC PROCESSING

When synthesizing the NMT compositions, small batch sizes were needed as the material would expand becoming much like a coral in appearance. In Figure 4.1 two pictures of the resulting sol and gel is seen. In Figure 4.1(a) the sol is seen as a clear brown mixture with the consistency of taffy. This was obtained through drying at a relatively low temperature of 100°C. Once additional heat was added, this would undergo a reaction where nitrates and leftover solvent were released resulting in a much larger porous matrix growing vertically out of the solution (Figure 4.1(b)). The resulting matrix was amorphous and through simple gravimetric measurements it was found that it still contained organic material.

Initially the ethylene glycol method was the preferred route for ceramic processing due to the fact that the titanium source, titanium IV isopropoxide (TISO), could be atomically mixed in isopropanol. One of the major disadvantages of this compound was its instability in water. In this particular study Sr(NO₃)₂ was used for the strontium source. This particular salt had very low solubility in isopropanol (the solvent used with TISO). In an attempt to use the more desirable TISO source, the same processing route was used as the non-aqueous route stated above. To accommodate the strontium nitrate, water was
incrementally added until the strontium nitrate fully dissolved and then isopropanol was added along with the other nitrates. The composition $\text{Sr}_{0.3}\text{Nd}_{0.7}\text{Mg}_{0.35}\text{Ti}_{0.65}\text{O}_3$ (SNMT 0AB) was used to test this method and with a batch size of 20 g the amount of water needed to fully dissolve the strontium nitrate came to be approximately 100 mL.

Even though the TISO was stabilized by EG, as it was added to the solution of $\text{Sr(NO}_3\text{)}_2$ and water it began to decompose. Upon XRD analysis of the resulting powder some of the desired product and unreacted starting materials were found. In an attempt to help in the stabilization of the TISO, more polymer was added. In conjunction with this, the specific surface area was also measured to compare the two processing routes stated above. In addition to using the monomer EG, PEG was added to see if any affect occurred. In Figure 4.2, for the SNMT compositions, the specific surface areas were measured for varied amounts of organics. Starting with a 4:1 ratio of cation:OH functional charge, the organic amount was doubled, sextupled and also mixed with a 50/50 mixture of PEG and EG, in an attempt to see what affect the polymer would have on the resulting product and surface area. As would be somewhat expected with increased organic content the surface area did increase, but was found to double in magnitude with the addition of six times the amount of organic material. To compare the specific surface area values the aqueous route outlined in the experimental procedures was used to make the same composition as seen in Figure 4.2 (PVA data point). Using the PVA process, resulted in a slightly larger specific surface area than that obtained by the 4:1 EG process.
As was described in the methods section a secondary synthesis route utilizing the organic PVA was used. This was compared to the above processing experiment and the resulting XRD patterns of the crystallized powders are shown in Figure 4.3. Small peaks can be seen (indicated by arrows) in between the fundamental peaks which were attributed to secondary phases made up of the starting compositions. These would differ from batch to batch, but normally consisted of unreacted SrO₂ or SrCO₃. The secondary phases were not apparent when using the hybrid PVA method which was the main reason for changing the synthesis route. For the these reasons the aqueous route was used for the making all of the four component compositions (SNMT and SLMT)

It was reported through some earlier work that titanium based compounds made by the PVA and EG routes would produce very exothermic reactions during gelation and drying [45]. For the aqueous route the suggested starting cation to functional group charge ratio for new compositions was around 4:1. This ended up creating very exothermic reactions which were often described as explosive. Even though the resulting product was normally extremely porous resembling a snow-type consistency, it became clear that this reaction was unwelcome, as much of the final product was lost. As it was seen in the specific surface area analysis, the more organic normally lead to a more desirable higher specific surface area. Through trial and error, it was found that a 6:1 ratio of cation charge to functional group was ideal.
4.2 X-RAY DIFFRACTION

The crystallization temperature for NMT 0B was determined by sequentially increasing heat treatments from the amorphous 600°C up to 1500°C (Figure 4.4(a)). In Figure 4.4(b and c) the near amorphous product for the SNMT and SLMT compositions can be seen. Any peaks that were seen in the SNMT and SLMT compositions were unidentifiable as the peak widths were too wide and intensity was too low to accurately match with any databases.

