TITLE:

Lattice constant prediction of defective rare earth titanate perovskites.

AUTHOR(S):

Steven Letourneau¹, Zhen Zhen¹, Josh Owens², Kevin Tolman², Rick Ubic², Waltraud M. Kriven¹

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Abstract

Engineering defective structures in an attempt to modify properties is an 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 empirically derived predictive model, based solely on chemical composition and published ionic radii has been developed. 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 lanthanum-doped barium titanate and strontium-doped magnesium titanate were synthesized with vacancies engineered on the A- and B-sites. Effective vacancy sizes were then used in empirical models to predict changes in lattice constants. Experimentally refined bond lengths used in the derivation of an effective vacancy size seemed to overestimate the effect of the point defects. Conversely, using calculated vacancy sizes, derived from a previously reported predictive model, showed significant improvements in the prediction of the pseudocubic perovskite lattice.

1.1 Introduction

Perovskite type materials are ubiquitous in functional devices and are of great interest because of their properties (piezoelectric, pyroelectric, ferroelectric, etc.). The perovskite structure, of which cubic SrTiO_3 is the aristotype, is normally defined with cations at the corners (A-site) and body center (B-site) and with the anions occupying the face centers. The A-site cations are in 12-fold coordination with the surrounding anions, while the B-site cations are in six-fold coordination, creating corner-shared octahedra throughout the crystal; however the structure is highly susceptible to distortion. These distortions can be caused by the structure accommodating different atomic species (i.e., doping) which is a common tool used to tailor a desired material property. By doping with chemical species of different valance states it is possible to engineer cation vacancies while minimizing the oxygen vacancies. Strain-modulated properties has been gaining much interest recently, especially in multiferroic materials [1]. With the ability to prepare defective thin-films [2], tuning this strain through changing lattice constants could be accomplished simply by adjusting the vacancy concentrations. Predictive models based on easily accessible data (e.g., ionic radii [3]) could be particularly helpful in this; however, current models fail to cope with defective structures. Cerium doped strontium titanate was used to show that an effective vacancy size could be calculated, ultimately improving lattice constant predictions in defective compositions[4]. Ubic *et al.* [5] recently published a report of defect perovskites bringing together information about A-site vacancies and ultimately creating a predictive model for the pseudocubic lattice constant of $\text{Sr}_{1-3x}\text{Ln}_{2x}\text{TiO}_3$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Ce}$) using the reported ionic radii. The focus of the current study is to investigate the structural effects of B-site vacancies in $\text{NdMg}_{1/2-2y}\text{Ti}_{1/2+y}\text{O}_3$ and $\text{Ba}_{1-4y}\text{La}_{4y}\text{Ti}_{1-y}\text{O}_3$ and simultaneous A- and B-site vacancies in Sr-doped $(\text{La},\text{Nd})(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3$. Using experimentally measured lattice constants

from either rietveld refinements of neutron diffraction data or simple le bail fits of X-ray diffraction data, a model dependent solely on reported ionic radii was compared to the experimental data, in an attempt to determine the model's validity.

1.2 Tolerance Factor

In non-cubic perovskites a pseudocubic lattice constant can be defined as the cube root of the cell volume normalized by the number of ABX_3 formula units. This pseudocubic lattice constant can also be defined by the $\langle 110 \rangle$ (a') and $\langle 100 \rangle$ (a'') lengths, as seen in Equations 1 and 2, respectively. The variables r_A , r_B , and r_X are the ionic radii of the A- and B-site cations and the anion radii, respectively. The perovskite tolerance factor, t , is widely used to aid in predicting the stability of perovskite structures [6, 7] and can be viewed as a ratio of these two measurements of the pseudocubic lattice constant (Equation 3). It is a measure of the distortion of the octahedra and is a weighted ratio of the A-X and B-X bond lengths.

$$a' = 2/\sqrt{2}(r_A + r_X) \quad (1)$$

$$a'' = 2(r_B + r_X) \quad (2)$$

$$t = \frac{a'}{a''} = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \quad (3)$$

1.3 Structural Analysis

Glazer's pioneering work [8, 9] demonstrated 23 possible octahedral tilt systems in perovskite. Later, Howard *et al.* [10, 11] used group-theoretical analysis to determine that, of these 23 possible tilt systems, only 15 are possible for non-ordered systems and 12 for ordered ones. Electron diffraction is one of the most powerful techniques for analyzing perovskite structures because it has a far greater sensitivity to oxygen displacements than does X-ray diffraction (XRD) or even neutron diffraction, and the methods of analyzing structures via

electron diffraction have been well established [12, 13]. Ultimately neutron diffraction is needed to quantify the oxygen positions and tilt angles.

