Local Structure Investigation of Bulk and Nanophase Perovskites

A Dissertation submitted in partial satisfaction of the requirements for the degree

Doctor of Philosophy

in

Materials

by

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December 2008
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November 2008
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for my family
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Y. -I. Kim, K. Page, and R. Seshadri, Synchrotron X-ray study of polycrystalline wurtzite Zn$_{1-x}$Mg$_x$O ($0 \leq x \leq 0.15$): Evolution of crystal structure and polarization, *Applied Physics Letters* **90** (2007) 101914 (1-3). DOI Link


Abstract

Local Structure Investigation of Bulk and Nanophase Perovskites

by

Katharine L. Page

Polar materials play an important role in science and engineering, and efforts to understand, characterize, design and engineer them are driven by a continued demand for robust ferroelectrics and the quest for practical multiferroics, among other noble pursuits. The intricate relationship between the properties of polar materials and their crystal structures is well established. While traditional crystallographic analysis relies on the long-range translational periodicity of structure and yields important average materials characteristics, it is becoming increasingly apparent in the exploration of functional materials that observed properties can arise from local correlations that are absent in this average information. In these cases, the length scale of interest is small enough that conventional techniques are inadequate, and we are obliged to consider information beyond the unit cell and Bragg diffraction.

In this work a combination of Bragg scattering analysis and real-space
atomic pair distribution function methods for neutron and synchrotron X-ray total scattering data are presented to investigate the role local structure plays in the polar properties of several bulk and nanophase inorganic materials systems based on the perovskite structure. First we visit the effects of particle size on ferroelectric distortions in nanoparticles of BaTiO$_3$. We uncover a surprising trend that significantly contrasts the accepted wisdom that BaTiO$_3$ becomes less distorted for smaller particle sizes. We then explore the structures of bulk Nb substituted SrTiO$_3$ and BaTiO$_3$ and present the subtle yet critical difference we believe underpins the distinct electronic properties in the fascinating materials. Finally we investigate short-range chemical ordering, atomic displacements and octahedral tilting in a family of bulk perovskite oxynitrides, ATaO$_2$N (A = Ba, Sr, Ca). We suggest that differences in structure across the A cation series strongly influence the dielectric properties of the materials. The work herein will demonstrate that a combined approach in reciprocal space and real space provides unique insight into local atomic configurations that influence material properties.
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Chapter 1

The Pair Distribution Function and the Perovskite Structure

A great deal of excitement in condensed matter science in recent years has arisen from the recognition that many functional materials are inhomogeneous, either compositionally or electronically, and can possess structure at the mesoscale.[1] Examples of such mesoscale structure are charge stripes in lightly doped Mott insulators and the various charge-ordering patterns seen in manganites. As our understanding of these materials has advanced, so has the imperative for more powerful and precise structural tools.[2]

There are numerous direct and indirect methods applied to local structure determination, and many are complementary. Some, like STM, AFM, trans-
mission electron microscopy and electron diffraction probe small volumes of samples. Others, such as small angle scattering and tomographic imaging sample larger volumes, but are limited to surfaces and interfaces. There are many indirect structural methods which sample large volumes, including forms of spectroscopy and NMR. A few local techniques offer direct probes of large sample volumes. Among these are diffuse scattering from single crystals, EXAFS and total scattering techniques. An overview of various experimental tools available for local structure exploration is provided in Table 1.1.

In practice, a combination of analytical techniques is undertaken to explore local materials structure. The work herein explores the use of the atomic pair distribution function (PDF) formalism of total X-ray and neutron scattering to address local structure in functional perovskite oxides and related materials. The work conveys an improved understanding of the crystal chemistry, local structure and inhomogeneities, bonding, and properties in these materials, and proffers the advancement of X-ray and neutron scattering capabilities necessary for their understanding.
Table 1.1. Various experimental probes of local structure categorized into those that probe the whole sample or small sections of sample, and those that are direct or indirect measures of structure. Techniques limited to interfaces and surfaces are shown in italics. Adapted from [2].

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1.1 Local Structure and Total Scattering

Conventional approaches to structure determination involve elucidating crystal structure by electron or X-ray diffraction, where lattice symmetry and constants can be deduced from the position of Bragg peaks. These methods rely on the assumption of translational periodicity, the supposition that materials are perfectly ordered. However, in many materials, the real atomic structure contains a large amount of disorder. In these cases, the average crystal structure description is incomplete. Many materials properties depend critically on disorder, and an understanding of the nature of the disorder on the local scale helps us understand the properties of the material.

1.1.1 The Pair Distribution Function

Longer range (periodic) atomic structure gives rise to Bragg scattering, while local, aperiodic structure contributes to diffuse scattering. The PDF method[3] is a total scattering technique, utilizing both average (Bragg) diffraction and diffuse scattering components, and containing data pertaining to limited structural coherence.

The PDF has historically been applied to study liquids, glasses and amorphous materials.[4, 5] Early work suffered from inaccuracies associated with
the Fourier transformation, so-called termination errors. Many significant advances have been made in the development of short-wavelength radiation from third generation synchrotron sources and high resolution and high momentum transfer neutron diffraction, and over the last twenty years the technique has been applied increasingly to study a wide range of crystalline materials.[6, 7] Recently, the method has been implemented in describing nanocrystalline materials.[8, 9, 10] Egami and Billinge provide a comprehensive account of the details, history and advancement of total scattering and the PDF method in reference [3].

The PDF, $G(r)$, is a sine Fourier transform of the experimentally determined total-scattering structure function $S(Q)$:

$$G(r) = 4\pi r [\rho(r) - \rho_0] = \frac{2}{\pi} \int_0^\infty Q [S(Q) - 1] \sin(Qr) dQ, \quad (1.1)$$

where $r$ is the distance between pairs of atoms and $Q$ is the momentum transfer, or the amount of momentum that one particle gives to another during a scattering event. ($Q$ is often defined in terms of wavenumber units in reciprocal length as $Q = k_f - k_i$, where $k_f$ and $k_i$ are the wavevectors of the probe after scattering and before scattering. For this reason, $Q$ is also called the wavevector.) $Q$ can be related to the more familiar quantity $2\theta$ through the Bragg equation,

$$Q = \frac{4\pi \sin \theta}{\lambda} \quad (1.2)$$
showing that larger $Q$ corresponds to larger $2\theta$. The formalism in $Q$-space has the advantage of being independent of wavelength and type of radiation.

The macroscopic pair density (defined by Faber and Ziman), $\rho(r)$, can be defined

$$\rho(r) = \frac{1}{4\pi r^2} \sum_{ij} \frac{b_ib_j}{\langle b_i \rangle^2} \delta(r - r_{ij}), \quad (1.3)$$

and $\rho_0$ is the average pair density in the sample.[11] The pair density sum is taken over all atoms in the sample and $r_{ij} = |r_i - r_j|$ is the distance separating atoms $i$ and $j$. The construction gives the probability of finding two atoms separated by a distance $r$, weighted by the scattering lengths, and averaged over all pairs of atoms in the sample. Thus $G(r)$ can be thought of as a distribution of all the pairs of distances in the structure, appropriately weighted by the scattering of the atoms in each pair. With the PDF method material structures are refined in terms of the distances between atoms, and since infinite periodicity is not assumed, local structural descriptions result.

The collection of diffuse scattering data comes with some complications. Scattering from disorder is low in intensity compared to Bragg scattering, often on the order of background scattering. In a diffuse scattering experiment considerable corrections are made to scattering intensity data to obtain the total scattering structure function $S(Q)$. Additive distortions that must be corrected for include background scattering, scattering from an empty can, and multiple
Figure 1.1. The room temperature PDF of Nb-substituted SrTiO$_3$ determined by time-of-flight neutron diffraction, compared with the PDF calculated from a cubic perovskite model structure. The first peak at 1.95 Å is negative due to the negative neutron scattering lengths of Ti.

An experimental PDF data set from time-of-flight neutron diffraction data is given in Figure 1.1 for Nb-substituted SrTiO$_3$ at room temperature. The experimental $G(r)$ is shown with circles and an orange line shows a calculated...
PDF from a cubic perovskite structure model as a fit to the data. Peaks in the PDF correspond to atomic separations in the structure in real space. For example, the first peak at 1.95 Å corresponds to the nearest-neighbor Ti-O atom-atom pairs in TiO$_6$ octahedra. The peak is negative due to the negative neutron scattering length of Ti. The small oscillations at low $r$ are termination errors. The data shown here will be discussed in detail in Chapter 4.

### 1.1.2 Facilities

As mentioned previously, diffuse scattering intensities are weak in comparison to Bragg scattering intensities, making measurement of the data used in PDF methods (and other diffuse diffraction techniques) often time consuming. Along with high radiation intensity, a high $Q$ vector is necessary to obtain the necessary resolution in real space. As such, the use of the PDF method relies on user programs at synchrotron sources and at spallation neutron sources.

Access to a combination of available data collection resources and techniques is important. The work presented in this thesis relied heavily on measurements at the Los Alamos National Laboratory Lujan Scattering Center for the collection of neutron powder diffraction data and at the Argonne National Laboratory Advanced Photon Source for collection of high energy synchrotron X-ray powder diffraction data. Neutron diffraction can be sensitive to lighter
Figure 1.2. Two-dimensional contour plots obtained from a MAR345 image plate detector. The data in (a) are for 3.5 nm gold nanoparticles in a diamond anvil cell at \( \approx 4.0 \) GPa measured using incident X-rays of 90 keV at the Advanced Photon Source. The bright spots are Bragg peaks from the single-crystal diamond anvil cell and pressure-sensitive rubies while the diffuse rings show the diffraction pattern for nanoparticles of gold. The same pattern is (b) is shown with a mask applied to the Bragg peaks, blotting out crystalline contributions. This masked plot is integrated to provide scattering data from small nanoparticles of gold under pressure. (Data from the Parise group at Stonybrook University.)
elements and can often differentiate between atom types that are difficult to
distinguish using an X-ray source. $Q_{\text{max}}$ in excess of 100 Å$^{-1}$ are possible using
the time-of-flight method, offering unprecedented resolution in real space.[13]
However, neutron scattering is often complicated by absorption and incoherent scattering from various elements, and experiments require large sample volumes and long data collection times. Synchrotron X-ray sources offer high intensity (allowing for small sample volumes), flexibility in radiation wavelength, and are particularly useful for probing heavy elements and compounds composed of elements that are well-separated by their atomic weights. Furthermore, the recent development of the so-called “Rapid Acquisition Pair Distribution Function Method” (RAPDF) at synchrotron sources (which involves integration of diffraction collected via an area detector) has recently shortened the collection time required for the technique to less than a minute, opening the door to in situ diffraction experiments in real space.

A demonstration of the flexibility the RAPDF method offers is conveyed in Figure 1.2. Raw diffraction data are shown in (a) for 3.5 nm gold nanoparticles dispersed in an alcohol pressure medium inside a diamond anvil cell at $\approx$ 4 GPa. Bragg scattering contributions from the single-crystal diamond anvil cell and pressure-sensitive rubies have been masked out in (b). Only contributions from the diffuse rings of the nanoparticles are integrated to provide
Figure 1.3. Diagrams comparing $S(Q)(a,b)$ and $G(r)(c,d)$ data for 2 nm (left panels) and 3.5 nm (right panels) gold nanoparticles compressed in a diamond anvil cell at $\approx 4\ \text{GPa}$. The data are shown with Rietveld refinement (a,b) and PDF refinement (c,d) fits using fcc gold models.
the total scattering $S(Q)$ data. The details of such an experimental set-up are
given in reference [14]. Resulting data for 2 nm and 3.5 nm particles of gold
are displayed in Figure 1.3(a) and (b), respectively, with Rietveld refinements
using a fcc gold model. The corresponding nanoparticle $G(r)$s are given in (c)
and (d) with PDF refinements using fcc gold models. Programs used for data
extraction and refinement are described below.

1.1.3 Software

Diffraction data are normally analyzed in $k$-space, with the Rietveld
method[15] as embodied in a program such as GSAS-EXPGUI,[16, 17]
FullProf,[18] or XND.[19] A crystallographic description of structure is used
to create a model for the refinement of data, and parameters (lattice param-
eters, atomic positions, atomic displacement parameters, background func-
tions, scale factors, profile parameters, etc.) are varied to achieve a model
that generates a scattering pattern best matching the data. It is common for
many crystallographic models to be tried in this process. In these programs,
the goodness of fit factor, $R_w$, is used to assess the quality of the refinement. It
is calculated as the weighted difference between observed $y_i^{obs}$ and calculated
$y_i^{calc}$ data points.

$$R_w = \left[ \frac{\sum w_i (y_i^{obs} - y_i^{calc})^2}{\sum w_i (y_i^{obs})^2} \right]^{1/2}. \quad (1.4)$$
The experimental PDF is typically extracted from total scattering data using the program PDFGetN[20] or PDFGetX2[21], depending on whether the radiation is from a pulsed neutron source or a synchrotron X-ray source. If synchrotron data are collected using the RAPDF method, the \( S(Q) \) data must first be extracted from image plate data using the program Fit2D.[22]

Full structure profile refinements can be carried out on PDF data in the program PDFFIT[23] or with the newly developed PDFfit2 and PDFgui programs.[24] In a manner similar to Rietveld refinement,[15] a structure is provided and parameters are selectively varied to achieve a model that best generates features of the data. Again, it is common for many models to be tried in the analysis. These programs assess goodness of fit similar to the Rietveld programs, with

\[
R_w = \left[ \frac{\sum w_i (G_{i}^{\text{exp}} - G_{i}^{\text{calc}})^2}{\sum w_i (G_{i}^{\text{exp}})^2} \right]^{1/2}. \tag{1.5}
\]

Additionally, several reverse Monte Carlo (RMC) programs exist for analyzing PDF data with large structure models. The programs DISCUS[25] and RMCprofile[26] are examples. Bréger et al. have authored several papers demonstrating a combination of NMR spectroscopy and X-ray and neutron PDF and RMC methods to explore local environments and short-range ordering in Li-ion battery electrode materials. [27, 28]
1.1.4 Illustrative Examples

The power of total scattering techniques for studying local structural features can be demonstrated by first considering materials without any long-range order. Such a case is conveyed in Figure 1.4, where the experimental $G(r)$ for Fountainebleau sandstone, which is more than 97% quartz, at the top of the figure and the $G(r)$ for amorphous silica at the bottom of the figure are compared. In the left panel of the figure it can be seen that the crystalline sandstone sample has extended long-range structure (pairs of atoms extend to high-$r$), while the amorphous sample has no atom-atom correlation beyond 5 Å of $r$. However, the structure of rigid SiO$_4$ tetrahedra are intact and common to both materials, as displayed in the low $r$ region of the PDFs in the right panel of the figure. The sensitivity of the PDF method to amorphous components is discussed in [29] and several examples are given in the literature.[30, 31]

A more relevant topic to this thesis work is the application of total scattering to nanomaterials, which can be thought of as intermediate between amorphous and extended crystalline materials. Aside from our own work, some of which will be discussed in Chapters 2 and 3, a number of groups have explored the application of the PDF to quantitatively describe the structure of nanoparticle systems.[3, 8, 9, 32]

Conventional diffraction methods with X-rays or neutrons give informa-
Figure 1.4. A comparison of the $G(r)$s for crystalline Fountainebleau sandstone (97 % quartz) (top) and amorphous silica (bottom). The absence of any extended structure in silica is evident in the bottom half on the pane, and provides a striking contrast to the crystalline sandstone structure in the top half of the pane. The views at right show the similarity in the first and second nearest neighbor atom-atom correlations. (Amorphous SiO$_2$ data from Sylvia McLain.)
tion of poor quality for nanomaterials. The primary use of X-ray diffraction from sub-micron powders has traditionally been to estimate particle sizes from the Scherrer broadening[33], though for nanoparticles the reflections are often too broad to achieve this with any reliability.

As an example Figure 1.5 displays powder patterns for bulk, 2.5 nm, and 1.0 nm gold particles in capillary tubes collected with an image plate detector[34] at the Advanced Photon Source. The wavelength of incident radiation used was $\lambda = 0.15489 \text{Å}$, enabling a large number of Bragg reflections. The data has been refined using fcc gold structure models. The particle sizes have been estimated from Scherrer broadening of the diffraction data,

$$\beta = \frac{K\lambda}{t \cos \theta}$$  \hspace{1cm} (1.6)

where $\beta$ is the broadening of the X-ray beam due to crystallite size $t$. The correction factor $K$ accounts for particle shape. The broadening associated with decreasing crystalline correlation length clearly demonstrates that especially in the extremes of size reduction, high quality, high resolution data are important.

As an example of the information total scattering can bring to nanomaterial studies we show results of our study on a 2 g batch of fluorothiol-capped fcc gold nanoparticles, with a mean diameter of approximately 4 nm, using total scattering powder neutron diffraction. Data were collected at 15 K and 300
Figure 1.5. Rietveld refinements for gold powder diffraction data collected at the APS. The profiles top to bottom correspond to bulk gold, 2.5 nm particles, and 1.0 nm particles. Particle sizes were estimated from Scherrer broadening (Equation 1.6). Expected peak positions for the gold fcc structure are given in the top panel. (Data collected by the Parise group.)
K on the NPDF[13] diffractometer for the nanoparticles and for a bulk gold reference. The results were originally published in reference [10].