Preliminary synchrotron X-ray diffraction data (Figure 4.5) suggested that the stability limit of B-site vacancies in NMT fell between vacancies concentrations of 1.5 % and 2 %, as unidentified peaks were seen for [V] of 2 % and above. Visual observations of the powder and test pellets for compositions above \( y = 0.02 \) showed a slight color change which may have been indicative of \( \text{Ti}^{4+} \) reduction to \( \text{Ti}^{3+} \).

Both \( \text{NdMg}_{\frac{1}{2}}\text{Ti}_{\frac{1}{2}}\text{O}_3 \) and \( \text{LaMg}_{\frac{1}{2}}\text{Ti}_{\frac{1}{2}}\text{O}_3 \) have been reported with an ordered B site \([52, 53]\). Ordering of the Mg and Ti on the B-site caused doubling of the perovskite cell and could be seen in XRD patterns most readily as the \( \frac{1}{2}\{111\}_{\text{pc}} \) reflection. Seabra et al. reported that for compositions with cation doping greater than 30 wt %, the resulting crystal structure will be disordered \([41]\).
4.3 NEUTRON AND ELECTRON DIFFRACTION

Neutron-diffraction and XRD data confirmed the ordered $P2_1/n$ structure for NMT compositions $0 \leq [V] \leq 0.015$ with octahedra tilted both in-phase and anti-phase. As previously reported by Groen et al. [52] a mixing of B-site cations lattice sites was seen in these compositions. On the $2d$ site Mg = 0.953(2) and Ti = 0.047(2) while on the $2c$ site Mg = 0.045(2) and Ti = 0.955(2). The cell volume decreased slightly as vacancy concentration increased, as summarized in Table 4.1.

Evidence of ordering can also be seen using the TEM by finding $\frac{1}{2}\{111\}_{pc}$ reflections. These reflections can be indirectly caused by anti-phase tilting, but the intensities in that case are typically very weak. Summaries of the electron diffraction results for both SLMT and SNMT compositions are shown in Figure 4.6. The $\frac{1}{2}\{111\}_{pc}$ reflections shown were much less intense than the fundamental reflections, which would indicate that the spots were most likely due to oxygen displacements.

To determine the oxygen tilt systems, and ultimately the space group, electron diffraction is ideal because of its sensitivity to oxygen displacements. Both $\alpha$ and $\beta$ superlattice reflections were observed in the selected-area diffraction patterns (SADPs) in Figure 4.5(a-c) for the SNMT composition. According to Glazer’s analysis [3], these reflections indicate a tilt system including anti-phase and in-phase tilts. The pseudo-cubic $<100>_{pc}$ diffraction pattern (Figure 4.6(a)) show superlattice reflections labeled $\beta$ corresponding to $\frac{1}{2}\{even,even,odd\}$ indicating anti-phase tilting. Determining the number
of axes about which octahedra are tilted in-phase can be accomplished succinctly by recording the \(<111>_{pc}\) pattern (Figure 4.6(c)). Twinning was observed in some grains and was attributed to growth twinning accommodating strains during reactions/sintering, making the investigation a little more ambiguous; however, by using a small selected-area aperture and recording multiple patterns on a single grain it was determined that there was one set of superlattice reflections caused by in-phase tilting about only one axis. This observation alone reduced the likely space groups to \(Cmcm\) \((a^0b^+c^-)\), \(Pnma\) \((a^+b^-b^-)\) or \(P2_1/m\) \((a^-b^-c^-)\). The \(<110>_{pc}\) diffraction patterns can be used to detect anti-phase tilting by the presence of \{odd, odd, odd\} superlattice (\(\alpha\)) reflections, which were observed in all \(<110>_{pc}\) patterns eliminating the \(Cmcm\) space group. On closer inspection the \(Pnma\) model can be ruled out by looking down the \([210]\) \((<111>_{pc})\) as the forbidden reflections of type \(hkl: h=2n\) and \(00l: l=2n\) are seen. For completeness, models in both the \(Pnma\) \((a^+b^-b^-)\) and \(P2_1/m\) \((a^-b^-c^-)\) space groups were created and successfully refined. It was found the \(P2_1/m\) model yielded a lower residual (\(R_p\)) of 7.65\% compared to \(Pnma\) of 7.99\% which would suggest that \(P2_1/m\) was the correct space group.