1.4 Lattice Constant Prediction

Using lattice constants from 132 perovskites, Ubic [14] developed a simple equation depending solely on the cation (r_A and r_B) and anion ionic radii (r_X) which yielded an absolute error of 0.60% based on Shannon ionic radii [3]. A more recent equation has been developed (Equation 4) using the same approach.

$$a_{pc} = 0.01153 + 0.5098r_A + r_X + 1.270(r_B + r_X). \quad (4)$$

This was expanded upon from cubic structures to orthorhombic structures later by Ubic *et al.* where the three orthorhombic axes could be predicted [15].

Still a serious drawback to Equation 4 and the work done on the orthorhombic structures is that they result in significant errors for defective crystals. Ubic *et al.* demonstrated that in cerium doped strontium titanate compositions an effective vacancy size could be calculated which greatly improved the errors for that particular defective composition [4].

1.5 Effective Vacancy Size

Using accurate bond lengths allows for calculations of an effective vacancy size which will be denoted r_{veff} . Even though a vacancy does not occupy any physical space, it would be wrong to suggest that it has no effect on the surrounding ions. While bond relaxation will allow coordinating ions to collapse towards the vacant site (simulating the effect of a dopant of smaller size than the host ions), coulombic repulsion will tend to push anions away (simulating the effect of a dopant of larger size than the host ions). Using average A-O and B-O bond lengths, the

pseudocubic cell parameter (a_{pc}), and stoichiometry, one can easily calculate this effective vacancy size.

For A-site deficient perovskites, it is possible to use cell volumes from neutron diffraction to derive a pseudocubic lattice constant. Using this and Equation 2, the anion radius (r_X) can be calculated using published ionic radii [3] for r_B assuming it remains unchanged as doping levels change. The average r_A can in turn be derived from Equation 1. Considering that the A-site is comprised of a stoichiometric mixture of A-site cations and vacancies, it is then possible to calculate the effective size of vacancies. For compositions in this study, Equation 1 can be rewritten with the corresponding compositional specifics for the A-site:

$$a_{pc} = \sqrt{2} \left((1.35(1-3x)r_{Sr} + (2.7x)r_{(Nd,La)} + [V]r_{Veff} + r_O) \right) \quad (5)$$

The effective vacancy size can be calculated for the B-site using Equation 2, as seen in Equation 6, 7, and 8, with the assumptions that the B-site cation and oxygen ionic radii remain unchanged. This is assumed to be true because of the low dopant levels in the compositions.

$$a_{pc} = 2 \left((1/2 - 2y)r_{Mg} + (1/2 + y)r_{Ti} + [V]r_{Veff} + r_O \right) \quad (6)$$

$$a_{pc} = 2 \left(1.3(1-4y)/3r_{Mg} + ((10.4y+7.3)/12)r_{Ti} + [V]r_{Veff} + r_O \right) \quad (7)$$

$$a_{pc} = 2 \left((1-y)r_{Ti} + [V]r_{Veff} + r_O \right) \quad (8)$$

2.1 Experimental Procedures

Compositions of $[Ba_{1-4y}La_{4y}][Ti_{1-y}]O_3$ (BLT, $y = 0.01, 0.02, 0.03, 0.04, 0.05, 0.06$), $Nd[Mg_{1/2-2y}Ti_{1/2+y}]O_3$ (NMT, $y = 0, 0.005, 0.01, 0.015, 0.02, 0.03, 0.04, 0.05$), and eight

compositions in the $[\text{Sr}_{1.35(1-3x)}(\text{La,Nd})_{2.7x}][\text{Mg}_{1.3(1-4y)/3}\text{Ti}_{(10.4y+7.3)/12}]\text{O}_3$ (SLMT and SNMT $x = 7/27, 71/270, 4/15, 37/135; y = 5/104, 7/130, 31/510, 31/520$) family were synthesized.

The BLT compositions were synthesized using conventional solid-oxide routes starting with high-purity BaCO_3 (99% Fischer Scientific), La_2O_3 (99.9% Fischer Scientific), and TiO_2 (99.5% Fischer Scientific) powder. The lanthanum oxide powder was hydroxylated by mixing with an excess of deionized water to form $\text{La}(\text{OH})_3$ and dried overnight. Stoichiometric amounts of these powders milled using a roll jar mill in deionized water for 12 h using cylindrical YSZ media in a high-density nylon pot. Slurries were dried, ground, and calcined at 1300 °C for 8 h.