Figure 1.6 compares the time-of-flight neutron scattering patterns of (a) bulk and (b) 4 nm nanoparticles of gold, and illustrates the vast difference in scattering intensity and profile typically displayed for such systems. The additional background scattering peaked around $Q = 5\,\text{Å}^{-1}$ in the nanoparticle data is due to incoherent scattering from hydrogen present in the capping material, a significant complication for neutron studies of nanoparticles.

A real space analysis of the structure of the materials was performed using the Pair Distribution Function. The PDFs for $T = 15$ K are shown out to 100 Å in Figure 1.7(a) and 1.7(b) for bulk and nanoparticles of gold, respectively. The PDF patterns for nanoparticles are significantly attenuated compared to bulk patterns due to the finite size of the particles. Refinements are shown in Figure 1.7(c) and 1.7(d) using a regular fcc structure. The features of the nearest atom-atom distances in the 4 nm particles were similar to those in bulk gold, however, quantitative determination from refinement indicated significant differences. For instance, the lattice parameters for the nanoparticles were smaller than the bulk lattice parameters. Further, the neutron PDF was sensitive to the vector between surface Au atoms and the sulfur of the thiol cap layer, observed at $2.4\,\text{Å}$. This structural feature is marked by an arrow in Figure 1.7(e). The de-
Figure 1.6. Normalized scattered intensities, $S(Q)$, for bulk gold (a) and the 4 nm gold nanoparticles (b). Note the different intensity scale in both panels. Reproduced with permission from reference [10]. © 2004, Elsevier.
tails of the experiment and the results of the structure analysis are reported in detail in reference [10].

Simulations of the $G(r)$ for cuboctahedral nanoparticles [35, 36] of different diameters (Figure 1.8) demonstrate that the PDF method is sensitive to nanoparticle size, since the $G(r)$ clearly cannot contain vectors that are longer than the maximum diameter of the particle. It can be seen that the experimental pattern (bottom trace) lies somewhere between the simulated patterns for particles of diameters 3.5 nm and 5.8 nm. This result demonstrates that complete structural “fingerprints” of nanomaterials up to several nanometers in size can be measured using total neutron scattering.

An extension has been made whereby particle size is refined as a parameter in the PDF analysis of total scattering data.[37] This capability is now incorporated in the PDFFIT[23] and PDFgui[24] software. For this application, the intrinsic dampening of the PDF data due to instrument resolution must be well-characterized.

The studies on small particles of gold point to the great power of total scattering in ensemble-averaged analysis of structure in the nano regime. While the only refinable parameter for correlation length applies to nanoparticles, many studies incorporate $r$-range dependent refinements to probe the length-scale of local structure correlations: over short $r$ ranges, local correlations are
Figure 1.7. $G(r)$ of bulk gold (a) and gold nanoparticles (b) measured on NPDF at $T = 15$ K. In both cases the maximum momentum transfer used to obtain $G(r)$ was $Q = 30\,\text{Å}^{-1}$. Refinement results for (c) bulk gold and (d) gold nanoparticles at $T = 15$ K. The filled circles represent the data and the solid grey line the model PDF. (e) shows the nearest neighbor region of the PDF. A structural feature can be seen at $r = 0.235$ nm marked by the arrow. This distance corresponds to the expected Au-S bond length. Reproduced with permission from reference [10]. © 2004, Elsevier.
Figure 1.8. Simulated PDFs for cuboctahedral $fcc$ gold nanoparticles clusters of different (indicated) sizes, compared with the total scattering pair distribution function $G(r)$ data from perfluorothiol-capped gold nanoparticles (displayed at the bottom). The experimental data clearly indicates a particle size range between 3.5 and 5.8 nm. Reproduced with permission from reference [10]. © 2004, Elsevier.
distinct, but over longer refinement ranges, the signature of these configurations steadily damp out and the atom-atom interactions correspond increasingly well to the average structure.

1.2 Perovskite Oxides

It is prudent to consider the particular class of materials that will encompass the bulk of the work herein: perovskite oxides and related phases. Perovskite-phase mixed metal oxides exhibit outstanding and wide-ranging chemical and physical properties. A few examples are ferroelectricity, colossal magnetoresistance, superconductivity, non-linear optical behavior, pyroelectricity, and piezoelectricity.

The perovskite unit cell has the general formula AMX$_3$. Perovskite can be regarded as a framework structure made up of corner-sharing (MX$_6$) octahedra with A ions occupying twelve-coordinate interstices, or as a ccp array of A and X atoms with M atoms occupying octahedral holes. The M site can be occupied with elements across the transition series, giving rise to a rich property variation. The basic unit cell with cubic symmetry $Pm\bar{3}m$ is shown in Figure 1.9, depicted with a white M atom at the center of a MX$_6$ octahedra, and green A atoms at the cell corners.
Many types of distortions modify the structure of the basic perovskite unit cell. Among the most common are octahedral tilting, cation site ordering, and the off-centering of atoms. As an introduction to the work of this thesis, common perovskite structure distortions, and examples of prior total scattering work exploring them, will be discussed.

Octahedral tilting distortions of the perovskite structure occur when a size mismatch of the constituent atoms is present. With smaller than ideal A-site cations, the octahedra tilt, resulting in a structure of lower symmetry. The Goldschmidt tolerance factor, $\tau$, is used to parameterize how well the sizes of the ions match. It is defined as

$$\tau = \frac{r_A + r_X}{\sqrt{2}(r_M + r_X)} \quad (1.7)$$
Table 1.2. Tolerance factors for several perovskite oxides.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\tau$</th>
<th>Space Group</th>
<th>Tilt System</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTiO$_3$</td>
<td>1.071</td>
<td>$P4mm$</td>
<td>$a^0a^0c^0$</td>
</tr>
<tr>
<td>BaNbO$_3$</td>
<td>1.031</td>
<td>$Pm\bar{3}m$</td>
<td>$a^0a^0a^0$</td>
</tr>
<tr>
<td>SrTiO$_3$</td>
<td>1.009</td>
<td>$Pm\bar{3}m$</td>
<td>$a^0a^0a^0$</td>
</tr>
<tr>
<td>NaTaO$_3$</td>
<td>0.974</td>
<td>$Pnma$</td>
<td>$a^+b^-b^-$</td>
</tr>
<tr>
<td>CaTiO$_3$</td>
<td>0.973</td>
<td>$Pnma$</td>
<td>$a^+b^-b^-$</td>
</tr>
</tbody>
</table>

where $r_A$, $r_M$, and $r_X$ are the radii of the A, M, and X ions respectively.[38]

An ideal perovskite has a tolerance factor of unity. As $\tau$ departs from 1, the cubic structure becomes increasingly less stable relative to lower symmetry structures and tilting occurs to attain maximized electron stabilization. In perovskite structures with tolerance factors greater than unity, cation displacements are commonly observed. Table 1.2 gives Goldschmidt tolerance factors for common perovskite compounds.

A useful notation has been developed by Glazer[39] and refined by Woodward [40] and Howard and Stokes[41] to describe both the tilting and out of center distortions present in perovskite systems. In Glazer’s classification scheme, three letters are accompanied by a superscript of 0, + or −. The letters correspond to the $x$, $y$ and $z$ axes of the $Pm\bar{3}m$ cubic perovskite structure. If two or more letters are the same, this indicates the magnitude of the tilts...
are equal along the axes represented. The superscripts + and − refer to tilts about a given axis in the $x$, $y$, and $z$ direction. A + indicates that successive tilts about an axis are equal in the same direction (in phase) and a − indicates the successive tilts about an axis are equal in magnitude but opposite in direction (out of phase). A superscript of 0 is used when a given structure does not display any tilting. For example, $a^+b^-b^-$, notation used to describe the tilting in $Pnma$ perovskites denotes in phase tilting about the $x$ axis, and out of phase tilting about the $y$ and $x$ axes. It also indicates that tilts about the $y$ and $z$ axes are equal in magnitude.

The modified Glazer notation introduced by Howard and Stokes[41] provides information about out of center displacements of the $M$ cations in perovskites. This notation includes subscripts of 0, + or − to indicate $M$ cation displacements in the three crystallographic directions. The structure of tetragonal BaTiO$_3$ (space group $P4mm$) is denoted $a^0a^0c^0$ in the standard Glazer notation. The structure has a displacement along the [001] direction giving rise to ferroelectricity. The modified notation $a^0_0a^0_0c^0_+$ indicates Ti displaces in the $+z$ direction. A notation of $a^0_0a^0_0c^0_-$ would indicate Ti displacement in the $−z$ direction.

If MX$_6$ rotation is small, the PDF can be insensitive. In these cases, changes in mean positions are smaller than the widths of the peaks in the distribution.
functions, or the resolution of the data, and long-range order and average positions provide a better characterization. Total neutron scattering and reverse Monte Carlo studies have been used to characterize the displacive phase transition in SrTiO$_3$, for example, whereby the material transitions from an $a_0^0a_0^0a_0^0$ perovskite to an $a_0^0d_0^0c_0^-$ perovskite below 105 K.[42]

Many perovskite materials have been engineered to incorporate ions with a propensity to distort, thereby increasing the likelihood of polarizability. This includes perovskites with lone pair species, such as Pb$^{2+}$ and Bi$^{3+}$, on the A site. There are numerous examples of local structure studies on such systems. For example, Egami and co-workers have examined the relaxor ferroelectric Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN) and found that the local structure of the compound determined by the PDF was markedly different than the average crystal structure.[43] The important piezoelectric system Pb(Zr,Ti)O$_3$ has also been examined using PDF methods by Egami et al.[44] A review of local structure studies on ferroelectric materials is given in reference [45].

Other perovskite structures contain ions that exhibit first-order Jahn-Teller effects, such as Cu$^{2+}$, which has a $d^9$ configuration, or Mn$^{3+}$, with $d^4$ configuration. Examples of PDF studies characterizing local Jahn-Teller distortions include work by Rodriguez et al.[46] on the rare-earth manganese oxide perovskite La$_{0.5}$Ca$_{0.5}$MnO$_3$. Recent additional work by Božin et al. has
helped map out the different electronic and magnetic phase boundaries in the temperature-composition plane in the La$_{1-x}$Ca$_x$MnO$_3$ system.\[47\]

Further systems contain $d^0$ ions such as Ti$^{4+}$ and Nb$^{5+}$, and exhibit second-order Jahn-Teller effects. Petkov et al.\[48\] have recently demonstrated the use of the PDF to understand local structure distortions and polar behavior in Ba$_x$Sr$_{1-x}$TiO$_3$ nanocrystals. We visit BaTiO$_3$ at length in Chapters 2 and 3 of this thesis, where we explore local atomic correlations in nanoparticles of three sizes using synchrotron X-ray total scattering, and the structure of smaller particles using neutron total scattering.

While the PDF is sensitive to differences in atom-atom distances (displacive disorder), there are some types of disorder the PDF is less sensitive to. Figure 1.10 shows a 2-dimensional schematic comparing displacive and order-disorder phenomena. While the two scenarios depict distinct local structures, their crystallographic descriptions are the same. A classic system that displays order-disorder phenomena is BaTiO$_3$. This material transitions successively from cubic $Pm\bar{3}m$ to tetragonal $P4mm$ to orthorhombic $Amm2$ to, finally, a rhombohedral $R3m$ ground state as it is cooled from high temperatures.\[50, 51\] In the rhombohedral crystal structure, Ti in BaTiO$_3$ displace towards octahedral faces, resulting in three short and three long Ti-O distances, giving rise to a nearly bimodal first peak in the PDF. Figure 1.11 gives low-$r$ PDF data
Figure 1.10. A schematic comparing the displacive (left) and order-disorder (right) models of tetragonal BaTiO$_3$. The black circles represent Ba atoms and the heads of the arrows represent Ti atoms. Oxygen atoms have been left out. The top of the figure shows two distinct local structures. The displacive model has Ti displacements in the [01] direction. The order-disorder model has random Ti displacements in the [11] or [11] directions. While these models are locally distinct, the crystallographic unit cells for the two models are the same. The local model schematics are adapted from [49].
for tetragonal BaTiO$_3$ measured at room temperature on the NPDF instrument. The figure shows this local rhombohedral structure persists at room temperature despite the average structure tetragonal phase, supporting the order-disorder model.\[52\] While the PDF is sensitive to this local distortion, it is not sensitive to changes corresponding to the coherence of displaced sites. Thus, previous work has show that low-$r$ PDF data above and below structural phase transitions in BaTiO$_3$ appear unchanged.\[3, 52\] Chapter 4 of this work will uncover a related and crucial structural feature in the structures of bulk Nb-substituted BaTiO$_3$ and SrTiO$_3$, underpinning the distinct electronic properties in the two materials.

An additional route to polarization in perovskite structures is substitution on the anion sites, giving rise to lower symmetry structures. It is thought the increase in cation-anion covalency and the introduction of more polarizable ions into the lattice may influence dielectric properties and increase the likelihood of a second order Jahn-Teller distortion involving the $d^0$ cation. Ordered oxynitride and oxyfluoride perovskite materials (materials with partial replacement of O by N or F) have been explored to this end. The possibilities for polar crystal lattices in these compounds depend critically on the nature and extent of anion ordering. The ability of the PDF technique to extract chemical short range order from diffuse scattering components has been demon-
Figure 1.11. Experimental low-$r$ neutron PDF for bulk BaTiO$_3$ measured at room temperature compared with calculated PDFs for tetragonal $P4mm$ and rhombohedral $R3m$ models. The local rhombohedral structure supports the existence of the order-disorder model of BaTiO$_3$, where the long-range crystal structure corresponds to averaged domains.
strated by both simulation and experiment. Still, sensitivity to site ordering is dependent on the respective scattering lengths of the ions (they should be well-separated). Our work in the fifth chapter of this thesis investigates the local atomic correlations observed in the oxynitride perovskite BaTaO$_2$N. Chapter 6 will conclude this work by presenting octahedral tilting and O and N ordering in other members of the perovskite oxynitride family, SrTaO$_2$N and CaTaO$_2$N.
Chapter 2

Size Effects in BaTiO$_3$ from X-ray Total Scattering

Ferroelectricity in perovskite barium titanate (BaTiO$_3$) was reported in 1946, and since that time it has been one of the most exhaustively studied materials of its kind. It is used today in an array of applications such as multilayer ceramic capacitors,[54, 55] gate dielectrics,[56] waveguide modulators,[57, 58] IR detectors,[59] and holographic memory. [60]

The sweeping technological trend towards decreasing dimensions makes it of interest to examine the dielectric and ferroelectric properties of BaTiO$_3$ materials whose size is reduced down to the nanoscale. A growing body of experimental and theoretical work on the subject[61, 62, 63, 64, 65, 66] has re-
vealed a complex and sometimes controversial picture. Here we apply the total scattering tools demonstrated in Chapter 1 to examine size effects in a series of BaTiO$_3$ nanoparticles.

2.1 Introduction

Barium titanate (BaTiO$_3$) is a ferroelectric oxide with a transition from a ferroelectric tetragonal phase to a paraelectric cubic phase upon heating above 130 °C (there are further transitions below room temperature). In cubic perovskite BaTiO$_3$, whose structure is displayed in Figure 2.1(a), titanium atoms are octahedrally coordinated by six oxygen atoms. Ferroelectricity in tetragonal BaTiO$_3$ is due to an average relative displacement along the $c$-axis of Ti from its centrosymmetric position in the unit cell, and consequently the creation of a permanent electric dipole. The tetragonal unit cell is shown in Figure 2.1(b). The elongation of the unit cell along the $c$-axis and consequently, the deviation of the $c/a$ ratio from unity is used as an indication of the presence of the ferroelectric phase.[67, 68, 69]

Many experimental and theoretical[71, 72, 73, 74, 75, 76, 77, 78, 79] studies have indicated the phase transition temperature of BaTiO$_3$ is size-dependent, with the ferroelectric phase becoming unstable at room temperature when par-
Figure 2.1. Unit cell of BaTiO$_3$ in both the (a) cubic $Pm\bar{3}m$ structure and (b) tetragonal $P4mm$ structure. In the tetragonal unit cell, atoms are displaced in the $z$-direction, and the cell is elongated along the $c$-axis. Atom positions: Ba at (0, 0, 0); Ti at (1/2, 1/2, $z$); O1 at (1/2, 1/2, $z$); O2 at (1/2, 0, $z$). Displacements in (b) have been exaggerated for clarity. Reproduced with permission from reference [70]. © 2008, American Chemical Society.
ticle diameter decreases below a critical size. However, both theoretical and experimental reports of this critical dimension encompass a broad range of sizes. The experimental discrepancies may arise due to intrinsic differences between ferroelectric samples, as the transition is sensitive to conditions such as compositional variation,[80] lattice defects,[62] strain,[81] or surface charges.[74] Furthermore, the differences in cell parameters between the two phases are small compared to other sources of broadening in diffraction data, likely leading to an overestimation of the critical size. Recent work by Fong et al. on perovskite PbTiO$_3$ thin films indicates ferroelectric behavior persists down to a thickness of only three unit cells,[79] a value significantly less than suggested by previous experimental studies.