Determining the SLMT oxygen octahedral tilt system was not as straightforward as that of the SNMT compositions. Upon investigation of the \(<100>_{pc}\) diffraction patterns a lack of \(\beta\) reflections indicated a system with anti-phase tilting but no antiparallel cation displacements. The only space groups with anti-phase tilting given by Howard and Stokes [5] are: \(I4/mcm\) \((a^0d^0c^-)\), \(Imma\) \((a^0b^-b^-)\), \(R\bar{3}c\) \((a^-a^-a^-)\), \(C2/m\) \((a^0b^-c^-)\), \(C2/c\) \((a^-b^-b^-)\), and \(P\bar{1}\) \((a^-b^-c^-)\). There was no evidence of a \(<110>_{pc}\) SADP with an absence of \(\alpha\) superlattice
reflections, thereby eliminating \( \text{I}4/\text{mcm} \). Dynamical conditions in the TEM make the determination of a single tilt system difficult, but the possible tetragonal and orthorhombic systems were eliminated by measuring the non-orthogonality of angles in the \(<100>_{\text{pc}}\) diffraction patterns, which were all found to be at least 0.8° from orthogonal. The trigonal case was put through the same scrutiny by measuring the angles of the \(<111>_{\text{pc}}\) patterns checking for proper 3-fold symmetry. Again, these angles were also found to be off by approximately 0.5 degrees. What remained were monoclinic or triclinic systems corresponding to the three possible tilt systems: \( a^0b^0b^0 \), \( a^0b^0b^0 \), or \( a^0b^0c^0 \). \( \text{C}2/\text{m} \) is a very common space group for perovskite crystal systems [7, 14] and was used as a first approximation, but subsequent models were made in \( \text{I}4/\text{mcm} (a^0a^0c^0) \), \( \text{Imma} (a^0b^0b^0) \), and \( \text{R}3\overline{2}c (a^0a^0a^0) \). It was found that the data were refined most successfully in \( \text{C}2/\text{m} \). As expected, refinements in \( \text{C}2/c \) and \( \text{P}\overline{1} \) were also successful; however, because all three of these options returned low Rp values (8.31%, 8.26%, and 7.49% respectively) it was the highest-symmetry group, \( \text{C}2/\text{m} \), which would be the most appropriate description for the SLMT compositions.
4.4 VACANCY SIZES

As discussed previously, the pseudocubic lattice constant can be defined in two ways (Equations 2.2 and 2.3). Using these two definitions of the pseudocubic, a compositionally specific equation could be created:

\[ a_{pc} = \sqrt{2} \left( (1.35(1-3x)r_{Sr} + (2.7x)r_{(Nd,La)} + r_O \right) \]  \hspace{1cm} (4.1)
\[ a_{pc} = 2 \left( 1.3(1-4y)r_{Mg} + ((10.4y+7.3)/12)r_{Ti} + r_O \right) \]  \hspace{1cm} (4.2)

where the variables \( r_A \), \( r_B \) and \( r_X \) from the generic forms become specific to the compositions to this study.

When using empirically derived equations as predictive models, normally \( \bar{r}_A \), \( \bar{r}_B \) and \( r_O \) are tabulated values where the A-site is in 12 fold coordination, B-site in 6-fold, and the oxygen anion is in 2-fold. The oxygen radius can be defined by Equation 4.3 where \( \bar{r}_B \) is defined in Equation 4.4 and \( r_{Mg} \) equals 0.72 Å and \( r_{Ti} \) is 0.605 Å [54].

\[ r_O = 0.5a_{pc} - \bar{r}_B \]  \hspace{1cm} (4.3)
\[ \bar{r}_B = [Mg]r_{Mg} + [Ti]r_{Ti} \]  \hspace{1cm} (4.4)

In the compositions where \([V] = 0\) the B-site and A-site are fully occupied, allowing for a more accurate measurement of \( r_O \). This value was used for the compositions in that particular series. Even though the effective oxygen radius will change with different doping levels and so this assumption results in some error, it has been reported
that the oxygen radius does not deviate very much from that tabulated as 1.35 Å [54, 55]. Calculating the average $\bar{r}_A$ and $\bar{r}_B$ now becomes trivial using the A-O and B-O bond lengths determined via neutron diffraction. Adding the term $[V]r_{\text{Veff}}$ to Equations 4.1 and 4.2 yields Equations 4.5 and 4.6, allowing for the calculation of an effective vacancy size ($r_{\text{Veff}}$).