The NMT, SLMT, and SNMT compositions were synthesized using the organic-inorganic steric entrapment method [16]. High-purity salts of $\text{Sr}(\text{NO}_3)_2$ (99.0% Alfa Aesar), $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9% Alfa Aesar), $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9% Alfa Aesar), and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.0% Fluka Analytic) were used in conjunction with TiO_2 nano-powder (99.5% Sigma Aldrich) or titanium isopropoxide $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$ (TISO) (99.995% Alfa Aesar) for powder synthesis. Two powder synthesis routes were used, the details of which have been reported previously [16-19]. For the rest of this study the compositions will be referred to by their corresponding vacancy concentrations, [V]. In addition “A” or/and “B” will be added to the name to indicate what site the vacancies are located in the perovskite sublattice (i.e. $\text{NdMg}_{0.490}\text{Ti}_{0.505}\text{O}_3$, where $y = 0.005$, will be referred to as NMT 0.5B).

2.2 Non-Aqueous Synthesis Route

For the compositions $\text{Nd}[\text{Mg}_{1/2-2y}\text{Ti}_{1/2+y}]\text{O}_3$ (NMT) a nonaqueous route was used. This process utilized the organic monomer ethylene glycol (EG) (Fisher Scientific) to aid in the stabilization of titanium isopropoxide (TISO) and other cation salts. To deal with the

hygroscopic nature of the neodymium and magnesium nitrates, standardized solutions were made with deionized (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. The neodymium and magnesium nitrate salts were dissolved in approximately 200 mL of isopropanol, and a stoichiometric amount of TISO was dissolved in isopropanol and mixed until the solution was clear. The amount of EG used was determined using a 2:3 ratio of moles of predicted final product to moles of 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 resulting mixture was heated on a hotplate (set to ~175 °C) until a minimal amount of solvent was left and then placed into a vented furnace at 250 °C to remove any remaining solvent. The dried gel was then crushed and calcined at 600 °C for 1 h, resulting in a very porous and amorphous (by XRD) powder.

2.3 Aqueous Synthesis Route

For the compositions with strontium doping, the minimal solubility $\text{Sr}(\text{NO}_3)_2$ in isopropanol called for a modification of the synthesis route. Standardized solutions were again used as the sources for the rare-earth cations. The strontium, lanthanum, neodymium, and magnesium nitrate salts were dissolved in approximately 200 mL of DI water. Next, polyvinyl alcohol (PVA)(Fisher Scientific, molecular weight 9,000-10,000) was added to the solution. Using a 1:1 molar ratio of NMT to PVA solution, the proper amount was added, utilizing a 5 wt % solution of polyvinyl alcohol in DI water prepared the day before. Increasing the organic amount resulted in 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 TiO₂ nanoparticles at a pH of approximately 2) was then added. The entire mixture was stirred for 1-2 hours, and then placed on a hot plate at 200-250 °C until almost all of the water was removed. Finally the mixture was placed in a vented oven at 250 °C, loosely covered, to remove any remaining solvent. Again, the dried gel was crushed and then calcined at 600 °C for 1 h producing an amorphous (by XRD) powder.

2.4 Test pellets and characterization techniques

BLT powders, synthesized at Boise State University, were prepared for X-ray diffraction from post-calcined batches. Diffraction data were acquired on a D8 Discover (Bruker AXS) operating in parallel-beam geometry. Le Bail fits to the data were conducted using DiffracPLUS TOPAS 4.2 (Bruker AXS Inc.).

Amorphous powders of the NMT, SNMT, and SLMT 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 the X14A powder diffractometer at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. Samples for the transmission electron microscope (TEM) were made via conventional methods and imaged at 200 keV (2100 HR and 2010, JEOL). Neutron diffraction

data of sintered powders were obtained at Oak Ridge National Laboratory (ORNL) 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 [20] and EXPGUI [21]. Parameters that were refined included scale factors, background coefficients, cell parameters, atomic positions, isotropic temperature factors for all atoms, zero-point correction and absorption.

3.1 Theory, Results, and Discussion

Preliminary X-ray data (Figure 1) suggested that the chemical stability limit of B-site vacancies in NMT fell between 1.5% and 2%, as unidentified peaks were seen for $[V] \geq 2\%$ and above. Visual observations of the powder and test pellets for compositions of which $y \geq 0.02$ showed a slight color change which may have been indicative of Ti^{4+} reduction to Ti^{3+} . As a result, structural refinements were not performed on the NMT compositions of $y \geq 0.02$.

Cell parameters of the BLT 0B composition were taken from PDF 00-005-0626 [22]. For all other BLT compositions Le Bail refinements were done in the $P4mm$ space group. The results are summarized in Table 1. Significantly higher vacancy concentrations seemed to be attainable, when compared to the NMT compositions, as there were no secondary phases apparent in the X-ray traces.

3.2 Neutron and Electron Diffraction

Neutron diffraction and XRD data confirmed the ordered $P2_1/n$ (#14) structure for NMT compositions $0 \leq [V] \leq 0.015$ with octahedra tilted both in-phase and anti-phase. As previously

1 reported a small intermixing of the B-site cations (Mg and Ti) was observed on the $2d$ and $2c$
2 sites [23]. The $2d$ site was primarily magnesium ($\text{Mg} = 0.953(2)$ and $\text{Ti} = 0.047(2)$) while the $2c$
3 site was dominated by titanium ($\text{Mg} = 0.045(2)$ and $\text{Ti} = 0.955(2)$). The cell volume decreased
4 slightly as vacancy concentration increased, as summarized in Table 1.