Several theoretical studies have been particularly useful in furthering the understanding of the observed behavior of ferroelectrics at small sizes.[71] However, ferroelectrics are particularly sensitive to surface effects, making modeling increasingly complicated as dimensions are reduced. Many models based on Landau theory[72] overestimate critical sizes, perhaps due to the use of bulk material parameters in the free-energy expression.[73] Spanier et al. have found that certain surface termination of thin films can stabilize polarization down to a thickness of only several unit cells.[74] Their calculations, which take into account experimentally determined nanoscale materials pa-
rameters, estimate the critical size for a BaTiO$_3$ sphere to be 4.2 nm. Other theoretical treatments such as effective Hamiltonian and \textit{ab initio} calculations have predicted the presence of ferroelectricity in perovskite films as thin as three unit cells.[77, 78]

Various experimental probes of the structure of BaTiO$_3$ have lead to substantial controversy. In particular, the disagreement of Raman and diffraction studies suggests that the phase transition in BaTiO$_3$ is complex, with order-disorder as well as displacive character (see Figure 1.10).[62, 82, 83] As explained in Chapter 1, in bulk BaTiO$_3$, structural transformations are explained by averaging domains that are locally rhombohedral, supporting a dominant order-disorder component to the structural phase transitions.[51, 49] For the tetragonal phase, the Ti atoms are distorted in several $<111>$ directions, oriented with a net displacement in the $c$-direction. A number of studies, including our own work displayed in Figure 1.11, provide evidence for disorder within BaTiO$_3$ above the transition temperature, proving the existence of local distortions within the cubic phase.[84, 85, 86]

For nanoparticles, X-ray diffraction studies produce data that are consistent with an increasingly cubic structure at smaller particle sizes, not distinguishing between average and local structure.[62, 87] In contrast, Raman results have supported the existence of tetragonal symmetry at small dimensions.[88]
In EXAFS and XANES analysis of 10, 35, and 70 nm BaTiO$_3$ particles,[89] Frenkel et al. find Ti displacements for all samples studied, in contrast to their cubic macroscopic crystal structures from lab X-ray diffraction. Petkov et al.[48] have recently made use of the pair distribution function approach to understand local structure distortions and polar behavior in Ba$_x$Sr$_{1-x}$TiO$_3$ ($x = 1, 0.5, 0$) nanocrystals. They found that 5 nm BaTiO$_3$ is on average cubic, but that tetragonal-type distortions in the Ti-O distances are present within the cubic structure. They did not, however, find the distortions to be inherent to small particles as they were not found in nanoparticles of perovskite SrTiO$_3$.

We have studied particles with average sizes of 70 nm, 45 nm, and 26 nm by temperature dependent Raman spectroscopy, variable temperature X-ray diffraction, and with room temperature Rietveld and atomic pair distribution function (PDF) analysis of high-energy, high momentum-transfer synchrotron X-ray diffraction data. These results were previously published in reference [70]. We have additionally explored a surprising experimental result with Density Functional Theory (DFT) calculations.

The complementary structural methods we employ provide information on different time and length scales. Raman spectra reflect the local symmetry around the scattering sites, and are averaged over different parts of the sample. The diffraction techniques allow both an average depiction of the structure
(through pattern matching and Rietveld analysis) as well as information on the near-neighbor length scale through PDF analysis.

2.2 Preparation

Several preparation strategies have been reported in recent years for high quality, well-defined BaTiO$_3$ nanocrystalline samples. Hydrothermal or solvothermal methods have been systematically used to make nanocrystalline BaTiO$_3$.[90, 91, 92, 93] O’Brien et al.[94] and Urban et al.[75, 95] have produced BaTiO$_3$ particles and rods respectively from the reaction of a bimetallic alkoxide precursor with hydrogen peroxide. Niederberger et al. report a solvothermal preparation of 5 nm particles of BaTiO$_3$ and SrTiO$_3$ from titanium isopropoxide and metallic barium or strontium in benzyl alcohol.[96]

For the X-ray study presented here, particles of BaTiO$_3$ with average diameters of 70, 45 and 26 nm were prepared by Millicent Smith of the Brus group at Columbia University. Anhydrous benzene, isopropanol, dendritic barium (99.99%), and titanium isopropoxide (99.999%) were obtained from Aldrich Chemical Co. and used as received. The bimetallic precursor BaTi[OC$_3$H$_7$]$_6$ was prepared according to Urban et al.[95] Parr acid digestion bombs with 23 mL Teflon liners were used for the solvothermal reaction. The effects of reac-
tion conditions such as temperature, precursor concentration, solvent composition and the addition of surfactants were explored. In a typical synthesis, 10 mmol (5.4 g) of the precursor, BaTi[OC\(_3\)H\(_7\)]\(_6\), was added to the Teflon liner of a digestion bomb under an inert atmosphere. 10 mL of solvent was added to the precursor under flowing argon according to the water and isopropanol ratios in Table 2.1, forming thick white suspensions in all cases. The Teflon liner was tightly sealed inside the acid digestion bomb, and the mixture was heated in an oven at 220 °C for 18 hours. The resulting white precipitate was collected by centrifugation, washed with ethanol and allowed to dry under ambient conditions. A white powder suitable for powder XRD and Raman measurements was produced with a typical yield of 1.93 g. Sintered pieces of BaTiO\(_3\) were also purchased from Aldrich Chemical Co. for use as a bulk standard.

TEM images taken on a JEOL 100CX instrument using an accelerating voltage of 100 kV were used to determine the particle size and morphology. Typical images are shown in Figure 2.2, with histograms of the particle size distributions displayed as insets. The particles were nearly spherical in shape with average sizes of 70, 45, and 26 nm. Table 2.1 gives the average particle size obtained with each solvent mixture as determined by TEM; the given error is plus or minus one standard deviation. The composition of the solvent played a critical role in determining the size of the particles, with pure water produc-
Figure 2.2. TEM images of BaTiO$_3$ nanoparticles. Histograms of individual particle sizes, shown as insets, correspond to (a) 70 +/- 10 nm, (b) 45 +/- 9 nm, and (c) 26 +/- 5 nm. The 200 nm scale bar is common to all three micrographs. (Micrographs from the Brus group.) Reproduced with permission from reference [70]. © 2008, American Chemical Society.
Table 2.1. The effect of solvent composition (water: isopropanol by volume) on BaTiO$_3$ particle size from solvothermal preparation. Estimated particle sizes are from TEM.

<table>
<thead>
<tr>
<th>Water: Isopropanol (v:v)</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0</td>
<td>70 +/- 10</td>
</tr>
<tr>
<td>40:60</td>
<td>60 +/- 10</td>
</tr>
<tr>
<td>30:70</td>
<td>45 +/- 9</td>
</tr>
<tr>
<td>20:80</td>
<td>26 +/- 5</td>
</tr>
<tr>
<td>0:1</td>
<td>10</td>
</tr>
</tbody>
</table>

The largest sizes and pure isopropanol producing the smallest. Scherrer analysis$^{[33]}$ (Equation 1.6) of the lab X-ray diffraction (111) peak at room temperature gave X-ray coherence lengths (grain sizes) of 33, 29, and 21 nm for the 70, 45 and 26 nm particles, respectively. The instrumental line width limits the determination of particle size to a maximum of 35 nm, preventing any conclusions about the single-crystallinity (grain size) of the 70 nm particles. However, for the two smaller sizes, the individual particles are likely single crystals. The sample particles are unstrained, as they are not thin-film samples, and are compositionally homogeneous with, in particular, no discernible OH impurities, that are known to plague many low-temperature solution preparations of ferroelectric oxides.$^{[62, 83, 87]}$
2.3 Raman and X-Ray Scattering Study

2.3.1 Raman Spectroscopy

Tetragonal BaTiO$_3$ has 10 Raman-active modes. When splitting of transverse and longitudinal optical modes, as well as splitting due to differing polarizability in each unit cell direction is considered, 18 Raman active phonons result.[97] Symmetry demands that cubic BaTiO$_3$ should be completely Raman-inactive. However broad peaks centered at 260 and 530 cm$^{-1}$ are still observed above the cubic-to-tetragonal phase transition temperature.[88] The Raman activity of the cubic phase is generally attributed in the literature to disorder of Ti in the nominally cubic phase.[97]

Raman spectroscopy was performed in air using a backscattering micro-Raman spectrometer with helium-neon laser (633 nm) excitation. A home-built thermoelectric heating stage was used for temperature-dependent measurements. Spectra were taken at temperatures ranging from room temperature to above 150 °C. The 300 cm$^{-1}$ peak[82] was fit to a Lorentzian line shape on a sloping baseline and from this fit, the scaled peak area and linewidth were determined.

Figure 2.3 shows the Raman spectrum of (a) bulk, (b) 70 nm, (c) 45 nm and (d) 26 nm BaTiO$_3$ over a range of temperatures between 25 °C and 150 °C.
Figure 2.3. Raman spectra at different, indicated temperatures, for bulk (a) BaTiO$_3$, (b) 70 nm particles, (c) 45 nm particles, and (d) 26 nm particles. Temperatures increase from top to bottom in each panel. Temperatures are specified to be within a range of up to +/- 3°C. The locations of Raman modes are indicated at the top of the figure. The features below 200 cm$^{-1}$ are due to a trace BaCO$_3$ impurity, and these are not found in the bulk sample. (Data from the Brus group.) Reproduced with permission from reference [70]. © 2008, American Chemical Society.
The assignments given to the Raman modes at the top of Figure 2.3 are those reported in the literature.[88] Below 200 cm\(^{-1}\) we find some weak scattering in the nanoparticle samples due to a BaCO\(_3\) impurity. As seen by others, the BaTiO\(_3\) Raman spectra have the broad features characteristic of Ti disorder in the unit cell at all temperatures, and at all sizes. In the bulk BaTiO\(_3\) spectra in Figure 2.3(a) the intensities of the \(E(\text{LO+TO}), B_1\) peaks at 300 cm\(^{-1}\), and \(E(\text{LO})\) and \(A_1(\text{LO})\) peaks at 715 cm\(^{-1}\) decrease rapidly as the temperature is increased through the bulk \(T_C\), an observation consistent with prior reports.[82] We interpret the disappearance of the 300 cm\(^{-1}\) peak as an indicator of the tetragonal phase and use two characteristics as a gauge of the phase transition. The first is an increase in peak width at the phase transition temperature similar to that reported by Hoshina et al.,[65] and the second is the loss of peak-intensity with increasing temperature. These values are given in Figure 2.4(a-d).

In the panels of the figure the linewidth for the \(E(\text{LO+TO}), B_1\) peak (shown with solid circles) increases both with increasing temperature and as particle size decreases. The schematic in Figure 2.5 summarizes this relationship. The much larger linewidths of the Raman peaks of the nanoparticles suggest that the tetragonality present is accompanied by a significantly decreased structural coherence. It is interesting to note that bulk BaTiO\(_3\) near the cubic to
Figure 2.4. Results from fits to the Raman data. Filled circles show variation of the linewidth of the 300 cm\(^{-1}\) Raman signal as a function of temperature. Open squares are intensities of the 300 cm\(^{-1}\) Raman signal normalized to intensity at 280 cm\(^{-1}\). Displayed for (a) bulk powder, (b) 70 nm particles, (c) 45 nm particles, and (d) 26 nm particles. (Data from the Brus group.) Reproduced with permission from reference [70]. © 2008, American Chemical Society.
tetragonal phase transition displays a Raman linewidth that is similar to the linewidth displayed by the 26 nm particles at all temperatures.

The linewidth analysis is complemented by the analysis of scaled peak area. The open squares in Figure 2.4(a) show that near the expected phase transition temperature of 130 °C there is a sharp drop in the Raman intensity of the 300 cm\(^{-1}\) peak for the bulk sample, but a more gradual decrease in intensity over the entire temperature range for the 70 nm and 45 nm particles. In contrast, the peak area of the 26 nm particles in Figure 2.4(d) is nearly constant over the entire temperature range. These results indicate a phase transition that becomes increasingly diffuse in temperature as the particle size decreases.

The lack of a sharply defined phase transition in nanosized samples is also observed using differential scanning calorimetry (DSC). Differential scanning calorimetry was performed on a Perkin Elmer Pyris 1 DSC. For each scan, 3-4 mg of sample was used. The heating profile consisted of two cycles of heating from 0 °C to 150 °C at a rate of 10 °C per minute and then cooling from 150 °C to 0 °C at the same rate. For bulk BaTiO\(_3\), the DSC trace exhibits a peak near 130 °C indicative of the phase transition. Similar features are not observed in the DSC of nanoparticle samples. Together with the Raman results, these findings support the idea that the phase-transition is distributed over a wide range of temperatures in the nanoparticles although it is sharply defined in the
Figure 2.5. A schematic drawing a parallel between the loss of structural coherence observed in BaTiO$_3$ either upon heat treatment through a phase transition (horizontal axis) or through a decrease in particle size (vertical axis).

2.3.2 Laboratory Thermodiffraction

Laboratory X-ray diffraction (XRD) data were obtained using a Rigaku rotating anode together with a custom built four-circle diffractometer. Graphite monochromated CuK$_\alpha$ radiation (1.39217 Å), together with a matched graphite analyzer, was used in Bragg-Brentano geometry. In this way, a well-defined powder diffraction profile was obtained for all reflections, allowing a detailed analysis of the profile changes associated with the paraelectric-to-
ferroelectric phase transition. The intensities were normalized to the incident beam to eliminate drift over the data acquisition time. A home-built heating stage was used to reach temperatures up to 150 °C. X-ray patterns above 143 °C were collected to obtain a cubic reference for the expected increase in the peak widths with 2θ. Full pattern refinements were executed in the program Winprep[98] using the profile parameters obtained from the cubic phase above 143 °C.

The splitting of the X-ray diffraction peaks is well-defined in terms of symmetry, allowing analysis of systematic changes for different (hkl) indices. Figure 2.6 shows diffraction data for 70 nm BaTiO$_3$ at room temperature and at 148 °C over a small 2θ range. In the high symmetry cubic phase no reflections are split. In the tetragonal phase, (222) remains a single peak while the (400) reflection is divided into (400/040) and (004) peaks with intensity ratio 2:1. Since the c/a ratio is larger than 1, the (004) reflection shifts to a lower 2θ value, and the (400/040) reflection correspondingly to a higher 2θ value. In spite of changes in symmetry, the cubic to tetragonal phase transition is usually not well-resolved in diffraction studies of nanosized BaTiO$_3$ because of inherent line broadening due to small particle size.

In our study, the phase evolution of BaTiO$_3$ particles was determined by pattern matching to the laboratory X-ray diffraction data. Patterns taken above
Figure 2.6. 70 nm BaTiO$_3$ particle lab XRD data shown over a small 2$\theta$ range. (a) was recorded at room temperature and (b) was recorded at 148$^\circ$C. Reflections have been labeled for the cubic phase in (b). The (222) peak does not split in the tetragonal phase and consequently the peak width is constant with temperature. Peaks which are degenerate in the cubic phase but not in the tetragonal phase, for example cubic (400), widen and lose intensity upon cooling. (Data from Theo Seigrist and Millicent B. Smith.) Reproduced with permission from reference [70]. © 2008, American Chemical Society.
Figure 2.7. Change in cell $a$ and $c$ parameters, and the pseudocubic cell parameter for (a) bulk, (b) 70 nm particles, (c) 45 nm particles, and (d) 26 nm particles from pattern matching to variable temperature lab diffraction data. Uncertainty in temperature for all data points is $+\/- 2^\circ$C. (Data from Theo Seigrist and Millicent B. Smith.) Reproduced with permission from reference [70]. © 2008, American Chemical Society.
$T_C$ were matched to the cubic phase to determine the intrinsic peak profile resulting from particle size and instrumental effects. To investigate structural changes with temperature, all data sets were pattern-matched with a tetragonal unit cell, even above the phase transition, using this fixed profile function.

Figures 2.7(a-d) show the refined values of the length of the $a$ and $c$ cell parameters at each temperature for bulk, 70 nm, 45 nm, and 26 nm particles, respectively. The pseudocubic cell parameter (the cube root of the unit cell volume) is also shown. In Figure 2.7(a) we see that for the bulk particles, there is at first a gradual change in $a$ and $c$ cell parameters as temperature increases. The rate of change becomes greatest at the transition temperature, at which point the $c/a$ ratio drops to its cubic-phase value of unity. This behavior is well known for the bulk material and has been explained as a second order phase transition followed by a first order phase transition.[69] In contrast to the behavior of the bulk material, the three sizes of particles studied here (Figure 2.7(b-d)) undergo more gradual changes in cell parameters, without a dramatic increase in slope at the phase transition temperature.

At room temperature, the $c/a$ ratio for the bulk sample was calculated to be 1.010, close to the value of 1.011 reported in the literature.[51] The ratio diminishes for decreasing particle size, with values of 1.0058(1), 1.0055(1) and 1.0040(2) for particle sizes of 70, 45, and 26 nm, respectively. For 26 nm parti-
cles the deviation of \( c/a \) from unity is about 40\% of that for the bulk tetragonal phase. Depressed \( c/a \) values have been modeled as a result of decreased polarization near the particle surface.[76] The picture of an increasingly broadened phase transition behavior with decreasing particle size is consistent across the analysis of Raman spectra, DSC measurements, and laboratory X-ray diffraction.