$$a_{pc} = \sqrt{2} \left( (1.35(1-3x)\bar{r}_{\text{Sr}} + (2.7x)\bar{r}_{\text{(Nd,La)}}) + [V]r_{\text{Veff}} + r_O \right)$$  (4.5)

$$a_{pc} = 2 \left( 1.3(1-4y)\bar{r}_{\text{Mg}} + ((10.4y+7.3)/12)\bar{r}_{\text{Ti}} + [V]r_{\text{Veff}} + r_O \right)$$  (4.6)

Solving for $[V]r_{\text{Veff}}$ simply yields:

$$a_{pc}/\sqrt{2} - (1.35(1-3x)\bar{r}_{\text{Sr}} - (2.7x)\bar{r}_{\text{(Nd,La)}}) - r_O = [V]r_{\text{Veff}}$$  (4.7)

$$a_{pc}/2 - 1.3(1-4y)\bar{r}_{\text{Mg}} - ((10.4y+7.3)/12)\bar{r}_{\text{Ti}} - r_O = [V]r_{\text{Veff}}$$  (4.8)

Rearranging this, we can simplify the equation by adding a few definitions:

$$a_{pc}/\sqrt{2} - r_O = r_{(\bar{A},\bar{B})}$$  (4.9)

$$(1.35(1-3x)\bar{r}_{\text{Sr}} + (2.7x)\bar{r}_{\text{(Nd,La)}}) = r_{\text{Aideal}}$$  (4.10)

$$1.3(1-4y)\bar{r}_{\text{Mg}} + ((10.4y+7.3)/12)\bar{r}_{\text{Ti}} = r_{\text{Bideal}}$$  (4.11)
This simple arithmetic (numerator) has been demonstrated before by Ubic et al. [55] and the resulting equation is repeated here:

\[
\frac{r_{\text{Veff}}[V]}{r_{(A,B)\text{ideal}}} = \frac{(r_{(A,B)} - r_{(A,B)\text{ideal}})}{r_{(A,B)\text{ideal}}} \quad (4.12)
\]

where \(r_{(A,B)\text{ideal}}\) (also added for normalization) can be easily calculated using Equations 4.10 and 4.11 with \(r_{\text{Veff}} = 0\). Normalizing the corresponding A- and B-sites by their ideal lengths indicates that if the value of \(r_{\text{Veff}}\) is greater than one, the oxygen ions are repelled by Coulombic forces (larger than the ideal). The smaller the host cation, the closer will be coordinating anions; therefore, vacancies in the cation sublattice will result in strong Coulombic repulsion and a large effective vacancy size. Conversely, if \(r_V\) is less than one, the cations are dominating the structure and pushing the oxygen ions towards the vacancy (less than \(r_{(A,B)\text{ideal}}\)). Equation 4.12 can then be arranged so that there is an inverse relationship to \(r_{\text{Veff}}\) and \([V]\) making it possible to include a datum at \([V] = 0\), and thereby allowing to fit a line of form: \(r_{\text{Veff}} = (A + B r_{\text{Veff}} + C/[V])r_{(A,B)\text{ideal}},\) such that:

\[
r_{\text{Veff}} = \frac{(r_{(A,B)} - r_{(A,B)\text{ideal}})}{r_{(A,B)\text{ideal}}} \frac{1}{[V]} * r_{(A,B)\text{ideal}} \quad (4.13)
\]

This form will become important when investigating the B-site vacancies as the experimental space of stable compositions is small.

After plotting \(r_{\text{Veff}}/r_{A\text{ideal}}\) vs. \([V]\) and \(r_{\text{Veff}}/r_{B\text{ideal}}\) vs. \([V]\) (Figure 4.6) the fit line can be refined. The coefficients and corresponding error are shown in Table 4.2. Due to the
very limited solubility of B-site vacancies, a pinning point was used corresponding to a theoretical and impossible composition of LnMg$_{1/2}$TiO$_3$. Because in the B-site vacant compositions NdMg$_{1/2-2y}$Ti$_{1/2+y}$O$_3$ y = [V] this would mean that this composition would have a [V] = 50%. However, this composition should have a zero vacancy as there is no Mg (actually negative) in the theoretical compound. Using this we can assume then in Equation 4.12 that $r_A = r_{A\text{ideal}}$ driving $r_{V\text{eff}}/r_{B\text{ideal}}$ to zero thereby allowing for a pinning point to be added to the Figure 4.6(b). A summary of [V]r$_{V\text{eff}}$ values is shown in Table 4.3.