5 Both $\text{NdMg}_{1/2}\text{Ti}_{1/2}\text{O}_3$ and $\text{LaMg}_{1/2}\text{Ti}_{1/2}\text{O}_3$ have been reported as possessing an ordered B site
6 [23, 24]. Ordering of the Mg and Ti on the B site causes doubling of the perovskite cell and can
7 be seen in XRD patterns most readily as the $\frac{1}{2}\{111\}_{\text{pc}}$ reflection. Upon the combination of B-
8 site and A-site doping, this ordering peak disappears, suggesting a disordered structure. Similar
9 results were found by Seabra *et al.* [25] at these dopant levels. Evidence of ordering can also be
10 seen using the TEM, by the presences of $\frac{1}{2}\{111\}_{\text{pc}}$ reflections. These reflections can also be
11 indirectly caused by anti-phase tilting, but the intensities in that case are typically very weak.
12 Summaries of the electron diffraction results for both SLMT and SNMT compositions are shown
13 in Figure 2. The $\frac{1}{2}\{111\}_{\text{pc}}$ reflections shown are much less intense than the fundamental
14 reflections, which would indicate that the spots are most likely due to oxygen displacements.

15 To determine the oxygen tilt systems, and ultimately the space group, electron diffraction
16 is ideal because of its sensitivity to oxygen displacements. Superlattice reflections were
17 observed in the selected-area diffraction patterns (SADPs) in Figure 2(a-c) for the SNMT
18 composition. Three distinct types of superlattice reflections were seen. According to Glazer's
19 analysis [9] two of these reflection types, $\frac{1}{2}\{\text{odd},\text{odd},\text{odd}\}$ and $\frac{1}{2}\{\text{even},\text{odd},\text{odd}\}$, arise from
20 anti-phase and in-phase tilting of the TiO_6 octahedral, respectively. Reaney *et al.* [13] showed
21 the third type of reflections, $\frac{1}{2}\{\text{even},\text{even},\text{odd}\}$, arises from anti-parallel A-site cation
22 displacements. He developed a simple notation to aid in the indexing of electron diffraction
23 patterns equating the symbols α , β , and γ to anti-phase oxygen octahdra tilting, anti-parallel A-

1 site cation displacements, and in-phase oxygen octahdra tilting, respectively. The pseudocubic
 2 $\langle 100 \rangle_{pc}$ diffraction pattern (Figure 2(a)) shows superlattice reflections labeled γ and β indicating
 3 in-phase oxygen octahedral tilting and anti-parallel A-site cation displacements. Determining the
 4 number of axes about which octahedra are tilted in-phase can be accomplished succinctly by
 5 recording the $\langle 111 \rangle_{pc}$ pattern (Figure 2(c)). Twinning was observed in *some* grains and was
 6 attributed to growth twinning accommodating strains during reactions/sintering, making the
 7 investigation a little more ambiguous; however, by using a small selected-area aperture and
 8 recording multiple patterns on a single grain it was determined that there was one set of
 9 superlattice reflections caused by in-phase tilting about only one axis. This observation alone
 10 reduces the likely space groups to $Cmcm$ ($a^0b^+c^-$ #63), $Pnma$ ($a^+b^-b^-$ #62) or $P2_1/m$ ($a^+b^-c^-$ #14).
 11 The $\langle 110 \rangle_{pc}$ diffraction patterns can be used to detect anti-phase tilting by the presence of
 12 $\frac{1}{2}\{odd, odd, odd\}$ superlattice (α) reflections, which were observed in all $\langle 110 \rangle_{pc}$ patterns,
 13 thereby eliminating the $Cmcm$ space group. On closer inspection, the $Pnma$ model can be ruled
 14 out by looking down the $[210]_o$ ($\langle 111 \rangle_{pc}$), as the forbidden reflections of type $hk0:h=2n$ and
 15 $00l:l=2n$ are seen. For completeness, models in both the $Pnma$ ($a^+b^-b^-$) and $P2_1/m$ ($a^+b^-c^-$) space
 16 groups were created and successfully refined. It was found the $P2_1/m$ model yielded a lower Rp
 17 and χ^2 value of 7.65% and 12.33 compared to $Pnma$ of 7.99% and 13.27 respectively, which
 18 would suggest that $P2_1/m$ is the correct space group.