### 2.3.3 Rietveld and PDF Synchrotron Scattering Study

Synchrotron powder diffraction data were collected in transmission mode at beamline 11-ID-B of the Advanced Photon Source, Argonne National Laboratory utilizing high energy X-rays (90.6 kV, \( \lambda = 0.13648 \text{ Å} \) ) at room temperature. Samples were loaded in Kapton tubes and scattering data were collected on an image plate system (amorphous silicon detector from General Electric Healthcare) with sample-to-detector distances of 660 mm for Rietveld refinement data and 150 mm for PDF data. The raw data sets were processed to one-dimensional X-ray diffraction data using the program FIT2D.[22] A bulk internal standard was used to calibrate the processed data, to supply an effective wavelength of \( \lambda = 0.13648 \text{ Å} \) for refinements. Rietveld refinement of the synchrotron data was carried out in the XND program.[19] Lattice parameters, atomic positions, and atomic displacement parameters were refined. The
Table 2.2. Results of Rietveld refinement of the synchrotron X-ray diffraction data, collected at a wavelength of $\lambda = 0.13648$ Å. A second BaCO$_3$ phase was also refined, and the mole-fractions of the second phase are presented.

<table>
<thead>
<tr>
<th></th>
<th>70 nm</th>
<th>45 nm</th>
<th>26 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>4.0003(2)</td>
<td>4.0044(3)</td>
<td>4.0125(5)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>4.0265(4)</td>
<td>4.0254(6)</td>
<td>4.030(1)</td>
</tr>
<tr>
<td>$c/a$</td>
<td>1.0065(10)</td>
<td>1.0054(3)</td>
<td>1.0044(4)</td>
</tr>
<tr>
<td>Vol. ($Å^3$)</td>
<td>64.43(1)</td>
<td>64.55(1)</td>
<td>64.88(2)</td>
</tr>
<tr>
<td>$z$(Ti)</td>
<td>0.518(1)</td>
<td>0.524(1)</td>
<td>0.534(1)</td>
</tr>
<tr>
<td>$z$(O1)</td>
<td>0.008(8)</td>
<td>0.004(10)</td>
<td>0.003(9)</td>
</tr>
<tr>
<td>$z$(O2)</td>
<td>0.490(5)</td>
<td>0.506(5)</td>
<td>0.508(5)</td>
</tr>
<tr>
<td>BaCO$_3$ mole-%</td>
<td>3</td>
<td>6</td>
<td>11</td>
</tr>
<tr>
<td>$R_w$ (%)</td>
<td>1.92</td>
<td>2.00</td>
<td>2.68</td>
</tr>
</tbody>
</table>

PDF was extracted from the processed scattering data as described by Chupas et al.[34] with a maximum momentum transfer of $Q = 24$ Å$^{-1}$ using the program PDFGETX2.[21] Full structure profile refinements were carried out in the programs PDFfit2 and PDFgui.[24] The scale factor, lattice parameters, atomic displacement parameters, and atomic positions, as well as broadening from the sample and the instrument resolution were refined.

Rietveld refinement results of high energy, long wavevector ($Q$) syn-
chrotron X-ray diffraction for the three sizes of nanoparticles in this study are given in Table 2.2 and the corresponding fits are shown in Figure 2.8. The data have been fit with the $P4mm$ tetragonal model, as established from the pattern matching analysis. An orthorhombic BaCO$_3$ impurity phase was included in the refinements. The right panels in Figure 2.8 show the respective phase contributions to the fits from BaTiO$_3$ and BaCO$_3$. Table 2.2 includes results of a quantitative phase analysis from the refinement. Phase impurities of 11, 6 and 3 mole-% for particle sizes of 26, 45 and 70 nm are determined, in agreement with the relative increase of BaCO$_3$ scattering in the Raman data of the smaller particles. We do not expect any influence of this separate phase on Raman and X-ray results.

Synchrotron Rietveld refinement results suggest several trends as particle sizes are reduced, and are displayed graphically in Figure 2.9. For reference, previous neutron studies of the bulk material give a cell volume of 64.271(14) Å$^3$, a $c/a$ ratio of 1.011, and a Ti(z) position of 0.5224(6).[51] Lattice parameters are shown in Figure 2.9(a), indicating larger $a$ and $c$ values for smaller particle sizes. In Figure 2.9(b) the $c/a$ ratio is shown. The $c/a$ values decrease for smaller particle sizes: 1.0065(10), 1.0054(3), and 1.0044(4) for 70, 45, and 26 nm particles. Cell volume is presented in Figure 2.9(c), increasing for the same series as 64.43(1), 64.55(1), and 64.88(2) Å$^3$. These results are consistent with
Figure 2.8. Rietveld fits of the synchrotron X-ray data for (a) 70, (b) 45, and (c) 26 nm particles. Data are shown as circles and the solid orange lines are fits using two phases: BaTiO$_3$ and BaCO$_3$. Phase contributions from BaTiO$_3$ and from the BaCO$_3$ impurity are displayed across a small $2\theta$ region at the right of each panel. In the (a) and (b) panels the most intense peak has been cut off in order to show all data sets at the same scale. Reproduced with permission from reference [70]. © 2008, American Chemical Society.
pattern matching results. The increase in unit cell volume is well established in
the literature for many metal oxides,[99, 100, 101, 102] and has been observed
in studies of small particles of BaTiO$_3$.[102] This is in contrast to metals such
as Au whose cell parameters shrink as their size is diminished.[103] The most
consistent explanation for such a volume expansion in small oxide particles
is the effect of truncation on the attractive Madelung potential that holds the
oxide lattice together.[104]

The Ti(z) positions from the Rietveld refinements are plotted in Figure 2.9d.
Surprisingly, the Ti displacements increase with decreasing particle size, cor-
responding to 0.0725(1), 0.0966(2), and 0.1370(3) Å displacements in the unit
cells of 70, 45, and 26 nm particles. This result seems contradictory to the more
cubic lattice found with reduced size and motivates us to look at the local
structure.

Local structure analysis was carried out in the $P4mm$ space group, with
only the Ti(z) position refined. Our PDF analysis is based entirely on metal-
metal distances (metal positions are reliable for X-ray scattering) and was not
changed by including the refinement of O1 and O2 oxygen positions. We per-
formed tetragonal model fits from 8 to 28 Å of real-space, in 4 Å supplements.
Table 2.3 presents the PDF results of the 20 Å refinements and Figure 2.10 dis-
plays the first 10 Å of 20 Å fits to the experimental nanoparticle PDFs, $G(r)$,
Figure 2.9. Rietveld refinement results for synchrotron data for the different (indicated) particle sizes. (a) cell parameters (c is the larger value), (b) c/a ratio, (c) cell volume, and (d) z position of Ti in the tetragonal $P4mm$ phase. Reproduced with permission from reference [70]. © 2008, American Chemical Society.
Table 2.3. Results of real-space PDF refinements over a 20 Å range using a tetragonal $P4mm$ model, with fixed O1 and O2 positions. Refined parameters are given with error.

<table>
<thead>
<tr>
<th></th>
<th>26 nm</th>
<th>45 nm</th>
<th>70 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>3.9972(5)</td>
<td>3.9961(5)</td>
<td>3.9926(4)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>4.041(1)</td>
<td>4.029(1)</td>
<td>4.0294(8)</td>
</tr>
<tr>
<td>$c/a$</td>
<td>1.0109(4)</td>
<td>1.0082(4)</td>
<td>1.0092(3)</td>
</tr>
<tr>
<td>Vol. (Å³)</td>
<td>64.56(6)</td>
<td>64.34(4)</td>
<td>64.23(4)</td>
</tr>
<tr>
<td>$z$(Ti)</td>
<td>0.518(2)</td>
<td>0.516(2)</td>
<td>0.514(1)</td>
</tr>
<tr>
<td>$z$(O1)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$z$(O2)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>$U_{iso}$(Ba) (Å²)</td>
<td>0.00415(6)</td>
<td>0.00365(5)</td>
<td>0.00325(4)</td>
</tr>
<tr>
<td>$U_{iso}$(Ti) (Å²)</td>
<td>0.0090(4)</td>
<td>0.0078(3)</td>
<td>0.0072(2)</td>
</tr>
<tr>
<td>$U_{iso}$(O1,O2) (Å²)</td>
<td>0.0227(3)</td>
<td>0.0227(3)</td>
<td>0.0224(2)</td>
</tr>
<tr>
<td>$R_w$ (%)</td>
<td>16.0</td>
<td>14.8</td>
<td>19.1</td>
</tr>
</tbody>
</table>
in real space. The first atom-atom distance manifested in the BaTiO₃ PDF corresponds to Ti-O distances near 2 Å. Ba-O distances come next around 2.8 Å, followed by Ba-Ti distances at around 3.5 Å and the first Ba-Ba distances around 4 Å. Qualitatively, the intensity of atom-atom peaks decrease and the widths increase with decreasing particle size.

In the $P4mm$ space group Ba-Ba distances are manifested in $a$ and $c$ cell parameters and Ba-Ti distances depend on both the cell parameters and Ti off-centering. Consequently, cell parameters, the atom $z$ positions, and the $c/a$ ratio could all be used as metrics of departure from a centrosymmetric structure. Since $c/a$ and Ti($z$) are likely to be correlated in an analysis, this is perhaps best captured through examination of atom-atom distances. The off-centering of Ti creates four long and four short Ba-Ti distances within each unit cell. We have parameterized the off centering using a distortion parameter, $\delta$, defined here as

$$\delta = \frac{(Ba - Ti)_{long} - (Ba - Ti)_{short}}{(Ba - Ti)_{long} + (Ba - Ti)_{short}}.$$ (2.1)

The sensitivity of the PDF to short-range structure and local bond distance, rather than to long-range periodic structure is the particular strength of the technique. This is traditionally most apparent when refinements are carried out over short $r$-ranges. Figure 2.11(a) shows the extracted Ba-Ti distances and Figure 2.11(b) the distortion parameter for the various $r$-ranges used in this
Figure 2.10. PDF fits of the total X-ray scattering data for the different particles. Circles correspond to the experimental PDFs and the fits are orange lines through the data. The difference curves are displayed in each panel, and have been offset for clarity. Reproduced with permission from reference [70]. © 2008, American Chemical Society.
Figure 2.11. PDF refinement results with varying $r$-range: (a) long and short Ba-Ti distances, and (b) a distortion parameter based on Ba-Ti distances as defined in Equation 2.1.

Reproduced with permission from reference [70]. © 2008, American Chemical Society.
study, and shows an unexpected result. The distortion is largest in the high $r$-range (relatively constant for $r \geq 16\,\text{Å}$, the distance across approximately four unit cells) and is essentially absent in the lowest $r$ region. The dependence on $r$-range is similar for all three particle sizes, suggesting this is related to the type of modeling we have used or the disorder present in the system, and not to any size effect. This result perhaps supports the notion of decreased sensitivity of the local structure to the order-disorder picture first envisioned by Comes and Lambert[85, 86] and discussed in Chapter 1. Previous PDF studies of bulk BaTiO$_3$ phases above and below phase transitions have demonstrated small or negligible effects on the experimental $G(r)$.[3, 52] As discussed in Chapter 1, the PDF is better poised to probe changes in displacive disorder than changes to the orientation of displacements, especially over low $r$ ranges. Thus, the behavior of our fits at low $r$ may suggest the length scale at which correlated order-disorder distortions in the particles may be captured.

Figure 2.12 shows the long and short Ba-Ti distances in (a) and the distortion parameter in (b) for the particle sizes, as extracted from Rietveld, 12 Å and 20 Å PDF analyses. It is again displayed that measured distortion increases with the length scale of the probe used for analysis. This is a counterintuitive result, as we expect atomic distortions to be manifested most strongly in the low $r$ region of the PDF, and become less and less apparent at high $r$. 

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Figure 2.12. (a) Long and short Ba-Ti distances and (b) the distortion parameter, $\delta$, defined in Equation 2.1. Results from synchrotron Rietveld refinements as well as the PDF analysis for different $r$ ranges are displayed. Reproduced with permission from reference [70]. © 2008, American Chemical Society.
Despite these questions, both Rietveld and PDF suggest that as particle size is decreased, the unit cell becomes metrically more cubic but the displacement of Ti is actually enhanced. These results are reconciled if we consider that for the smaller particles, the distortions from one unit cell to another become less correlated in much the same manner as is seen when bulk samples are heated to near the phase transition temperature (see Figure 2.5). Two physical explanations for an increasing distortion at smaller particle sizes suggest themselves. The first supposes the increase in cell volume in smaller particle sizes allows more space within the unit cell for Ti off-centering. The second presumes the reduction in periodicity in the lattice of smaller particles diminishes the restoring Coulombic force on movable atoms. The former notion is explored in the following section where we use density functional theory calculations to explore the effect of lattice expansion on atom positions in metrically cubic BaTiO$_3$.

### 2.4 Density Functional Theory Calculations

We have used first principles density functional theory calculations as implemented in the program Quantum-ESPRESSO[105] to explore the relationship between cell volume and atom-atom distortions in cubic BaTiO$_3$. The interactions between ions and valence electrons were described using the ul-

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trasoft (non-norm-conserving) pseudopotentials\cite{106} Ba.pw91-nsp-van.UPF, Ti.pw91-nsp-van.UPF and O.pw91-nsp-van.UPF from the distribution. Convergence testing was completed to determine suitable energy cutoffs for the plane-wave basis set and the expansion of augmentation charges (necessitated by the use of pseudopotentials), and a suitable \( k \)-point mesh for a cubic unit cell of BaTiO\(_3\). The lattice parameter corresponding to minimum energy was found to be 3.9768 \( \text{Å} \), within 1\% of the experimentally determined cubic lattice parameter of 4.0106(8) \( \text{Å} \) from laboratory X-ray diffraction at 148\( ^\circ \text{C} \), indicating acceptable parameters. Relaxations were performed on all atom positions using a plane-wave basis set with a cutoff of 41 Ry, a cutoff of 200 Ry for the expansion of augmentation charges, and a \( 6 \times 6 \times 6 \) Methfessel-Paxton\cite{107} \( k \)-point mesh. Relaxations of atomic positions were performed for metrically cubic unit cells of BaTiO\(_3\) with fixed \( a \) lattice parameters between 3.985 and 4.020 \( \text{Å} \), in 0.005 \( \text{Å} \) intervals.

Figure 2.13(a) shows theoretical and experimental Ba-Ti distances as a function of (pseudo)cubic cell parameter. For the calculations (blue circles) the cell parameters correspond to the fixed \( a \) values used in cubic unit cell relaxations. For the Rietveld (orange square) and PDF (green triangle) results cell parameters are the pseudocubic cell parameter (\( V^{1/3} \)) from refinement. Larger cell parameters correspond to smaller particle sizes. In all three sets of data, the
Figure 2.13. (a) Long (open symbols) and short (filled symbols) Ba-Ti distances and (b) the distortion parameter, δ, defined in Equation 2.1 from density functional theory calculations together with experimental results from this study. Theoretical results are shown with blue circles and correspond to cubic unit cells of fixed size. Results from synchrotron Rietveld refinements (orange squares) as well as 20 Å PDF analysis (green triangles) are given for the three experimental nanoparticle sizes, as a function of the experimentally determined pseudocubic cell parameters ($V^{1/3}$).
bond lengths increase as the unit cell dimension is increased. Both sets of experimental bond lengths display a greater dependence on lattice expansion than the calculated bond lengths.

Figure 2.13(b) shows the parameterized bond distortion as defined in Equation 2.1 for the same set of calculations and experiments. The theoretical results show a dependence on distortion with increasing unit cell size, in qualitative agreement to the trend in experimental results we found for nanoparticles. There is again a greater dependence on cell parameter in the experimental results than in the theoretical results.

The theoretical results corresponding to a unit cell with $a = 4.010 \, \text{Å}$ are close to the average structure results for the largest (70 nm) particles, with $V^{1/3} = 4.0090(3) \, \text{Å}$. For the smaller particle sizes (larger $a$ values) the calculated behavior departs significantly from the experimental findings. Discrepancies between the theoretical and experimental results here are not unexpected. The nanoparticles we have studied have surfaces, while the relaxations assume an extended cubic lattice. Also, the ground state of BaTiO$_3$ is known to be rhombohedral, and we have performed density functional theory calculations on cubic structures. These results merely show there is more at play in determining the higher distortion in smaller particles than a simple lattice expansion. A whole-particle first principles approach may be needed to gain further insight
into the problem.