If the A-site cation dopant is large, e.g. Sr$^{+2}$, the $r_{V\text{eff}}$ size is small, even negative at low vacancy concentrations. However, for small A-site cations, e.g., Nd$^{+3}$, the A-site effective vacancy size is very large. The opposite trend is observed on the B-site for obvious reasons. If the A-site effective size is large (small ionic radii) then a vacancy leaves a large hole into which oxygen anions will relax, resulting in an effective negative size as seen in the SNMT compositions.
4.5 CELL PREDICTION

To improve the accuracy of predicted lattice constants one can include modified values of \( r_A \) which account for \( r_{\text{Veff}} \) into Equation 2.8 resulting in:

\[
a_{\text{pc}} = 0.0544 + 0.47016 \left( (1.35(1-3x)r_{\text{Sr}} + (2.7x)r_{\text{(Nd,La)}}) + [V]r_{\text{Veff}} + r_0 \right) + ... \\
... + 1.29212(1.3(1-4y)r_{\text{Mg}} + ((10.4y+7.3)/12)r_{\text{Ti}} + r_0)
\]  

(4.13)

The corrected and uncorrected values can be seen in Figure 4.7 including a perfect-fit line for which \( a_{\text{pc}}(\text{exptl}) = a_{\text{pc}}(\text{calc}) \). The results are not ideal, with an absolute error of 2.31%. Errors are exacerbated at low [V] owing to uncertainties in the \( r_{\text{Veff}} \) values which become exaggerated by the \( 1/[V] \) term at low [V].

In an attempt to understand where these discrepancies arose in the compositions under investigation, rather than solving for the \( r_{\text{Veff}} \), an ideal \([V]r_{\text{Veff}}\) was calculated by using experimental \( a_{\text{pc}} \) in Equation 4.13. A single value was given for the total vacancy concentration, \( V_{\text{tot}} \), combining the effect of both the A site and B site vacancy concentrations and the corresponding size. This approximation is valid because the two values should be related due to the push and pull of the oxygen anions from both the A-site and B-site. These values of \( r_{\text{Veff}}(\text{calc}) \), plotted in Figure 4.8(a), yielded Equation 4.14 after a linear regression.

\[
V_{\text{tot}} = 0.30536 [V] - 0.00284
\]  

(4.14)
Inserting these values into Equation 4.13, yields Equation 4.15, significantly reducing the errors. The resulting predicted $a_{pc}(\text{calc})$ are shown in Figure 4.8(b).

$$a_{pc} = 0.0064783988 + 0.50978926 \, r_A + 1.2695858 \, r_B + \ldots$$
$$\ldots+1.7793751 r_O + 0.543349975 \, V_{tot} \tag{4.15}$$

The resultant predicted lattice constants yielded an absolute error of 0.28% with the resulting data shown in Figure 4.8(b).

Upon further inspection it should not be unexpected that using real bond lengths could cause such a large discrepancy. Discrepancies can also be seen when calculating tolerance factors from real bond lengths. Normally, when calculating tolerance factors, tabulated values of the ionic radii are used in an attempt to predict the structure; however, when the same relationships are used with real bond lengths, the tolerance factor normally approaches unity even in tilted systems. As an example, using the real A-O and B-O bond lengths from SNMT and SLMT as seen in Table 4.4, the values would suggest structures of much higher symmetry. As a comparison $t$ was calculated using tabulate values for the ionic radii. This anomaly can be attributed to the relaxation of real crystals, which distort such that ions maintain symmetrical coordination environments in order to minimize local strain. The empirical equations under investigation in this study used tabulated values for $r_A$, $r_B$ and $r_X$ for prediction.
4.6 FIGURES