19 Determining the SLMT oxygen octahedral tilt system was not as straightforward as that
 20 for the SNMT compositions. The $\langle 110 \rangle_{pc}$ diffraction patterns (Figure 2(e)) were the only
 21 recorded patterns with evidence of superlattice reflections suggesting the structure had anti-phase
 22 tilting. The only space groups with any anti-phase tilting given by Howard and Stokes [10] are:
 23 $I4/mcm$ ($a^0a^0c^-$ #140), $Imma$ ($a^0b^-b^-$ #74), $R\bar{3}c$ ($a^-a^-a^-$ #167), $C2/m$ ($a^0b^-c^-$ #12), $C2/c$ ($a^-b^-b^-$ #15),

and $P\bar{1}$ ($a^-b^-c^-$ #2). There was no evidence of a $\langle 110 \rangle_{pc}$ SADP with an absence of α superlattice reflections, eliminating $I4/mcm$. 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 $\langle 100 \rangle_{pc}$ diffraction patterns, which were all found to be at least 0.8° from orthonormal. The trigonal case was put through the same scrutiny by measuring the angles of the $\langle 111 \rangle_{pc}$ 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: $a^0b^-b^-$, $a^-b^-b^-$, or $a^-b^-c^-$. $C2/m$ is a very common space group for perovskite crystal systems [12, 26] and was used as a first approximation, but subsequent models were made in $I4/mcm$ ($a^0a^0c^-$), $Imma$ ($a^0b^-b^-$), $R\bar{3}c$ ($a^-a^-a^-$), and it was found that the data were refined most successfully in $C2/m$. As expected, refinements in $C2/c$ and $P\bar{1}$ were also successful. All three of these options returned low Rp values: 8.31%, 8.26%, and 7.49% respectively and the resulting χ^2 values: 17.90, 27.58 and 22.73 suggested that $C2/m$ would be the most appropriate description for the SLMT compositions.

3.3 Vacancy Sizes

As discussed previously, the pseudocubic lattice constant can be defined in two ways (Equations 1 and 2). When using empirically derived equations as predictive models, normally r_A , 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 9 where $\bar{r}_B$ is

1 simply $(1-y)r_{Ti}$ for the BLT compositions and $[Mg]r_{Mg}+[Ti]r_{Ti}$ for the NMT, SNMT and SLMT
 2 compositions. For both of all of these r_{Mg} equals 0.72 Å and r_{Ti} is 0.605 Å [3].

$$r_O = 0.5a_{pc} - \bar{r}_B \quad (9)$$

3 In the compositions where $[V] = 0$ the B-site and A-site are fully occupied, allowing for a
 4 more accurate measurement of r_O . This value was used for the compositions in that particular
 5 series. This assumption will result in some error because the effective oxygen radius changes
 6 with different doping levels. However, it has been reported that the oxygen radius does not
 7 deviate very much from the tabulated 1.35 Å in 2-fold coordination [3, 5]. Calculating the
 8 average $\bar{r}_A$ and $\bar{r}_B$ now becomes trivial using the A-O and B-O bond lengths determined via
 9 neutron diffraction. Adding the term $[V]r_{Veff}$ to Equations 1 and 2 allows for the calculation of
 10 an effective vacancy size, r_{Veff} . This has been done for the general cases using Equations 1 and 2
 11 below:

$$r_{Veff} = (a_{pc}/\sqrt{2} - \bar{r}_A - r_X)/[V] \quad (10)$$

$$r_{Veff} = (a_{pc}/2 - \bar{r}_B - r_X)/[V] \quad (11)$$

12 It should be noted that the stoichiometry must be considered in both $\bar{r}_A$ and $\bar{r}_B$ because the X-ray
 13 powder diffraction performed in this study did not probe the local environment. As an example,
 14 for the composition $[Ba_{0.96}La_{0.04}][Ti_{0.99}]O_3$ the value of $\bar{r}_B$ used in Equation 11 was:
 15 0.99×0.605 Å.

16 This simple arithmetic has been demonstrated before for A-site vacancies by
 17 Ubic *et al.* [5]. It can be shown that the $r_{Veff}[V]$ is the difference between the average radius of
 18 the A-site or B-site cation (derived from Equations 10 and 11) and what we define as $\bar{r}_{(A,B)ideal}$

which is simply where $r_{\text{Veff}}=0$. For both the A- and B-site vacancies the equation is of the same form allowing for the (A, B) subscript, resulting in:

$$\frac{r_{\text{Veff(A,B)}}[V]_{(\text{A,B})}}{\bar{r}_{(\text{A,B})\text{ideal}}} = \frac{(\bar{r}_{(\text{A,B})} - \bar{r}_{(\text{A,B})\text{ideal}})}{\bar{r}_{(\text{A,B})\text{ideal}}} \quad (12)$$