2.5 Summary

While somewhat surprising, the outcomes of the study presented in this chapter are consistent between the various techniques. Raman spectroscopy of 26, 45 and 70 nanoparticulate BaTiO$_3$ indicate that small particles undergo a more diffuse phase transition than is observed in the bulk, although the $T_C$ remains nearly unchanged. Careful temperature-dependent XRD studies show that all sizes of particles are tetragonal until close to the bulk $T_C$, and the smaller particles have $c/a$ ratios closer to unity than bulk BaTiO$_3$. Average (Rietveld) and local (PDF) structure analysis of X-ray synchrotron data show that as particle size is reduced, there is a clear and surprising trend towards increasing structural distortion. The increase in the off-centering of the Ti cation as particle size is decreased in conjunction with the decrease in the $c/a$ ratios is consistent with diminished structural coherence in smaller particles. Our preliminary density functional theory calculations qualitatively follow the dependence on distortion with changing unit cell volume observed experimentally, but indicate more effects should be incorporated to understand the experimental result. Overall, we conclude that although smaller particles of BaTiO$_4$ show greater distortion, a loss of coherence relative to the bulk material is respon-
sible for decreased $c/a$ values. Our results significantly contrast the accepted wisdom that BaTiO$_3$ becomes less distorted for smaller particle sizes. In the next chapter we explore efforts to characterize the structure of smaller (5 nm) BaTiO$_3$ particles with neutron total scattering methods.
Chapter 3

The Structure of 5 nm BaTiO$_3$

Particles from Neutron Scattering

While the X-ray methods utilized in Chapter 2 provide reliable detection of metal sites, neutron diffraction methods offer greater sensitivity to oxygen positions and to atomic displacement parameters. We were motivated to pursue time-of-flight neutron diffraction total scattering studies of nanoparticles of BaTiO$_3$ in order to characterize metal-oxygen atom-atom distances. We were also motivated by a desire to understand the structure of smaller particles. In this chapter we present the room temperature structure of 5 nm BaTiO$_3$ particles and bulk BaTiO$_3$ using Rietveld and PDF analysis of time-of-flight neutron scattering data and compare the results to those in Chapter 2.
3.1 Preparation

The nanoparticles used in our neutron diffraction study were prepared by the Neiderberger group at the Max-Planck-Institute for Colloids and Interfaces in Berlin, Germany. The synthesis involves a solvothermal reaction of titanium isopropoxide and metallic barium in benzyl alcohol and is described in detail elsewhere.[96] The particles are single grains, nearly spherical in shape and range in diameter from 4 to 5 nm. The reaction produces no crystalline byproducts and can be scaled to produce gram quantities. A bulk BaTiO$_3$ standard was prepared by ceramic methods in our laboratory for comparison.

3.2 Rietveld and PDF Neutron Scattering Study

Neutron data were collected at room temperature for the (nominally) 5 nm particles as well as for bulk BaTiO$_3$ on the neutron powder diffractometer NPDF[13] at the Lujan Center at Los Alamos National Laboratory. 700 mg of the nanoparticles were loaded into a vanadium can and data were collected for 6 hours. 2 grams of the bulk sample were loaded into a vanadium can for 4 hours of data collection.

The diffraction data were analyzed with the Rietveld method as embodied in the GSAS-EXPGUI[16, 17] suite of programs. The bulk data were fit
Figure 3.1. Rietveld refinement of time-of-flight neutron scattering data for (a) bulk BaTiO$_3$ and (b) 5 nm BaTiO$_3$ particles. Data are given as black circles and orange lines represent fits to the data using tetragonal $P4mm$ models. Maroon difference curves and blue reflection markers for the $P4mm$ phase fall below the data and fits. Data are shown without the experimental backgrounds, which were fit during refinement and subtracted.
with the tetragonal $P4mm$ perovskite structure. Two models were tried for the nanoparticle data: the tetragonal $P4mm$ model and a cubic $Pm\overline{3}m$ model. The data (black circles) and fits (orange lines) using the $P4mm$ model are shown in Figure 3.1 for (a) bulk and (b) 5 nm BaTiO$_3$. A maroon difference curve and blue markers indicating expected peak positions for the $P4mm$ phase fall below the data and fits. There are no impurity phases detected and all reflections are indexed using the tetragonal phase. For the 5 nm particles the broadening of diffraction peaks is significant, and the quality of fit is almost unchanged using a cubic model during refinement. The refinement of atomic positions in the $P4mm$ model was not stable for the nanoparticle data, and these values were set to results obtained from refinement of the bulk BaTiO$_3$ data. Results from the analyses are given in Table 3.1.

Routine extraction steps were followed in order to obtain the experimental pair distribution function from scattering data of bulk BaTiO$_3$. The data were corrected for instrument background, incident neutron spectrum, absorption and multiple scattering, and finally normalized using the program PDFgetN.[20] The resulting scattering data, $S(Q)$, is shown in Figure 3.2(a). The corresponding PDF, $G(r)$, is shown in Figure 3.2(b). The extraction of the experimental pair distribution function from 5 nm particle data required additional steps. The raw 5 nm particle data (data from bank 4 of the NPDF instru-
Table 3.1. Results of Rietveld and 20 Å PDF analysis of time of flight neutron diffraction data for bulk and 5 nm BaTiO$_3$. Fits were made using a tetragonal $P4mm$ model for the bulk data, and both tetragonal $P4mm$ and cubic $Pm\bar{3}m$ models for the nanoparticle data. Refined parameters are given with error.

<table>
<thead>
<tr>
<th></th>
<th>Bulk Rietveld</th>
<th>Bulk PDF</th>
<th>5 nm ($P4mm$) Rietveld</th>
<th>5 nm ($P4mm$) PDF</th>
<th>5 nm ($Pm\bar{3}m$) Rietveld</th>
<th>5 nm ($Pm\bar{3}m$) PDF</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
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<td>4.0115(9)</td>
<td>4.009(3)</td>
<td>4.0261(3)</td>
<td>4.026(1)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>4.03288(4)</td>
<td>4.038(1)</td>
<td>4.057(2)</td>
<td>4.064(6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$c/a$</td>
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<td>1.0091</td>
<td>1.0113</td>
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<tr>
<td>Vol. (Å$^3$)</td>
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<td>65.317</td>
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<td>65.256</td>
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<td>0.487(2)</td>
<td>0.5135</td>
<td>0.47(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>z(O1)</td>
<td>-0.0219(5)</td>
<td>0.027(3)</td>
<td>-0.0219</td>
<td>0.98(1)</td>
<td></td>
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<tr>
<td>z(O2)</td>
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<td>0.488</td>
<td>0.49(2)</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>0.0046(4)</td>
<td>0.010(1)</td>
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<td>0.0064(8)</td>
<td>0.0029(8)</td>
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<td>0.0055(2)</td>
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<td>0.012(1)</td>
<td>0.0114(7)</td>
<td>0.015(3)</td>
</tr>
<tr>
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<td>5.47</td>
<td>1.55</td>
<td>28.0</td>
<td>1.55</td>
<td>29.6</td>
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</tbody>
</table>

*$U_{iso}$ are given in units of Å$^2$.  

75
Figure 3.2. Diagrams comparing time of flight neutron scattering $S(Q)$ (left) and $G(r)$ (right) for (a,b) bulk BaTiO$_3$ and (c,d) 5 nm BaTiO$_3$ particles. In (c) the raw nanoparticle $S(Q)$ is given in red for bank 4. Data after manual background subtraction is displayed in black and was used in the $G(r)$ transformation in (d). Note the differences in intensity between bulk and nanoparticle scattering.
ment is displayed in red in Figure 3.2(c) shows a large amount of incoherent scattering relative to Bragg scattering: the solution preparation strategies for nanoparticles inevitably result in H incorporation. The raw data were corrected manually so the baseline of the nanoparticle profile matched the baseline of the bulk profile. The experimental $S(Q)$ resulting from this correction is displayed in black in the same panel, and this data was used for conversion to $G(r)$, given in Figure 3.2(d). Data up to $Q = 30 \text{ Å}^{-1}$ were used for both bulk and nano Fourier transforms, giving a high real space resolution and allowing for direct comparison of the PDF data.

Figure 3.2(c) displays an important aspect in the analysis of nanomaterial diffraction data and how it is currently approached. Neutron diffraction from nanomaterials suffers from significant incoherent scattering, most likely arising from hydrogen incorporated in the capping or stabilization layer of nanomaterial surfaces. Small sample volumes exacerbate these complications. While neutron data has enhanced capabilities for probing light elements and the possibility of characterizing magnetic structures, synchrotron X-ray methods require much less sample, allow for shorter data collection times, and afford straightforward data extraction. For these reasons, synchrotron X-ray total scattering data is used almost exclusively in the nano-regime: our work on 4 nm gold nanoparticles presented in Chapter 1 represent, to our knowledge,
the only total scattering neutron study of nanoparticles to date.

Full profile structural refinements using the programs PDFfit2 and PDFgui[24] were carried out for the bulk and 5 nm BaTiO$_3$ $G(r)$s with the same models employed in the Rietveld refinement analysis. Lattice parameters, atomic displacement parameters, atom positions, and scale factors were refined. Parameters describing the instrument resolution were included in the analysis of bulk data, and the resulting parameters were applied and held constant for the analysis of 5 nm particle data. The refinement of particle size was not stable, but long range PDF data were well-fit by setting the particle size to 5 nm: this value was applied for all refinements. Results of 20 Å PDF refinements are given in Table 3.1, along with results from the Rietveld analysis.

As observed in 70, 45 and 26 nm particles from Rietveld and PDF X-ray diffraction analysis, we see an expanded lattice for the 5 nm particles. We also see larger atomic displacement values for 5 nm particle refinements, consistent with increased disorder in the lattice. In the Rietveld analysis there were not significant differences in the quality of the cubic and tetragonal refinements for the small particles. There is a slight improvement in the fitting of the PDF data using a tetragonal model over a cubic model. Figure 3.3 shows the first 10 Å of the 20 Å PDF refinements using $P4mm$ models. An inspection of the first, second and third nearest-neighbor atom-atom correlations shows that the
Figure 3.3. Full profile fitting of time-of-flight neutron PDF data for (a) bulk BaTiO$_3$ and (b) 5 nm particles of BaTiO$_3$. Data are given as circles, fits to $P4mm$ structure models are given in blue, and a difference curve has been offset below the data and fits.
nanoparticle PDF in (b) differs significantly from the bulk PDF in (a). Both PDFs show the characteristic rhombohedral-type distortion (a bimodal peak) in the Ti-O distances around 2 Å. However, in Figure 3.3(b) the bimodal Ti-O atom-atom peaks appear lower in r with respect to the bulk local structure, and there is additional splitting in second coordination shell (Ba-O) distances around 2.9 Å and the third coordination shell (Ba-Ti) distances around 4 Å. Figure 3.4 shows PDF refinement fits to both sets of data using a rhombohedral $R3m$ perovskite structure model. The low-r region of the bulk BaTiO$_3$ PDF data is well-fit by the rhombohedral structure in (a), but the model poorly describes the same region for 5 nm particle data in (b). The features observed in the 5 nm particle PDF are not captured with any of the simple crystallographic models we have tried. For these reasons, our refinement results understate the disorder present in these small particles, and further analysis is called for.

As explained in the previous chapter, refinement parameters are often correlated and thus it is useful to study atom-atom distances when analyzing local structure. Select atom-atom distances extracted from the neutron Rietveld and PDF refinement results for bulk and 5 nm BaTiO$_3$ data are given in Table 3.2. The PDF results for the $P4mm$ model show increased distortion (as defined in Equation 2.1) for 5 nm data compared to the bulk sample data. While the standard deviations associated with refined atomic positions and the similarity in
Figure 3.4. Full profile fitting of time-of-flight neutron PDF data for (a) bulk BaTiO$_3$ and (b) 5 nm particles of BaTiO$_3$ using a rhombohedral perovskite structure model. Data are given as circles, fits to $R3m$ structure models are given in green, and a difference curve has been offset below the data and fits.
quality of fit for cubic, tetragonal and rhombohedral models make this difference statistically insignificant, the poor fit of the low-\(r\) PDF in Figure 3.3(b) provide strong evidence for significant distortion in the small particles.
Table 3.2. Selected atom-atom distances from Rietveld and 20 Å PDF analysis of time of flight neutron diffraction data for bulk and 5 nm BaTiO$_3$.

<table>
<thead>
<tr>
<th></th>
<th>Bulk ($P4mm$)</th>
<th>5 nm ($P4mm$)</th>
<th>5 nm ($Pm3m$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rietveld</td>
<td>PDF</td>
<td>Rietveld</td>
</tr>
<tr>
<td>$d_{Ti-O}$ (Å)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1x)1.874(4)</td>
<td>(1x)1.86(2)</td>
<td>(1x)1.8849(9)</td>
<td>(1x)2.0(1)</td>
</tr>
<tr>
<td>(4x)2.0018(3)</td>
<td>(4x)2.005(1)</td>
<td>(4x)2.0084(4)</td>
<td>(4x)2.006(8)</td>
</tr>
<tr>
<td>(1x)2.159(4)</td>
<td>(1x)2.18(2)</td>
<td>(1x)2.1721(11)</td>
<td>(1x)2.1(1)</td>
</tr>
<tr>
<td>$d_{Ba-Ti}$ (Å)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(4x)3.441(2)</td>
<td>(4x)3.445(6)</td>
<td>(4x)3.4557(7)</td>
<td>(4x)3.42(5)</td>
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<td>(4x)3.505(2)</td>
<td>(4x)3.508(5)</td>
<td>(4x)3.5194(7)</td>
<td>(4x)3.56(6)</td>
</tr>
<tr>
<td>$δ$</td>
<td>0.0092</td>
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</tr>
</tbody>
</table>
The validity of the data correction used here and the implications for the resulting analysis of structure are not clear. The manual correction applied to the 5 nm particle may have stripped important contributions from the diffuse scattering. Other than giving a better indication of particle size, the resulting $G(r)$ may not provide any more information than the Rietveld analysis.

The same 5 nm particles studied here were the subject of a synchrotron X-ray total scattering study by Petkov et al.\cite{Petkov2015} A comparison of our results to the results obtained in that study give some measure of quality for our data. They found that locally, refining over the first 15 Å, the tetragonal model was the best fit to the experimental PDF; however over longer distances (15-28 Å), the cubic model was the best fit. Our results gave identical unit cell volume for the particles. Their analysis gave a greater $c/a$ ratio, but our atomic positions and atomic displacement parameters for O atoms are more reasonable.

### 3.3 Summary

We have explored time-of-flight neutron PDF analysis of data from 5 nm particles of BaTiO$_3$. We find an expanded lattice for small particles similar to our results for larger particles using X-ray total scattering in Chapter 2. We see significant distortion in the low-$r$ PDF corresponding to the three nearest-
neighbor correlations. This distortion is not captured with our simple crystallographic models. This work calls upon the need for further development of tools for analysis of structure in the nano regime; particularly for improved characterization of incoherent scattering to allow a more structured approach to background subtraction. The limitations incurred by excessive incoherent scattering do not allow for a conclusive structural analysis of the system, but results are consistent with our picture of decreasing structural coherence with decreasing particle size.

Together, Chapters 2 and 3 have illustrated the valuable information to be gained by analysis of high quality diffraction data from nanomaterials. In remaining chapters we will shift focus and explore local structure and property relationships in two families of bulk materials.
Chapter 4

Niobium Substituted BaTiO$_3$ and SrTiO$_3$

In Chapter 3 we discussed the rich ferroelectric and structural phase diagram of perovskite BaTiO$_3$ and remarked on its long and continuing technological importance. Perovskite SrTiO$_3$ is widely used as a substrate for epitaxial thin films, and lays claim to a rich set of phenomena in the resulting epitaxial heterointerfaces.[108, 109, 110, 111] SrTiO$_3$ is known amongst other things for its unusual paraelectric ground state,[112] in contrast to the ferroelectric ground state of BaTiO$_3$.[50]

Nb substituted BaTiO$_3$ and SrTiO$_3$ are reported to have similar structures and lattice parameters. At room temperature, both crystallize in the cubic
perovskite $Pm\bar{3}m$ structure, with a lattice constant $a$ that increases with Nb-substitution. It is now long known that electronic conductivity,[113, 114, 115] and even superconductivity[116] are brought about by substitution of Nb for Ti in SrTiO$_3$: it becomes metallic with just 0.03 to 0.1% substitution. On the other hand, BaTiO$_3$ is semiconducting to at least 20% Nb-substitution. Given the nearly identical structure and electron counts of the compounds, the distinct ground states in this regime have been a long-standing puzzle. In this chapter we present from neutron methods of average and local structure, the subtle yet critical difference that we believe underpins the distinct electronic properties in these fascinating materials. While SrTi$_{0.875}$Nb$_{0.125}$O$_3$ possesses a distorted non-cubic structure at 15 K, (Nb/Ti)O$_6$ octahedra in the structure are regular. BaTi$_{0.875}$Nb$_{0.125}$O$_3$ on the other hand shows evidence for local cation off-centering whilst retaining a cubic structure. These results were published previously in reference [117].

### 4.1 Introduction

Nb-substituted perovskite SrTiO$_3$ is a well-known electrical conductor finding widespread use as a conducting substrate in the growth of epitaxial perovskite thin films. The room temperature structure is cubic (see Figure 4.1), and there are no reported structural distortions. BaTiO$_3$ also substitutes Nb
Figure 4.1. Crystal structures of SrTiO$_3$ at (a) room temperature when it is cubic, and (b) at low temperatures when it is tetragonal. The structural parameters used to depict (b) were obtained from Rietveld refinement of the 15 K neutron diffraction data of SrTi$_{0.875}$Nb$_{0.125}$O$_3$.

on the Ti site, and is known to form almost a complete solid solution with BaNbO$_3$. Despite possessing the same cubic perovskite structure (at least for greater than 10 atom-% substitution) and identical electron counts, the Sr compounds display metallic behavior at 10% substitution[115] while the Ba compounds are semiconducting up to at least 20% substitution.[118]

4.2 Preparation

Samples were prepared by our collaborator. Dr. Taras Kolodiazhniy in Tsukuba, Japan, from high purity (99.99%) Ba(Sr)CO$_3$, TiO$_2$ and Nb$_2$O$_5$ pow-
ders purchased from Sigma Aldrich. The powders were heat treated at 500 °C to remove any adsorbed water and stoichiometric amounts of material were weighed for preparation of the $\text{Ba}_{1-x}\text{Sr}_x\text{Ti}_{0.9}\text{O}_3$ and $\text{Ba(Sr)Ti}_{0.875}\text{Nb}_{0.125}\text{O}_3$ target compounds. The powders were first wet-mixed using zirconia media and ethanol in Nalgene bottles, dried overnight, and screened through a 100 mesh nylon sieve. To reduce contamination with magnetic impurities, a WC die was used for pressing the powder and preparing green pellets. The pellets were placed in an $\text{Al}_2\text{O}_3$ boat on a coarse-grained $\text{ZrO}_2$ (99.99%) setter and calcined in a tubular furnace at 1100 °C for 20 h in flowing $\text{H}_2$, at a flow rate of 50 cm$^3$/min. After calcination the pellets were re-ground in an $\text{Al}_2\text{O}_3$ mortar and the powder was wet-milled with zirconia media and ethanol overnight. After drying, the powder was pressed again into pellets. To ensure a complete electronic compensation of Nb (donor) ions, a second heat treatment was performed at 1350 °C for 20 h in flowing $\text{H}_2$ (flow rate 50 cm$^3$/min). Sintering of the ceramic was performed at 1370 °C for 20 h. For neutron diffraction measurements the sintered pellets were ground in an $\text{Al}_2\text{O}_3$ mortar.