Figure 4.1. Both images are of a 20 g batch of NdMg$_{1/2}$Ti$_{1/2}$O$_3$ (a) is of the gelled solution while (b) is the dried powder which was very porous yet still contained organics.
Figure 4.2. The average specific surface area vs. organic content using the 4:1 charge ratio as 1xEG. For the last data using the total amount of calculated organic was made up of 50% EG and 50% PEG. The aqueous route using PVA was also measured.
Figure 4.3. Comparison of XRD patterns of crystallized SNMT 0AB for 2xEG, 6xEG, EG+PEG, and the PVA hybrid synthesis route. Secondary phases can be seen in the EG route but none were evident in the PVA hybrid route.
Figure 4.4. (a) Crystallization of NMT 0B from 600 °C to 1500 °C. (b) Calcined powder of SNMT 0AB. (c) Calcined powder of SLMT 0AB.
Figure 4.5. A selected two-theta range of synchrotron X-ray diffraction data showing the extra (secondary phase) reflections of the B-site vacant NMT compositions. The extra reflections arose between the vacancy concentrations of 2.0 and 5.0%.
Figure 4.6. SADPs of \( \text{Sr}_{0.3}\{\text{Nd,La}\}_{0.7}\text{Mg}_{0.35}\text{Ti}_{0.65}\text{O}_3 \) indexed according to the pseudocubic cell (a) \( \langle 100 \rangle_{\text{pc}} \) pattern where only \( \beta \) reflection are visible indicating anti-phase tilting, (b) \( \langle 110 \rangle_{\text{pc}} \) pattern showing \( \alpha \) reflections indicating anti-phase tilting, (c) \( \langle 111 \rangle_{\text{pc}} \) pattern summarizing the in-phase tilting which indicates a single tilt axis, (d) \( \langle 100 \rangle_{\text{pc}} \) pattern indicating no in-phase tilting, (e) \( \langle 110 \rangle_{\text{pc}} \) pattern showing strong \( \alpha \) reflections indicating ordering or more probably anti-phase tilting (see text), and (f) \( \langle 111 \rangle_{\text{pc}} \) pattern indicating no in-phase tilting because of the lack of superlattice reflections.
Figure 4.7. (a) Effective vacancy size on the A site for SNMT and SLMT overlaid on previous work. The vacancy size decreases with size of the dopant and will converge towards the pinning point of La$_{2/3}$TiO$_3$ [55]. (b) Effective vacancy size on the B site with a pinning point at the theoretical composition of y = 1/2.
Figure 4.8. Calculated $a_{pc}$(experimental) vs. $a_{pc}$(calc). Corrected values and uncorrected values are plotted together. The corrected values include $r_{\text{Veff}}$ from refined neutron diffraction (ND) data while the uncorrected values assumed a $r_{\text{Veff}}$ of zero.
Figure 4.9. (a) Using Ubic’s updated model from [56] refined values of \( a_{pc} \) were used to derive corresponding values of \( r_{V}[V] \). A line of best fit was applied and yielded an equation for a single variable to insert back into the model. (b) The resulting work shows the solid filled data which falls, as expected, closer to the line of \( a_{pc}(exp) \) vs. \( a_{pc}(calc) \).
### 4.7 TABLES