Normalizing the corresponding A- and B-sites by their ideal lengths indicates that if the value of $r_{\text{Veff}}/\bar{r}_{(\text{A,B})\text{ideal}}$ is greater than one, the oxygen ions are repelled by Coulombic forces (larger than the ideal). The smaller the host cation, the closer the coordinating anions will be. Therefore, vacancies in the cation sublattice will result in strong Coulombic repulsion and a large effective vacancy size. Conversely, if $r_{\text{Veff}}/\bar{r}_{(\text{A,B})\text{ideal}}$ is less than one, the cations are dominating the structure and pushing the oxygen ions towards the vacancy (less than $r_{(\text{A,B})\text{ideal}}$). Equation 12 can then be arranged so that there is an inverse relationship to r_{Veff} and $[V]$ (see in Equations 10 and 11), making it possible to include a datum point at $[V] = 0$ and thereby allowing to fit a line of form: $r_{\text{Veff}} = (A + B [V] + C/[V])r_{(\text{A,B})\text{ideal}}$. This form will become important when investigating the B-site vacancies as the experimental space for stable compositions is small.

After plotting $r_{\text{Veff}}/r_{\text{Aideal}}$ vs. $[V]$ and $r_{\text{Veff}}/r_{\text{Bideal}}$ vs. $[V]$ (Figure 3) the fitted line can be refined. The coefficients and corresponding errors are shown in Table 2. It should be noted that the values of r_{Veff} at low concentrations are large and would be many times larger than an ideal A- or B-site cation. This of course does not suggest that the actual vacancy size is this large but simply the difference of $(\bar{r}_{(\text{A,B})})$ and $\bar{r}_{(\text{A,B})\text{ideal}}$ as show in Equation 12. We explain these large differences as the structure accommodating the strain of the missing cations. Due to the very limited solubility of B-site vacancies, and ultimate improvement of the fits, a pinning point was used corresponding to a theoretical and impossible composition of $\text{LnMg}_{-1/2}\text{TiO}_3$. Because in the B-site vacant compositions $\text{NdMg}_{1/2-2y}\text{Ti}_{1/2+y}\text{O}_3$ $y = [V]$ 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. The lines converge as they approach a single composition which can easily be shown when using experimental data of $\text{La}_{2/3}\text{TiO}_3$ in Figure (3a). Using the impossible $[V] = 50\%$ composition Equation 11 yields $r_{\text{B}} = r_{\text{Bideal}}$ driving r_{Veff} to zero, and this pinning point is used in Figure 3(b). This pinning point was also used for the BLT compositions. A summary of $[V]r_{\text{Veff}}$ values is shown in Table 3. If the A-site cation dopant is large, e.g. Sr^{+2} , the r_{Veff} 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. It would be ideal to normalize by a material independent parameter to remove the cation to vacancy size correlation, but attempts to develop a single material parameter has yet to be found with the current data set.

3.4 Cell Prediction

To improve the accuracy of predicted lattice constants in Equation 4, one can include modified values of r_{A} and r_{B} which account for the r_{Veff} values. The corrected and uncorrected values can be seen in Figure 4(a-c), including a perfect-fit line for which $a_{\text{pc}}(\text{exptl}) = a_{\text{pc}}(\text{calc})$. The results are not ideal, where the calculated pseudocubic lattice constants yielded an absolute error of 2.3%. Errors are exacerbated at low $[V]$ owing to uncertainties in the r_{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_{Veff} an ideal r_{Veff} was calculated by using

experimentally measured a_{pc} in Equation 4. A single value was given for the total vacancy concentration, V_{tot} , combining the effects of both the A site and B site. 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 $r_{veff}(calc)$, plotted in Figure 5(a), yielded Equation 13 after a linear regression.

$$V_{tot} = 0.5949 [V] - 0.0037 \quad (13)$$

Inserting these values into Equation 4, yields Equation 12, significantly reducing the errors. The resulting predicted $a_{pc}(calc)$ are shown in Figure 5(b).

$$a_{pc} = 0.004948 + 0.5098r_A + 1.270r_B + 1.270r_O + 1.058 V_{tot} \quad (14)$$

The resultant predicted lattice constants yielded an absolute error of just 0.20% with the resulting data shown in Figure 5(b). The error seen as the deviation of the data points in Figure 5 (b-e) was contributed to uncertainties in the calculated oxygen ion radius. This be seen as the each data set gradually deviates from the ideal line. This error will become large as the vacancy concentrations increase, yet yield an acceptable error for the data range examined in this study.

After further inspection of the tolerance factor it became clear that using real bond lengths to calculate r_{veff} caused a large discrepancy. Traditionally calculated tolerance factors use Shannon ionic radii [3] in an attempt to predict the structure. However, when the ionic bond lengths from neutron diffraction are used, t normally approaches unity even in tilted systems. This was shown in Table 4 where the differences between the tolerance factors calculated using real A-O and B-O bond lengths and Shannon ionic radii. This anomaly was attributed to the relaxation of the real crystal. This distortion of ions maintains their symmetrical coordination

environments in order to minimize local strain. The empirical equations developed in this study use tabulated values from Shannon [3] for r_A , r_B and r_X .