### 4.3 Electronic Properties

The distinct properties below 20% substitution are amply illustrated by considering the temperature dependence of the electrical resistivity and the
Figure 4.2. Specific resistivity (a) and magnetic susceptibility (b) as a function of temperature for samples of Sr$_{1-x}$Ba$_x$Ti$_{0.9}$Nb$_{0.1}$O$_3$ demonstrates the metal-insulator transition as $x$ increases. The different values of $x$ for the various samples are indicated. The data in (b) have not been corrected for atomic diamagnetism. Reproduced with permission from reference [117]. © 2008, American Physical Society.
magnetic susceptibility of the solid solution series $\text{Sr}_{1-x}\text{Ba}_x\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_3$ displayed in the panels of Figure 4.2. Four-probe resistivity was measured on 95% dense ceramic samples cut into $2 \times 2 \times 9 \text{ mm}^3$ parallelepipeds and magnetic susceptibility in the 2 K to 400 K range was measured with a Quantum Design Magnetic Property Measurement System XL. As the value of $x$ (the amount of Ba) is increased across the solid solution, the resistivity (Figure 4.2(a)) displays an upturn at low temperatures; the change from a positive to negative temperature coefficient of resistivity takes place between $x = 0.25$ and $x = 0.50$, in a region where the resistivity values are somewhat smaller than the value suggested by Mott for the minimum conductivity.[119] In correspondence with electrical transport, the magnetic susceptibility of the Sr-rich side of the solid solution is largely temperature-independent, in keeping with its metallic transport properties, while the Ba-rich samples from the solid solution display a stronger temperature dependence, characteristic of moments on localized electrons. One explanation that has been proffered for the magnetic behavior is the formation of bipolarons.[120]

4.4 Rietveld and PDF Neutron Scattering Study

In order to unravel the possible structural underpinnings of the distinct behavior of the end-members in this solid solution series, we have prepared
and studied two special sample compositions with 12.5% Nb-substitution: SrTi$_{0.875}$Nb$_{0.125}$O$_3$ (STNO) and BaTi$_{0.875}$Nb$_{0.125}$O$_3$ (BTNO), and studied their average and local structures using time of flight neutron diffraction measurements. The compositions were chosen as an aid to model building for local structure studies; with 1/8 of the Ti atoms replaced by Nb, a $2 \times 2 \times 2$ cubic perovskite supercell allows explicit modelling of all the B-site cations. The supercell is shown in Figure 4.3, with the single NbO$_6$ octahedra colored in blue and a basic perovskite unit cell delineated with a dashed line.

Time of flight neutron diffraction measurements were carried out on powder samples at room temperature and at 15K in order to probe the average
and local structures of SrTi$_{0.875}$Nb$_{0.125}$O$_3$ and BaTi$_{0.875}$Nb$_{0.125}$O$_3$. High-Q resolution neutron powder diffraction data were collected for both samples on the NPDF instrument at the Los Alamos National Laboratory Lujan Neutron Scattering Center[13] at room temperature and at 15 K. Approximately 2 g of powder were loaded into vanadium cans for the experiment, and data were collected for a 3.5 hours at 15 K and for 2 hours at 298 K for each sample. Rietveld refinement with the scattering data was carried out in the GSAS-EXPGUI[16, 17] suite of programs. Backgrounds, scale factors, lattice parameters, isotropic displacement parameters, profile parameters, atom positions, and atom site occupancies were refined. The experimental pair distribution function was extracted from neutron total scattering data using the program PDFgetN.[20] Background scattering was subtracted from the raw data and corrections were made for detector deadtime, absorption, multiple scattering, inelasticity effects, and normalized by the incident flux and total sample scattering cross-section. The wavevector cutoff $Q_{\text{max}}$ used for the transform was 40 Å$^{-1}$. PDF refinements were carried out in the program PDFGui[24]; PDF refinement included a $Q$ broadening factor, a scale factor, lattice parameters, quadratic peak sharpening, and isotropic atomic displacement parameters.

Rietveld refinement confirms that the average structures of both STNO and BTNO at room temperature are cubic. The only significant difference is in the
Figure 4.4. A portion of the highest resolution bank of time-of-flight neutron scattering data for (a) $\text{SrTi}_{0.875}\text{Nb}_{0.125}\text{O}_3$ at 298 K (b) $\text{SrTi}_{0.875}\text{Nb}_{0.125}\text{O}_3$ at 15 K, (c) $\text{BaTi}_{0.875}\text{Nb}_{0.125}\text{O}_3$ at 298 K and (d) $\text{BaTi}_{0.875}\text{Nb}_{0.125}\text{O}_3$ at 15 K. Circles are data and the lines are Rietveld fits to the cubic $Pm\bar{3}m$ structures for (a), (c), and (d), and to the tetragonal $I4/mcm$ structure for (b). Vertical lines at the top of each panel indicate expected peak positions. Note the log scale. Reproduced with permission from reference [117]. © 2008, American Physical Society.
cell parameters, with $a = 3.9237(1) \text{ Å}$ and $a = 4.0147(1) \text{ Å}$ respectively for STNO and BTNO, in keeping with the much larger 12-coordinate radii of Ba$^{2+}$ ($r = 1.61 \text{ Å}$) compared with Sr$^{2+}$ ($r = 1.44 \text{ Å}$). Rietveld profile fits are displayed for STNO and BTNO at room temperature in Figure 4.4(a) and Figure 4.4(c). At 15 K, BTNO remains cubic (Figure 4.4(d)), while STNO transforms between 298 K and 15 K to a structure that is very well described using the low temperature structure of SrTiO$_3$ as a model, in the tetragonal $I4/mcm$ space group (Figure 4.4(b)).[121, 42] The tetragonal crystal structure of SrTi$_{0.875}$Nb$_{0.125}$O$_3$ is displayed in Figure 4.1(b). In contrast to SrTiO$_3$ where the Rietveld refined octahedral rotational order parameter at 20 K is 1.97$^\circ$ and at 5 K is 1.98$^\circ$,[42] the value obtained here for STNO at 15 K is 3.46(2)$^\circ$. This larger value for the Nb-substituted compound reflects the slightly decreased tolerance factor (see Equation 1.7. Results of the structure refinements are presented in Table 4.1.
Table 4.1. Average structures of SrTi$_{0.875}$Nb$_{0.125}$O$_3$ and BaTi$_{0.875}$Nb$_{0.125}$O$_3$ from Rietveld and 50 Å PDF refinement of time-of-flight neutron scattering data. Note the anomalously high $U_{iso}$ for the A site in the strontium compound, relieved at 15 K via the phase transition to the tetragonal structure. The high $U_{iso}$ for (Ti/Nb) for the barium compound remains at all temperatures.

<table>
<thead>
<tr>
<th></th>
<th>SrTi$<em>{0.875}$Nb$</em>{0.125}$O$_3$</th>
<th>BaTi$<em>{0.875}$Nb$</em>{0.125}$O$_3$</th>
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</thead>
<tbody>
<tr>
<td></td>
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<td>15 K, I4/mcm</td>
</tr>
<tr>
<td></td>
<td>300 K, Pm$\overline{3}$m</td>
<td>15 K, Pm$\overline{3}$m</td>
</tr>
<tr>
<td></td>
<td>Rietveld PDF</td>
<td>Rietveld PDF</td>
</tr>
<tr>
<td></td>
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<td>Rietveld PDF</td>
</tr>
<tr>
<td>$a$ (Å)</td>
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</tr>
<tr>
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<td>4.0147(1) 4.0165(1)</td>
<td>4.0084(1) 4.0100(1)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
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<tr>
<td>$U_{iso}(A)$ (Å$^2$)</td>
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<td>0.0028(1) 0.0021(1)</td>
</tr>
<tr>
<td>$U_{iso}(Ti/Nb)$ (Å$^2$)</td>
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<td>0.0042(3) 0.0028(1)</td>
</tr>
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<td>0.0093(3) 0.0080(2)</td>
<td>0.0070(2) 0.0059(1)</td>
</tr>
<tr>
<td>$U_{iso}(O)$ (Å$^2$)</td>
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<td>0.0054(1) 0.0042(1)</td>
</tr>
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<td>0.0053(1) 0.0040(1)</td>
</tr>
<tr>
<td>$x$(O2)</td>
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<td>occ.(Nb)</td>
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<td>0.123(2) 1/8</td>
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<tr>
<td>$R_{\text{w}}$ (%)</td>
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<td></td>
<td>3.0 7.4</td>
<td>3.4 8.5</td>
</tr>
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</table>
Local structure was analyzed in terms of the atomic pair distribution function, $G(r)$, using $A_8Ti_7NbO_{24}$ supercells, as well as single-unit cell models with appropriate partial Ti/Nb occupancies. Ti and Nb are amply separated in terms of their coherent neutron scattering lengths, with respective values of $-3.370(13)$ fm and $7.054(3)$ fm.[122] In Figure 4.5, we compare data and PDF fits to the average tetragonal structure of (a) SrTi$_{0.875}$Nb$_{0.125}$O$_3$ and the average cubic structure of (b) BaTi$_{0.875}$Nb$_{0.125}$O$_3$ to a maximum vector length of 50 Å. Both compounds are remarkably well described by the average structures, suggesting that local geometric effects due to replacing an eighth of all Ti by Nb are small in both compounds. The $2 \times 2 \times 2$ perovskite supercell with Nb at the center and Ti at all corners, edges, and faces shown in Figure 4.3 provided a model for probing whether the coordination of NbO$_6$ octahedra were distinct from those of TiO$_6$ octahedra. Within the resolution of these experiments, no differences were discernible, supporting the analysis using an average $B$-site (Ti/Nb) occupation unit cell. Results of 50 Å PDF refinement are displayed alongside results of the Rietveld refinement in Table 4.1. Significant anomalies are found in the isotropic displacement parameters, $U_{iso}$ for the two compounds. In SrTi$_{0.875}$Nb$_{0.125}$O$_3$ it is seen at room temperature that $U_{iso}$ is somewhat large on the $A$ site (Sr) compared to the value found for Ba in BaTi$_{0.875}$Nb$_{0.125}$O$_3$. This is a signature of the tilting instability that drives the cubic compound to transform to a tetragonal ground state, whereupon all
Figure 4.5. Neutron pair distribution functions (PDF) of (a) SrTi$_{0.875}$Nb$_{0.125}$O$_3$ and (b) BaTi$_{0.875}$Nb$_{0.125}$O$_3$ acquired at 15 K. Circles are data and lines are fits to the average tetragonal (SrTi$_{0.875}$Nb$_{0.125}$O$_3$) and cubic (BaTi$_{0.875}$Nb$_{0.125}$O$_3$) structure models. The difference between data and fit is displayed separately at the top of each panel, at a different (magnified) scale. Reproduced with permission from reference [117]. © 2008, American Physical Society.
values of $U_{iso}$ at 15 K are somewhat more reasonable.\[50\] In BaTi$_{0.875}$Nb$_{0.125}$O$_3$ on the other hand, it is the $B$ site (Ti/Nb) that has an anomalously large $U_{iso}$, both at 300 K and at 15 K.

Figure 4.6 (a through d) displays the short $r$ PDFs of SrTi$_{0.875}$Nb$_{0.125}$O$_3$ and BaTi$_{0.875}$Nb$_{0.125}$O$_3$ at room temperature and at 15 K. The first peak corresponding to the (Ti/Nb)-O vectors is negative as a result of the negative coherent neutron scattering length of Ti. For BaTi$_{0.875}$Nb$_{0.125}$O$_3$ at 300 K and more markedly at 15 K, this first coordination shell is clearly bimodal. In contrast, the local structure of SrTi$_{0.875}$Nb$_{0.125}$O$_3$ is regular and well-described by the crystallographic model. The PDF results here for BaTi$_{0.875}$Nb$_{0.125}$O$_3$ resemble previous work on BaTiO$_3$ where the local rhombohedral distortion persists across phase changes.\[52\] This local distortion explains the larger $U_{iso}$ seen both in Rietveld and PDF results. This is the principal finding of this work, and points to a subtle yet fundamental difference in the local structures of these two compounds. To better understand the bimodal first (Ti/Nb)-O peak in the PDF of BaTi$_{0.875}$Nb$_{0.125}$O$_3$, we show alongside in Figure 4.6(e), simulations of the first peak PDF of BaTiO$_3$ in its different crystalline structures. As explained in Chapter 1, BaTiO$_3$ transitions successively from cubic $Pm\bar{3}m$ to tetragonal $P4mm$ to orthorhombic $Amm2$ to, finally, a rhombohedral $R3m$ ground state as it is cooled from high temperatures.\[50, 51\] In the rhombohedral crystal struc-
Figure 4.6. Shortest (Ti/Nb)-O distances in the (a) 298 K PDF and (b) 15 K PDF of SrTi$_{0.875}$Nb$_{0.125}$O$_3$. Circles are experimental data and the lines are fits to the respective average structures. (c) and (d) show these distances for BaTi$_{0.875}$Nb$_{0.125}$O$_3$ at 298 K and 15 K respectively. (e) Calculated shortest Ti-O distance(s) in BaTiO$_3$ for the different crystallographic (cubic, tetragonal, orthorhombic, and rhombohedral) modifications. Note that the (Ti/Nb)-O distances are seen as negative peaks because of the negative neutron scattering length of Ti. Reproduced with permission from reference [117]. © 2008, American Physical Society.
ture, Ti in BaTiO₃ displace toward octahedral faces, resulting in three short and three long Ti-O distances, giving rise to a nearly bimodal first peak in the PDF. This is precisely the situation in BaTi₀.₈₇₅Nb₀.₁₂₅O₃. However in BaTiO₃ local distortions are strain-coupled and more coherent, and lead to phase transitions with associated changes in the average structure. In BaTi₀.₈₇₅Nb₀.₁₂₅O₃, the random substitution of Ti by 12.5-atom% Nb clearly is sufficient to frustrate long-range ordering, and indeed the quality of the PDF and Rietveld fits to the cubic structure over 50 Å support the idea that displacements of (Ti/Nb) in BaTi₀.₈₇₅Nb₀.₁₂₅O₃ are only very poorly correlated from one unit cell to the next. We note parenthetically, that random B-site substitution does not frustrate tilting in perovskites, and to achieve that, one requires random substitutions on the A-site.[123]

The PDF results here for BaTi₀.₈₇₅Nb₀.₁₂₅O₃ resemble previous work on BaTiO₃ where the local rhombohedral structure persists despite phase changes in the average structure.[52] The PDF is rather sensitive to atomic displacements. However, as discussed in Chapter 1, it is rather difficult to detect phase changes corresponding to the coherence of displaced sites. This is the case with order-disorder systems like BaTiO₃, where low-r PDF data above and below structural phase transitions can appear unchanged.[3]

The results of this work underpin the differences in the local structures of
SrTi$_{0.875}$Nb$_{0.125}$O$_3$ and BaTi$_{0.875}$Nb$_{0.125}$O$_3$ which draw from the distinct ground states of the undoped compounds. The introduction of random potentials \emph{via} Nb-substitution on the Ti site in BaTiO$_3$, in addition to the introduction of charge carriers due to the aliovalent nature of the substitution, result in dipole-dipole correlations being rapidly suppressed. In particular, the role of charge carriers in bringing this about is dramatic. In systems where the substitution is isovalent, for example, BaTi$_{1-x}$Sn$_x$O$_3$, ferroelectricity is suppressed only somewhat slowly.\cite{124} In keeping with ideas of “ferroelectric metals” (and their scarcity), charge carriers screen the long-range electrostatic interactions responsible for ferroelectric order.\cite{125, 126} However, local effects that are responsible for off-centering, namely the second-order Jahn-Teller distortion on Ti$^{4+}$, are quite robust to changing electron counts, and persist even when long-range ordering of dipoles has been suppressed. How is this distortion responsible for an insulating ground state in BaTi$_{0.875}$Nb$_{0.125}$O$_3$? Firstly, we anticipate significant narrowing of states near the Fermi energy, even in the one-electron band structure. In addition, since transport occurs through states involving (Ti/Nb) $d$ orbitals, the incoherent nature of the off-centering would induce electrons to localize. In BaTiO$_{3-\delta}$, metallic ground states are obtained even in systems where Ti displacements are seen, provided they are coherent,\cite{127} clearly pointing to the importance of incoherency in determining the electronic ground state of BaTi$_{0.875}$Nb$_{0.125}$O$_3$. In SrTi$_{0.875}$Nb$_{0.125}$O$_3$, 

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where no distortions are found, Ti/Nb $t_{2g}$ electronic degeneracy is retained, and there is no disorder-induced localization.