Table 4.1. Summary of cell parameters for NMT, SNMT and SLMT

<table>
<thead>
<tr>
<th>Composition</th>
<th>[V] (%)</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β (deg)</th>
<th>Vcell (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NdMg0.5Ti0.5O3</td>
<td>0B</td>
<td>5.47016(4)</td>
<td>5.57668(4)</td>
<td>7.78176(5)</td>
<td>89.998(2)</td>
<td>237.385(2)</td>
</tr>
<tr>
<td>NdMg0.490Ti0.505O3</td>
<td>0.5B</td>
<td>5.47086(3)</td>
<td>5.57741(3)</td>
<td>7.78346(4)</td>
<td>89.997(1)</td>
<td>237.499(2)</td>
</tr>
<tr>
<td>NdMg0.480Ti0.510O3</td>
<td>1.0B</td>
<td>5.47179(3)</td>
<td>5.57719(3)</td>
<td>7.78315(4)</td>
<td>89.995(1)</td>
<td>237.520(2)</td>
</tr>
<tr>
<td>NdMg0.470Ti0.510O3</td>
<td>1.5B</td>
<td>5.47258(5)</td>
<td>5.57387(5)</td>
<td>7.78243(7)</td>
<td>89.992(1)</td>
<td>237.391(5)</td>
</tr>
<tr>
<td>Sr0.3Nd0.7Mg0.35Ti0.65O3</td>
<td>0AB</td>
<td>5.49458(6)</td>
<td>5.51828(6)</td>
<td>7.78538(9)</td>
<td>89.932(2)</td>
<td>236.499(5)</td>
</tr>
<tr>
<td>Sr0.285Nd0.71Mg0.33Ti0.66O3</td>
<td>0.5A 1.0B</td>
<td>5.49309(6)</td>
<td>5.51860(6)</td>
<td>7.77727(8)</td>
<td>89.929(2)</td>
<td>235.618(5)</td>
</tr>
<tr>
<td>Sr0.27Nd0.72Mg0.33Ti0.66O3</td>
<td>1.0A 1.0B</td>
<td>5.49208(4)</td>
<td>5.52224(4)</td>
<td>7.77862(5)</td>
<td>89.924(2)</td>
<td>235.821(4)</td>
</tr>
<tr>
<td>Sr0.24Nd0.74Mg0.33Ti0.66O3</td>
<td>2.0A 1.0B</td>
<td>5.48792(4)</td>
<td>5.51812(4)</td>
<td>7.77293(5)</td>
<td>89.938(2)</td>
<td>235.466(5)</td>
</tr>
<tr>
<td>Sr0.3La0.7Mg0.35Ti0.65O3</td>
<td>0AB</td>
<td>5.56672(5)</td>
<td>7.83547(7)</td>
<td>5.54217(5)</td>
<td>89.964(3)</td>
<td>241.738(4)</td>
</tr>
<tr>
<td>Sr0.285La0.71Mg0.33Ti0.66O3</td>
<td>0.5A 1.0B</td>
<td>5.56347(6)</td>
<td>7.83514(5)</td>
<td>5.54131(5)</td>
<td>89.975(4)</td>
<td>241.549(4)</td>
</tr>
<tr>
<td>Sr0.27La0.72Mg0.33Ti0.66O3</td>
<td>1.0A 1.0B</td>
<td>5.56615(5)</td>
<td>7.83205(7)</td>
<td>5.53996(5)</td>
<td>89.956(2)</td>
<td>241.511(4)</td>
</tr>
<tr>
<td>Sr0.24La0.74Mg0.33Ti0.66O3</td>
<td>2.0A 1.0B</td>
<td>5.56693(5)</td>
<td>7.83267(7)</td>
<td>5.54049(5)</td>
<td>89.959(2)</td>
<td>241.578(4)</td>
</tr>
</tbody>
</table>
Table 4.2. Fitted lines to plotted $r_{\text{Veff}}/r_{(A,B)\text{ideal}}$ following the above equation.

\[
r_{\text{Veff}} = (A + B [V] + C/[V]) * r_{\text{Aideal}}
\]

<table>
<thead>
<tr>
<th>A-Site Vacancy</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>R-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>SNMT</td>
<td>1.55052</td>
<td>-0.2479</td>
<td>0.07706</td>
<td>0.9996</td>
</tr>
<tr>
<td>SLMT</td>
<td>1.09301</td>
<td>1.4869</td>
<td>0.0379</td>
<td>0.99831</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>B-Site Vacancy</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>R-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMT</td>
<td>0.48202</td>
<td>-0.96405</td>
<td>-6.08002E-5</td>
<td>0.98285</td>
</tr>
<tr>
<td>SNMT</td>
<td>-16.86874</td>
<td>34.86008</td>
<td>-0.28065</td>
<td>0.99955</td>
</tr>
<tr>
<td>SLMT</td>
<td>-5.11807</td>
<td>10.01273</td>
<td>0.05586</td>
<td>0.9998</td>
</tr>
</tbody>
</table>
Table 4.3. Summary of $[\text{V}]_{\text{Veff}}$ from refined neutron diffraction data.