4.1 Conclusions

Defect compositions allowing for vacancies to be engineered on the A- and B-sites of $\text{Nd}[\text{Mg}_{1/2-2y}\text{Ti}_{1/2+y}]\text{O}_3$, $[\text{Ba}_{1-4y}\text{La}_{4y}]\text{Ti}_{1-y}\text{O}_3$, and $[\text{Sr}_{1.35(1-3x)}(\text{La},\text{Nd})_{2.7x}][\text{Mg}_{1.3(1-4y)/3}\text{Ti}_{(10.4y+7.3)/12}]\text{O}_3$ systems were synthesized and their structure analyzed via X-ray, neutron, and electron diffraction. The previously reported structure of NMT was confirmed. Lattice parameters refined by Le Bail methods of the BLT compositions were reported. 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, determined from neutron diffraction, a vacancy size was calculated which yielded 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, attributed to the relaxation of the actual structure. A fitted model that incorporated the addition of a single factor for the total vacancy concentration was introduced and it was demonstrated to significantly improve the fit.

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1 Figures

2 Fig1

Figure 1. A selected two-theta range of synchrotron X-ray diffraction data showing the extra (secondary phase) reflections of the B-site defective NMT compositions. The extra reflections arose between the vacancy concentrations of 2.0 % and 5.0 %.

3

1

Fig2

(a)

(b)

(c)

(d)

(e)

(f)

Figure 2. SADPs of $\text{Sr}_{0.3}(\text{Nd},\text{La})_{0.7}\text{Mg}_{0.35}\text{Ti}_{0.65}\text{O}_3$ indexed according to the pseudocubic cell (a) $\langle 100 \rangle_{\text{pc}}$ pattern where γ and β reflections are visible indicating anti-phase tilting and antiparallel A-site cation displacements, respectively, (b) $\langle 110 \rangle_{\text{pc}}$ pattern showing α 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 α reflections indicating anti-phase tilting, and (f) $\langle 111 \rangle_{\text{pc}}$ pattern indicating no in-phase tilting because of the lack of superlattice reflections.

2

1 Fig3

(a)

(b)

Figure 3. (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 $\text{La}_{2/3}\text{TiO}_3$ [5]. (b) Effective vacancy size on the B-site with a pinning point at the theoretical composition of $y = 1/2$.

2

3

1

Fig4

Figure 4. Calculated $a_{pc}(\text{experimental})$ vs. $a_{pc}(\text{calc})$. Corrected and uncorrected values are plotted together, including a “perfect” line where $a_{pc}(\text{experimental}) = a_{pc}(\text{calc})$. The corrected values include r_{veff} from refined neutron diffraction (ND) data while the uncorrected values assumed an r_{veff} of zero. Figure (a) shows NMT, Figure (b) shows SLMT and Figure (c) shows SNMT.

2

3

Fig5

Figure 5. (a) Based on Ubic's updated model from [27] 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. This improved the results in Figures (b-e) (solid data points), being closer to the line of $a_{pc}(\text{exp})$ vs. $a_{pc}(\text{calc})$ where Figure (b) shows BLT, Figure (c) shows NMT, Figure (d) shows SLMT, and Figure (e) shows SNMT results.