Neutron studies of a more complete Nb substitution series may help illuminate whether the rhombohedral distortion in BaTi$_{0.875}$Nb$_{0.125}$O$_3$ disappears or becomes coherent as the series transitions to a metal. Patino et al.[128] have studied Nb doping in BaTiO$_3$ by quantum chemical methods, but have not considered rhombohedrally distorted ground states.

### 4.5 Summary

In Chapter 4 we have remarked upon the distinct properties of BaTi$_{0.875}$Nb$_{0.125}$O$_3$ and SrTi$_{0.875}$Nb$_{0.125}$O$_3$, and thoroughly explored their average and local structures. We have observed a low temperature tetragonal phase for SrTi$_{0.875}$Nb$_{0.125}$O$_3$ coinciding with the low temperature phase of SrTiO$_3$, but with increased octahedral tilting. Average and local structure analysis show regular (Ti/Nb)O$_6$ octahedra at room temperature and at 15 K. In contrast, the analysis of BaTi$_{0.875}$Nb$_{0.125}$O$_3$ at room temperature and at 15 K displayed average cubic structures and local atomic configurations similar to the rhombohedral ground state of BaTiO$_3$. While the work here strongly suggests local off-centering gives rise to localized electronic ground states in
Nb-doped BaTi$_{0.875}$Nb$_{0.125}$O$_3$, the precise relation should be further explored. In a larger context, this finding provides a poignant example of how a simple and yet difficult to characterize structural difference can have profound influences on property. This theme is carried to the following chapters, where we will explore the local atomic configurations in a family of transition metal perovskite oxynitrides.
Chapter 5

Local Displacements and O/N

Ordering in BaTaO$_2$N

There has been considerable interest recently in perovskite oxynitrides, the group of compounds formed by partial replacement of oxygen by nitrogen in ABO$_3$ perovskites.\cite{Kim2010, Kim2011, Kim2012, Kim2013, Kim2014, Kim2015, Kim2016} In these materials, the increase in negative charge upon replacing O by N is compensated by simultaneously replacing the B cation by metals with higher cationic charge. Thus compounds which are electronically equivalent to $d^0$ perovskites such as BaTiO$_3$ and BaZrO$_3$ can be envisaged, for example corresponding to BaNbO$_2$N and BaTaO$_2$N. The dielectric properties of BaTaO$_2$N were measured by Kim \textit{et al.}\cite{Kim2017} and found to be rather unusual: polycrystalline BaTaO$_2$N has a rel-
ative bulk permittivity in excess of 4500, with a moderate temperature coefficient, 1140 ppm K$^{-1}$ near room temperature. Such high permittivity values are reminiscent, for example, of those in BaTiO$_3$ near the paraelectric to ferroelectric phase transition. It is therefore somewhat surprising that neutron,[130] X-ray,[136] and electron[136] diffraction of polycrystalline BaTaO$_2$N all suggest the cubic $Pm\bar{3}m$ space group and show no evidence for O/N ordering. Neither does temperature-dependent X-ray diffraction suggest a phase transition to a lower symmetry structure at low temperatures.[136] This interesting dichotomy has motivated us to pursue total scattering neutron diffraction methods to characterize local structure in BaTaO$_2$N.

5.1 Introduction

Perovskite oxynitrides were first reported by Marchand et al.[129] The compounds are ideal candidates for applications: they are stable to air, water, and acids, their dielectric properties have a weak linear dependence on temperature, and they do not undergo phase transitions below 300 K. Oxynitrides and related phases have received considerable attention for their potential use as non-toxic replacements for inorganic pigments and photocatalysts.[137, 138, 139] Partial replacement of the O$^{2-}$ anions in the parent oxides by the less electronegative N$^{3-}$ anion can raise the valence band edge of the electromag-
netic spectrum into the visible region. It is furthermore thought the increase in cation-anion covalency and the introduction of more polarizable ions into the lattice may influence dielectric properties and increase the likelihood of a second order Jahn-Teller distortion involving the $d^0$ cation.

There have been several experimental and theoretical studies examining the structure of BaTaO$_2$N. The local structure of BaTaO$_2$N has previously been probed by extended X-ray absorption fine structure (EXAFS) at the Ta \textit{L}	extsubscript{3}-edge.[140] The nearest Ta(O,N)$_6$ shell from EXAFS appeared as a broad, bimodal peak in the radial distribution function, clearly indicating a low symmetry coordination geometry around Ta. This bimodal peak character was not observed in the fourth shell and beyond ($r > 4.5 \text{ Å}$), suggesting that any local ionic displacements occur with an extremely small correlation length. In the EXAFS analysis, the Ta-O and Ta-N bonds could not be distinguished because of the very similar X-ray scattering from O and N. The question of whether N are \textit{cis} or \textit{trans} in the TaO$_4$N$_2$ octahedra similarly could not be addressed.

Recently Withers and coworkers have completed an analysis of diffuse electron scattering in BaTaO$_2$N showing inherently polar, off-center, and oppositely directed displacements of Ta and neighboring O/N anions along $<001>$ directions.[141] The so-called ‘one-dimensional polar nano regions’ observed are identical to those previously reported in paraelectric BaTiO$_3$ and doped
BaTiO$_3$ relaxor ferroelectric systems. This suggests O/N ordering is not directly responsible for observed Ta off-centering, but rather supports an inherent displacive disorder.

Fang et al.[142] have reported density functional electronic structure calculations on BaTaO$_2$N with specific regard to its local structure. Both cis and trans arrangements of N in TaO$_4$N$_2$ octahedra were found by DFT to support formation of local dipoles. The energy of a cis configuration was found to be about 0.2 eV (per BaTaO$_2$N unit) lower than the energy of a trans arrangement. Disordered anion arrangements were found to be slightly favored energetically, although the authors mention that choice of cell volume can bias what emerges as the preferred structural motif.

While no experimental evidence for long range anion ordering has been seen in BaTaO$_2$N, there are some reports of anion ordering in other oxynitride perovskites. Günther et al.[131] have reported the preparation of O/N ordered SrTaO$_2$N in the $I4/mcm$ space group. Their preparation involved the use of a halide mineralizer, believed to assist in the ordering. Ebbinghaus et al.[134] have reported $\approx$85%-ordered SrNbO$_2$N also in the $I4/mcm$ space group. However, while the TaO$_4$N$_2$ octahedra have trans N atoms in the former, the N atoms are largely cis in SrNbO$_2$N. Reports of ordered oxynitride perovskite compounds seem to be the exception rather than the rule. How-
ever, given how sensitively O/N ordering can depend on preparative conditions, it should be recognized that the structural results presented here may not be universally valid for all BaTaO$_2$N samples.

We present the average and local crystal structure of BaTaO$_2$N as determined by the combination of Rietveld and PDF refinements of time-of-flight neutron powder diffraction data. The use of neutrons is particularly appropriate for the problem of O/N ordering since these elements are well-separated in terms of their scattering lengths, at 5.805 fm and 9.36 fm$^{[122]}$ respectively. We also present density functional calculations of the relative stabilities of the structural models that are employed in the PDF analysis. The work in this chapter was previously published in reference $^{[143]}$.

5.2 Preparation

The sample for the study was prepared by Young-Il Kim of Professor Woodward’s group at Ohio State University. The X-ray structure, dielectric properties and electron diffraction were reported in reference$^{[136]}$ for the same sample. The preparation involved ammonolysis of mixed powders of BaCO$_3$ (J. T. Baker, 99.8%), and Ta$_2$O$_5$ (Cerac, 99.5%). Stoichiometric measures of the reactants were mixed in acetone using an agate mortar and pes-
tle, placed in an alumina boat, and heated in flowing anhydrous ammonia
(99.99%, \( \approx 0.5 \) mL/sec) to between 1223 K and 1273 K at a rate of 5 K/min. Af-
fter holding for as long as 80 h, it was cooled down at 10 K/min.[136] The same
sample was used in the EXAFS study by Ravel et al.[140] and the study of
diffuse electron microscopy by Withers et al.[141]

5.3 Rietveld and PDF Neutron Scattering Study

Time of flight neutron powder diffraction data were collected on the NPDF
instrument at the Los Alamos National Laboratory Lujan Neutron Scattering
Center[13] at room temperature. Approximately 2 g of powder were loaded
into a vanadium can for the experiment, and data were collected for 12 hours.
The diffraction data were analyzed with the Rietveld method as embodied in
the GSAS-EXPGUI[16, 17] suite of programs.

The cubic perovskite structure \( Pm\bar{3}m \) was used as a starting point for all
refinements, with complete O/N disordering. For the \( Q \)-space Rietveld refine-
ment, background, scaling, profile parameters, lattice parameters, anion oc-
cupancy, and atomic displacement parameters were refined. Figure 5.1 shows
the Rietveld fit to the cubic structure for the bank of data with the largest \( d \)
spacings. All detector banks (four in total) were used in the refinement. The
Figure 5.1. Rietveld fit of the time-of flight neutron diffraction data. Experimental data are circles and the solid line is the fit to the average $Pm\bar{3}m$ structure. The difference curve is displayed at the bottom of the plot. Vertical lines in the top panel indicate expected peak positions. Reproduced with permission from reference [143]. © 2007, American Chemical Society.
(100) peak at the largest $d$-spacing is not very well fitted by Rietveld analysis.

Two causes suggest themselves. The first is the problem of neutron absorption by Ta, which is corrected for systematically in the PDF analysis but not in the Rietveld. The second could reflect shortcomings of assuming complete O/N disorder in the Rietveld model. Results of the refinement are presented in the first column of Table 5.1. The results and quality of fit are consistent with the findings of other neutron refinement studies. The occupancy of O and N, constrained to fully occupy the anion site, were refined to 0.687(5) and 0.313(5), respectively.

To model the local structure in real space, the experimental PDF was extracted from the total scattering data using the program PDFgetN.[20] Background contributions were subtracted and the data were corrected for detector dead-time, absorption, multiple scattering, and inelasticity effects. The data were also normalized by the incident flux and total sample scattering cross-section. The maximum $Q$ vector used for the extraction was $38 \text{ Å}^{-1}$. PDF refinements were carried out using the PDFfit program.[23]

Real-space refinements began with an analysis of the cubic perovskite structure. The pair distribution function offers the advantage of being able to probe structural correlations at different length scales.[3] As discussed in Chapter 1, local correlations are distinct over shorter $r$-ranges. Over longer
Table 5.1. Rietveld and PDF refinement results to the long-range (average) structure using cubic space group $Pm\overline{3}m$. Two $r$-range refinements are reported for the PDF: one terminating at 10 Å and the other at 20 Å. Note that the reliability factors, $R_w$ for Rietveld refinement and for the PDF cannot be directly compared. * indicate anisotropic atomic correlation factors, constrained to be equivalent for O and N in the Rietveld analysis. † indicate isotropic atomic displacement factors used in the PDF analysis.

<table>
<thead>
<tr>
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<th>Rietveld</th>
<th>1.5 to 10 Å PDF</th>
<th>1.5 to 20 Å PDF</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>4.1103(1)</td>
<td>4.113(2)</td>
<td>4.1128(1)</td>
</tr>
<tr>
<td>$U_{iso}(Ba)$ (Å²)</td>
<td>0.00674(9)</td>
<td>0.0110(3)</td>
<td>0.00606(5)</td>
</tr>
<tr>
<td>$U_{iso}(Ta)$ (Å²)</td>
<td>0.01058(8)</td>
<td>0.01162(2)</td>
<td>0.00928(3)</td>
</tr>
<tr>
<td>$U(O)$ (Å²)</td>
<td>0.0067(2)*</td>
<td>0.00845(1)†</td>
<td>0.00740(4)†</td>
</tr>
<tr>
<td></td>
<td>0.00965(9)*</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0165(9)*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$U(O)$ (Å²)</td>
<td>0.0067(2)*</td>
<td>0.00870(1)†</td>
<td>0.00733(5)†</td>
</tr>
<tr>
<td></td>
<td>0.00965(9)*</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0165(9)*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$O_{occ}$</td>
<td>0.687(5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$N_{occ}$</td>
<td>0.312(5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_w$ (%)</td>
<td>2.14</td>
<td>14.8</td>
<td>9.96</td>
</tr>
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</table>
refinement ranges, the signatures of these configurations steadily damp out and atom-atom distances correspond increasingly well to the average structure. We refined the average structure over two ranges: from 1.5 Å to 10 Å, and from 1.5 Å to 20 Å. PDF refinement included the scale factor, lattice parameters, quadratic peak sharpening, and isotropic atomic displacement parameters. For \( Pm\bar{3}m \) the occupancy of O and N at the cube faces was set to 2/3 and 1/3, respectively, allowing for a direct comparison to lower symmetry models in the study. Results of the \( Pm\bar{3}m \) structural refinement are given in the second and third columns of Table 5.1. The \( a \) lattice parameter is slightly larger than the one obtained in the Rietveld refinement. No significant difference in the lattice parameters was observed for the two \( r \)-ranges. The goodness of fit parameters, \( R_w \), show the average \( Pm\bar{3}m \) structure is not able to fit short-range correlations very well. The fit to the first 10 Å gave \( R_w = 14.8\% \) while the fit to 20 Å was significantly improved with \( R_w = 9.96\% \). This provides direct evidence for short-range structural correlations that lose coherence at high-\( r \).

In order to analyze the local structure of BaTaO\(_2\)N using the PDFfit program (which requires crystallographic descriptions of compounds) we considered several structural models. We report here, the detailed analysis of four different models, including the average \( Pm\bar{3}m \) crystal structure. The models we present were the most reasonable in terms of their size, the number of re-
Figure 5.2. *cis* and *trans* configurations of the TaO$_4$N$_2$ octahedron. The central sphere represents Ta, the small dark grey spheres N, and the small light grey spheres O. Reproduced with permission from reference [143]. © 2007, American Chemical Society.

The models considered can be classified as *cis* models where the 2 N on corners of TaO$_4$N$_2$ octahedron share a common edge, and *trans* models where N occupy positions on opposite vertices of an octahedron forming linear N-Ta-N bonds. These two configurations are displayed in Figure 5.2. Furthermore, with respect to Ta displacements (included in the models to account for the asymmetrical environments introduced), unit cells that have a net dipole moment are referred to as ‘polar’, whereas ‘antipolar’ models are those where the
dipoles cancel one another. We focused on comparing polar trans, antipolar trans, and antipolar cis structures. We were unsuccessful in constructing a polar cis structure on a reasonable size scale. Larger mixed models, such as those containing cis and trans, or variations of TaO$_{6-m}$N$_m$ with $m = 0, 1, 2, 3$, calculated by Fang et al.[142] contain too many atoms for PDF analysis as performed here, and were not considered.

The polar trans model allows ions in the average cubic structure to shift along the [001] direction, creating a tetragonal distortion and reducing the symmetry of the cell to $P4mm$. Such a model is displayed in Figure 5.3(a). In the figure, large black Ba atoms occupy the corners of the unit cell, and a large blue Ta atom is found near the center of the cell. O and N are at the cell faces with orange N in a trans arrangement and blue O in one $xy$ plane around the Ta. The Ta shift has been exaggerated in the figure to make the displacement visible.

The antipolar trans model can be envisioned if we again consider a trans arrangement of N and imagine that adjacent octahedra in the structure contain Ta atoms that displace in the opposite direction. In our model in the space group $I4/mmm$ displayed in Figure 5.3(b), each Ta is allowed to move towards one of its N neighbors, and farther away from the other, along the [001] direction. In Figure 5.3(b), two adjacent octahedra have been connected and the Ta
Figure 5.3. The structures considered for this study. Large black spheres are Ba, large blue spheres are Ta, small blue spheres are O, and small orange spheres are N. Ta shifts are exaggerated in the figures for clarity. (a) $P4_{2}121$ polar trans model, the Ta shift along [001] is evident; (b) $I4_{1}/mmm$ antipolar trans model, two adjacent octahedra have been connected and display opposite directional shifts along [001]; (c) $Pbm$ antipolar cis model, projected down the c-axis, the Ta are connected through O and N. Ta shifts towards the N-edges of octahedra. Reproduced with permission from reference [143]. © 2007, American Chemical Society.
Figure 5.4. Antipolar, cis $Pbmm$ structure projected down [001] showing the two kinds of TaO$_4$N$_2$ polyhedra corresponding to Ta displacements towards $-x$ (teal polyhedra) and towards $+x$ (dark blue polyhedra). Ba atoms (black spheres) are only displayed within the unit cell, which is outlined. Reproduced with permission from reference [143]. © 2007, American Chemical Society.

shift has again been exaggerated for clarity.