<table>
<thead>
<tr>
<th>Composition</th>
<th>A-Site $[\text{V}]_{\text{Veff}}$</th>
<th>B-Site $[\text{V}]_{\text{Veff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMT 0.0B</td>
<td>--</td>
<td>0.000000</td>
</tr>
<tr>
<td>NMT 0.5B</td>
<td>--</td>
<td>0.00336</td>
</tr>
<tr>
<td>NMT 1.0B</td>
<td>--</td>
<td>0.00715</td>
</tr>
<tr>
<td>NMT 1.5B</td>
<td>--</td>
<td>0.00973</td>
</tr>
<tr>
<td>SNMT 0A 0B</td>
<td>0.000000</td>
<td>0.000000</td>
</tr>
<tr>
<td>SNMT 0.5A 0.5B</td>
<td>0.106946</td>
<td>-0.56098</td>
</tr>
<tr>
<td>SNMT 1.0A 1.0B</td>
<td>0.118196</td>
<td>-0.67143</td>
</tr>
<tr>
<td>SNMT 2.0A 1.0B</td>
<td>0.133896</td>
<td>-0.68605</td>
</tr>
<tr>
<td>SLMT 0 VAC</td>
<td>0.000000</td>
<td>0.000000</td>
</tr>
<tr>
<td>SLMT 0.5A 0.5B</td>
<td>0.05995</td>
<td>0.04468</td>
</tr>
<tr>
<td>SLMT 1.0A 1.0B</td>
<td>0.06565</td>
<td>0.00812</td>
</tr>
<tr>
<td>SLMT 2.0A 1.0B</td>
<td>0.08345</td>
<td>0.00899</td>
</tr>
</tbody>
</table>
Table 4.4. Tolerance factors of the SNMT and SLMT using real A-O and B-O bond lengths.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Tolerance Factor using real A/B–O BLs</th>
<th>Tolerance factors using Shannon Radii</th>
</tr>
</thead>
<tbody>
<tr>
<td>SNMT 0A 0B</td>
<td>0.9902</td>
<td>0.947</td>
</tr>
<tr>
<td>SNMT 0.5A 0.5B</td>
<td>1.005</td>
<td>0.922</td>
</tr>
<tr>
<td>SNMT 1.0A 1.0B</td>
<td>0.9433</td>
<td>0.924</td>
</tr>
<tr>
<td>SNMT 2.0A 1.0B</td>
<td>1.009</td>
<td>0.926</td>
</tr>
<tr>
<td>SLMT 0 VAC</td>
<td>0.9991</td>
<td>0.969</td>
</tr>
<tr>
<td>SLMT 0.5A 0.5B</td>
<td>0.9994</td>
<td>0.922</td>
</tr>
<tr>
<td>SLMT 1.0A 1.0B</td>
<td>0.9988</td>
<td>0.924</td>
</tr>
<tr>
<td>SLMT 2.0A 1.0B</td>
<td>0.9988</td>
<td>0.926</td>
</tr>
</tbody>
</table>
Defect compositions allowing for vacancies to be engineered on the A- and B-sites of \( \text{NdMg}_{1/2-2y}\text{Ti}_{2+y}\text{O}_3 \) and \( \text{Sr}_{1.35(1-3x)}\text{(La,Nd)}_{2.7x}\text{Mg}_{1.3(1-4y)}\text{Ti}_{(10.4y+7.3)/12}\text{O}_3 \) were synthesized and their structure analyzed via X-ray, neutron, and electron diffraction. The previously reported structure of NMT was confirmed. The strontium-doped NMT was found to have the tilt system \( a^*b^*c^* \) with the corresponding space group \( P2_1/m \). The strontium-doped LMT was found to have the tilt system of \( a^0b^*c^* \) corresponding to space group \( C2/m \). Using real bond lengths a vacancy size was calculated which showed large values for A-site defects where the host ion had a small ionic radius. Conversely, the B-site vacancy size was small, even negative, if the A-site cation size was small. The real values were found to cause large errors in predicted lattice constants, which was attributed to the relaxation of the actual structure. A fitted model that incorporates the addition of a single factor for the total vacancy concentration was introduced and it significantly improved the fit.

Much more work is needed to fully understand the contributions both A- and B-site vacancies have on both properties and structure. To help accomplish this two important avenues should be explored:
1) Observations seen in the effective vacancy sizes show a type of inflection in the normalized $r_{\text{eff}}$. This would suggest then that there are compositions where the effective vacancy sizes do not change as the vacancy concentration increases. This will be of great importance as the effects of just the increasing vacancy concentration can be hopefully isolated from structural changes. This can then be extended to looking at dielectric properties as function of vacancy concentrations. Because dielectric properties are affected by structural changes, the ability to isolate this effect will give insight into possible ways to improve dielectric performance through adding vacancies.

2) Investigating B-site vacancies is still another area which needs more exploration. In this study there seemed to be a minimal effect that the B-site vacancies had on the crystal structure. This was explained by the inability to synthesize compositions with large quantities of vacancies on the B-site. However, it was discovered that as the A-site cation size was increased, the B-site $r_{\text{eff}}$ seemed to become largely negative. This could indicate that if the A-site cation was large, the amount of vacancies on the B-site could have a higher solubility limit. By making compositions with large cations on A-site, such as yttrium or lanthanum, this solubility limit could be explored with the goal of improving future models.

A final implementation which should be added is the inclusion of the tolerance factor into the predictive model. Because the tolerance factor is dependent only on composition, its contributions to the effective vacancy size should be minimized. This may allow for a single polynomial fit line to be applied to various compositions.
REFERENCES