1 Tables

2 Table1

Table 1. Summary of cell parameters for BLT, NMT, SNMT and SLMT

Composition	[V] (%)	a (Å)	b (Å)	c (Å)	β (deg)	V _{cell} (Å ³)
BaTiO ₃ (PDF 00-005-0626)	0	3.994	3.994	4.038	90	64.41
Ba _{0.96} La _{0.04} Ti _{0.99} O ₃	0.01B	3.99941(4)	3.99941(4)	4.01416(7)	90	64.204(2)
Ba _{0.92} La _{0.08} Ti _{0.98} O ₃	0.02B	4.00218(4)	4.00218(4)	4.00039(4)	90	63.999(2)
Ba _{0.88} La _{0.12} Ti _{0.97} O ₃	0.03B	3.99424(9)	3.99424(9)	3.99633(6)	90	63.748(4)
Ba _{0.84} La _{0.16} Ti _{0.96} O ₃	0.04B	3.99437(1)	3.99437(1)	3.99546(6)	90	63.710(1)
Ba _{0.80} La _{0.20} Ti _{0.95} O ₃	0.05B	3.99086(9)	3.99086(9)	3.99028(8)	90	63.473(4)
Ba _{0.76} La _{0.24} Ti _{0.94} O ₃	0.06B	3.98918(4)	3.98918(4)	3.99095(3)	90	63.536(2)
NdMg _{0.5} Ti _{0.5} O ₃	0B	5.47016(4)	5.57668(4)	7.78176(5)	89.998(2)	237.385(2)
NdMg _{0.490} Ti _{0.505} O ₃	0.5B	5.47086(3)	5.57741(3)	7.78346(4)	89.997(1)	237.499(2)
NdMg _{0.480} Ti _{0.510} O ₃	1.0B	5.47179(3)	5.57719(3)	7.78315(4)	89.995(1)	237.520(2)
NdMg _{0.470} Ti _{0.515} O ₃	1.5B	5.47258(5)	5.57387(5)	7.78243(7)	89.992(1)	237.391(5)
Sr _{0.3} Nd _{0.7} Mg _{0.35} Ti _{0.65} O ₃	0AB	5.49458(6)	5.51828(6)	7.78538(9)	89.932(2)	236.499(5)
Sr _{0.285} Nd _{0.71} Mg _{0.33} Ti _{0.66} O ₃	0.5A 0.5B	5.49309(6)	5.51860(6)	7.77727(8)	89.929(2)	235.618(5)
Sr _{0.27} Nd _{0.72} Mg _{0.33} Ti _{0.66} O ₃	1.0A 1.0B	5.49208(4)	5.52224(4)	7.77862(5)	89.924(2)	235.821(4)
Sr _{0.24} Nd _{0.74} Mg _{0.33} Ti _{0.66} O ₃	2.0A 1.0B	5.48792(4)	5.51812(4)	7.77293(5)	89.938(2)	235.466(5)
Sr _{0.3} La _{0.7} Mg _{0.35} Ti _{0.65} O ₃	0AB	5.56672(5)	7.83547(7)	5.54217(5)	89.964(3)	241.738(4)
Sr _{0.285} La _{0.71} Mg _{0.33} Ti _{0.66} O ₃	0.5A 0.5B	5.56347(6)	7.83514(5)	5.54131(5)	89.975(4)	241.549(4)
Sr _{0.27} La _{0.72} Mg _{0.33} Ti _{0.66} O ₃	1.0A 1.0B	5.56615(5)	7.83205(7)	5.53996(5)	89.956(2)	241.511(4)
Sr _{0.24} La _{0.74} Mg _{0.33} Ti _{0.66} O ₃	2.0A 1.0B	5.56693(5)	7.83267(7)	5.54049(5)	89.959(2)	241.578(4)

3

1 Table2

Table 2. Fitted lines to plotted $r_{\text{Veff}} / r_{(\text{A,B})\text{ideal}}$ following the above equation.

$r_{\text{Veff}} = (A + B [V] + C/[V]) * r_{\text{Aideal}}$				
A-Site Vacancy	A	B	C	R-Value
SNMT	1.55052	-0.2479	0.07706	0.9996
SLMT	1.09301	1.4869	0.0379	0.99831
B-Site Vacancy	A	B	C	R-Value
NMT	0.48202	-0.96405	-6.08002E-5	0.98285
SNMT	-16.86874	34.86008	-0.28065	0.99955
SLMT	-5.11807	10.01273	0.05586	0.9998

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3

1 Table3

Table 3. Summary of $[V]r_{\text{Veff}}$ in Å from refined neutron diffraction data.

Composition	A-Site $[V]r_{\text{Veff}}$	B-Site $[V]r_{\text{Veff}}$
NMT 0.0B	--	0.00000
NMT 0.5B	--	0.00336
NMT 1.0B	--	0.00715
NMT 1.5B	--	0.00973
SNMT 0A 0B	0.000000	0.00000
SNMT 0.5A 0.5B	0.106946	-0.56098
SNMT 1.0A 1.0B	0.118196	-0.67143
SNMT 2.0A 1.0B	0.133896	-0.68605
SLMT 0A 0B	0.00000	0.00000
SLMT 0.5A 0.5B	0.05995	0.04468
SLMT 1.0A 1.0B	0.06565	0.00812
SLMT 2.0A 1.0B	0.08345	0.00899

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1 Table4

Table 4. Tolerance factors of the SNMT and SLMT using real A-O and B-O bond lengths.

Composition	Tolerance Factor using real A/B–O BLs	Tolerance factors using Shannon Radii
SNMT 0A 0B	0.9902	0.947
SNMT 0.5A 0.5B	1.005	0.922
SNMT 1.0A 1.0B	0.9433	0.924
SNMT 2.0A 1.0B	1.009	0.926
SLMT 0 VAC	0.9991	0.969
SLMT 0.5A 0.5B	0.9994	0.922
SLMT 1.0A 1.0B	0.9988	0.924
SLMT 2.0A 1.0B	0.9988	0.926

2