In the antipolar cis model, N atoms occupy cis positions in the $xy$ plane. The structure of the model used, corresponding to space group $Pbmm$, is shown projected down the $c$-axis in Figure 5.3(c). It has linear stripes of N atoms running along the [010] direction. The Ta shift towards the (N-containing) edges
of the octahedron, in the $x$ and $-x$ directions, causing the sense of the Ta displacements to cancel. This structure is displayed in greater detail in Figure 5.4.

We have refined the orthorhombic cell with $a = b$, to allow for a comparable number of parameters in the refinement with respect to the other models. Other $cis$ structures were considered with more than one Ta plane in the unit cell, but with no improvement to the results.

All models were constructed by ordering O and N on the cubic perovskite lattice as described above. The atom positions were explicitly input into the program Isotropy[144] in order to obtain the crystallographic descriptions of the ordered structures described here.

Refinement results for these models to 10 and 20 Å of $r$, including atomic positions, are given in Tables 5.2, 5.3, and 5.4. Since PDF results are sensitive to the number of parameters refined, for these different models, positional parameters were refined only when they were found to strongly influence results. In the $P4mm$ model, Ba was held fixed, but all other ions were allowed to move in the [001] direction. In the two other models, only Ta displacements in specific directions were allowed.

In all cases, the sub-10 Å regime is better fitted with short-range order models than it is by the average structure model. A PDF refinement using the polar $trans$ $P4mm$ model results in a sizable improvement over the first 10 Å in real
Table 5.2. PDF refinement results to 10 and 20 Å in $r$ along with atomic positions for the polar trans ($P4mm$) BaTaO$_2$N model. General positions are shown in italics. When these are refined positions, errors are shown.

<table>
<thead>
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<th>$P4mm$</th>
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<tr>
<td></td>
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<tr>
<td>$a$ (Å)</td>
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<td>$c$ (Å)</td>
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<tr>
<td>$R_w$ (%)</td>
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<td>$c$ (Å)</td>
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<tr>
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Table 5.3. PDF refinement results to 10 and 20 Å in r along with atomic positions for the antipolar trans \( \text{I}4/\text{mmm} \) BaTaO\(_2\)N model. General positions are shown in italics. When these are refined positions, errors are shown. † indicate atomic displacement parameters that were constrained to be equivalent.

<table>
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<td></td>
<td>atom</td>
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<td>( a ) (Å) 5.8145(9)</td>
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</tr>
<tr>
<td>( c ) (Å) 8.228(3)</td>
<td>Ta</td>
</tr>
<tr>
<td>( R_w ) (%) 11.1</td>
<td>O</td>
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<td></td>
<td>N1</td>
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<td></td>
<td>N2</td>
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<table>
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<tr>
<th>( \text{I}4/\text{mmm} )</th>
<th>20 Å refinement, 9 parameters</th>
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<td>( a ) (Å) 5.8141(2)</td>
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<tr>
<td>( c ) (Å) 8.2329(5)</td>
<td>Ta</td>
</tr>
<tr>
<td>( R_w ) (%) 9.70</td>
<td>O</td>
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<tr>
<td></td>
<td>N1</td>
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<td></td>
<td>N2</td>
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</tbody>
</table>
Table 5.4. PDF refinement results to 10 and 20 Å in $r$ along with atomic positions for the antipolar cis ($Pbmm$) BaTaO$_2$N model. General positions are shown in italics. When these are refined positions, errors are shown. † indicate atomic displacement parameters that were constrained to be equivalent.

<table>
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<td>$a, b$ (Å)</td>
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<td>$c$ (Å)</td>
<td>4.1411(8)</td>
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<tr>
<td>$R_w$ (%)</td>
<td>9.52</td>
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<td></td>
<td>O2</td>
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<td></td>
<td>N</td>
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<table>
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<tr>
<th>Pbmm</th>
<th>20 Å refinement, 9 parameters</th>
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<td>8.2022(2)</td>
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<td>$R_w$ (%)</td>
<td>8.99</td>
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<tr>
<td></td>
<td>O2</td>
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<td></td>
<td>N</td>
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</tbody>
</table>
Figure 5.5. Sub-10 Å real space PDF refinement results, corresponding to (a) the average structure $Pm\bar{3}m$ model, and (b) the antipolar cis $Pbmm$ structure. Black circles correspond to the experimental PDF and the fits are given as orange lines through the data. The difference curves are presented at the bottom of each panel. Reproduced with permission from reference [143]. © 2007, American Chemical Society.
space. $R_w$ improves to 11.9%, compared to 14.8% for the average structure. The results for the antipolar *trans I*$_4$/mmm show further improvement. $R_w$ improves to 11.1%, while using fewer refinement parameters (9 vs. 11 in the previous model). The best model over 10 Å was the antipolar *cis* model, using *Pbmm*. Here $R_w$ is 9.52%, also with only 9 refined parameters. Figure 5.5 shows the experimental PDF fit with the average structure in (a) and the best fit with the antipolar *cis* (*Pbmm*) model in (b) to 10 Å.

The difference in the reliability factor between the local structures and the average structure dies out quickly; it is much less significant over 20 Å than over 10 Å. The PDF fit to the polar *trans* model over 20 Å gave $R_w = 10.6\%$ compared to 9.96% for the average *Pm*$_3$m structure, indicating that distortions of this kind, if present, would have to be very short-range. For the antipolar *trans* and antipolar *cis* structures, there were slight improvements over the *Pm*$_3$m result, with $R_w = 9.70\%$ and 8.99% respectively. Thus we suggest that the local structure of this BaTaO$_2$N sample shows a tendency for *cis* rather than *trans* TaO$_4$N$_2$ polyhedra, and the correlation length for this kind of ordering is on the scale of 10 Å.

In molecules oxygen and nitrogen ligands have the same effect in terms of $\sigma$ donation, but a considerable difference is seen in $\pi$ donation. For nitrogen, $\pi$ orbitals are larger and the overlap with the transition metal $d$ orbitals are
greater compared to those of the more electronegative oxygen ligand. In a \textit{trans} configuration along the $z$-axis, the $\pi$ orbitals on the nitrogen compete with each other over the electron density in the $d_{xy}$ and $d_{yz}$ orbitals on the transition metal cation, but in the \textit{cis} variant the alignment of the nitrogen $\pi$ orbitals allow for greater $\pi$ donation, stabilizing the isomer.[145] A similar stabilization is seen in the solid state and may have an effect here.

Table 5.5 presents bond lengths from the PDF results. In the $P4mm$ structure, Ta-O and Ta-N bond lengths show a slight shortening of the four equivalent Ta-O bonds [2.0525(3) Å] compared to the $Pm\bar{3}m$ structure [2.0565(1) Å], and one long and one short Ta-N bond arising from the $c$-axis displacements. Bond lengths from the $I4/mmm$ refinement show Ta-O bonds identical to those in the $Pm\bar{3}m$ structure, and one lengthened and one shortened Ta-N bond. In fact, the bond lengths for the Ta-N bonds are refined to be the same (within error) for both \textit{trans} models. For the antipolar \textit{cis} structure, the Ta-O bonds are split into two very similar lengths, at 2.06 Å and 2.07 Å. Both Ta-N distances are slightly shorter within the octahedra, at 2.03 Å.
Table 5.5. Atom-atom distances from PDF structural refinements of the neutron data, shown with reliability factors for the models.

The refinement results are for the first 10 Å in real space.

<table>
<thead>
<tr>
<th></th>
<th>Rietveld</th>
<th>Pm3m</th>
<th>P4mm</th>
<th>I4/mmm</th>
<th>Pbmm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{Ta-O}$ (Å)</td>
<td></td>
<td>(4×) 2.05516(6)</td>
<td>(4×) 2.0565(1)</td>
<td>(4×) 2.0525(3)</td>
<td>(4×) 2.0566(5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(2×) 2.06(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$d_{Ta-N}$ (Å)</td>
<td></td>
<td>(2×) 2.05516(6)</td>
<td>(2×) 2.0565(1)</td>
<td>(1×) 2.126(7)</td>
<td>(1×) 2.112(7)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>(1×) 2.005(7)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_w$ (%)</td>
<td></td>
<td>14.8</td>
<td>11.9</td>
<td>11.1</td>
<td>9.52</td>
</tr>
</tbody>
</table>
5.4 Density Functional Theory Calculations

Density functional theory calculations were completed by Matthew Stoltzfus in the Woodward Group at Ohio State University using the Cambridge Serial Total Energy Package (CASTEP) as embodied in Accelrys Materials Studio.[146] Norm-conserving non-local pseudo-potentials were generated using the Kerker scheme with a kinetic energy cutoff of 400 eV. A convergence criterion of 0.00002 eV was applied for the energy change per atom, 0.001 Å for the root-mean-square atomic displacement, and 0.05 eVÅ$^{-1}$ for the root-mean-square residual force on movable atoms. Electron exchange and correlation were described using the Perdew-Wang (PW91) generalized gradient approximation (GGA).[147] Geometry optimization utilized the Broyden-Fletcher-Goldfarb-Shanno Scheme[148] in a manner which permitted both the lattice parameters and atomic coordinates to be optimized.

DFT calculations provide information on the energetics of different ordered structures, and details of atom positions as a result of geometry optimization. An important distinction between the PDF and DFT results presented here is that in the DFT studies, all general positions were allowed to displace in the geometry optimization, unlike in the PDF refinements where many general positions were held fixed, and furthermore, $a$ and $b$ were constrained to be equal in the $Pbmm$ structure. A total of seven parameters were refined in this model.
Tables 5.6 and 5.7 give the DFT results for the three ordered BaTaO$_2$N structures in the study and Table 5.8 presents bond lengths with the corresponding relative energies for the structures. Since the number of formula units per unit cell were not the same for the three structures, the relative energy is expressed per BaTaO$_2$N formula unit.

The trends (long-medium-short) in the DFT predicted bond lengths agree with those obtained from the PDF refinements for the $P4mm$ and $Pbmmm$ models but not for $I4/mmm$, although the exact lengths differ. In the $I4/mmm$ models, the calculated bond lengths are essentially all the same. In the polar trans model ($P4mm$) both calculations and experiment indicate a structural distortion leading to a short Ta-N bond and a long Ta-N bond. However, the difference between long and short bonds is quite large in the calculations, associated with an unusually large $c$ parameter. The long-short bond alternation predicted by the calculations effectively lowers the coordination number of the tantalum from octahedral to square pyramidal. This is reminiscent of the structure of PbVO$_3$.[149] In sharp contrast the two Ta-N bonds are almost identical in the antipolar trans model ($I4/mmm$). This can be understood from simple bond valence considerations.[150] In the $P4mm$ model each nitrogen makes one short, strong bond with tantalum and one long, weak bond with tantalum. This preserves the net bonding at each nitrogen site. If there were
Table 5.6. DFT results for trans BaTaO$_2$N models in the present study. Calculated positions are shown in italics. (Data from the Woodward group.)

<table>
<thead>
<tr>
<th></th>
<th>atom</th>
<th>Wyck.</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>P4mm (polar trans)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>4.0564</td>
<td>Ba</td>
<td>1a</td>
<td>0</td>
<td>0</td>
</tr>
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<td>$c$ (Å)</td>
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<td>Ta</td>
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</tr>
<tr>
<td>$E$ (eV)</td>
<td>-7997.88</td>
<td>O</td>
<td>2c</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>vol (Å$^{-3}$)</td>
<td>76.628</td>
<td>N</td>
<td>1b</td>
<td>0.5</td>
<td>0.5</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>I4/mmm (antipolar trans)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>$a$ (Å)</td>
<td>5.8764</td>
<td>Ba</td>
<td>4c</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>8.3024</td>
<td>Ta</td>
<td>4e</td>
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<td>0</td>
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<tr>
<td>$E$ (eV)</td>
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<td>O</td>
<td>8f</td>
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<tr>
<td>vol (Å$^{-3}$)</td>
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<td>N1</td>
<td>2a</td>
<td>0</td>
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</table>
similarly large displacements of the tantalum atoms in the $I4/mmm$ model one nitrogen would end up with two short, strong bonds to tantalum and the other nitrogen would end up with two long, weak bonds to tantalum. To avoid this unfavorable local bonding scenario the structure effectively ends up keeping all six tantalum-anion bonds nearly equidistant. The local distortion calculated for the antipolar $cis$ structure ($Pbmm$) is somewhat larger than the distortion observed from the PDF refinements. This is to be expected given the lack of long range order in the samples. Nevertheless, the shift of the Ta$^{5+}$ ion toward the edge of the octahedron containing nitrogen is seen both for calculations and experiments. The fact that the calculations show that $cis$ ordering leads to a much smaller local distortion than does the polar $trans$ ordering may
provide a clue as to why cis ordering is favored in samples where long range anion ordering is absent. The energetics of a structure containing the highly distorted polyhedra associated with polar trans ordering will be very sensitive to the orientation of the resulting square pyramids. Unlike PbVO$_3$ or PbTiO$_3$ the orientation of the long and short bonds is dependent upon the anion distribution, which presumably does not change much once the compound forms at high temperature. In contrast, the cis geometry preserves a polyhedron whose dimensions are only mildly distorted from an octahedron. Given the lack of long range N/O order this would seem to be a more favorable local bonding situation.

One interesting result that has not been previously discussed is the fact that for simple ordering schemes a trans arrangement is needed to generate cooperative displacement that is polar. Therefore, in order to obtain a polar structure that may exhibit ferroelectricity or pyroelectricity it would seem to be essential to find a route to an ordered trans structure. One possible route to stabilizing a trans ordering would be to take advantage of epitaxial lattice matching in thin film architectures to orient the long Ta-N bonds perpendicular to the substrate.
Table 5.8. Bond lengths and relative energies per formula unit from DFT calculations of the BaTaO$_2$N structures in the study. (Data from the Woodward group.)

<table>
<thead>
<tr>
<th></th>
<th>$P4mm$</th>
<th>$I4/mmm$</th>
<th>$Pbmmm$</th>
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<tbody>
<tr>
<td>$d_{Ta-O}$ (Å)</td>
<td>$4(4×)$ 2.060</td>
<td>$4(4×)$ 2.078</td>
<td>$2(2×)$ 2.176</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$(2×)$ 2.068</td>
</tr>
<tr>
<td>$d_{Ta-N}$ (Å)</td>
<td>$1(1×)$ 2.787</td>
<td>$1(1×)$ 2.076</td>
<td>$2(2×)$ 2.007</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$(1×)$ 1.870</td>
</tr>
<tr>
<td>$ΔE$ (meV)</td>
<td>0</td>
<td>−482</td>
<td>−508</td>
</tr>
</tbody>
</table>

5.5 Summary

In conclusion, we have experimentally demonstrated that short range ordering of O and N exists in BaTaO$_2$N, as the average $Pm\bar{3}m$ structure is unable to capture the local correlations embodied in the sub-10 Å pair distribution function. These local correlations die out quickly over distance, and the average structure is a good model for the 1.5 to 20 Å PDF. The sub-10 Å PDF is best fitted by an antipolar cis configuration of N in TaO$_4$N$_2$ octahedra. Further insight is provided by the DFT calculations which support the experimental conclusion that the cis TaO$_4$N$_2$ octahedra are more stable. In Chapter 6 we will examine local structure correlations in other members of the oxynitride family; SrTaO$_2$N and CaTaO$_2$N.
Chapter 6

O/N Ordering and Octahedral

Tilting in SrTaO$_2$N and CaTaO$_2$N

In the previous chapter the local structure and oxygen/nitrogen ordering of the high permittivity perovskite BaTaO$_2$N was discussed. While the average structure as revealed by neutron diffraction Rietveld analysis was cubic $Pm\bar{3}m$ with no evidence of O/N ordering, the local structure as revealed by pair distribution function analysis of the total neutron scattering favored a cis configuration of the TaO$_4$N$_2$ polyhedra with small Ta displacements toward the N atoms. SrTaO$_2$N has a dielectric constant more than half that of BaTaO$_2$N, while the dielectric constant of CaTaO$_2$N is quite small and typical for an insulating perovskite oxide. Materials possessing high permittivities are typically
associated with polar behavior and often display phase transitions to lower symmetry structures. Structural studies on these additional compounds will allow a more complete understanding of the relationship between structure and property in these particular oxynitride perovskite compounds.

6.1 Introduction

Kim et al. [136] measured the dielectric properties of BaTaO$_2$N, SrTaO$_2$N, and CaTaO$_2$N and his results were quite unusual, particularly for BaTaO$_2$N and SrTaO$_2$N. As discussed in Chapter 5, polycrystalline BaTaO$_2$N has a relative bulk permittivity in excess of 4500 near room temperature. SrTaO$_2$N also has a high permittivity (around 2900), while CaTaO$_2$N has a constant of only 30.[136] In contrast to other high-permittivity materials, such as a material near a ferroelectric transition, no evidence of lower symmetry structures are detected in any of these materials on cooling from room temperature.

Previous neutron studies have reported the crystal structure of SrTaO$_2$N as tetragonal, in the $I4/mcm$ space group, and the crystal structure of CaTaO$_2$N as orthorhombic, in the $Pnma$ space group. The crystallographic unit cells are depicted in Figure 6.1.

The calculated tolerance factors (Equation 1.7) for SrTaO$_2$N and CaTaO$_2$N
Figure 6.1. (a) The SrTaO$_2$N $I4/mcm$ crystal structure and (b) the CaTaO$_2$N $Pnma$ crystal structure. Ta(O/N)$_6$ octahedra are shown in blue, Sr and Ca atoms are dark and light grey, respectively, and the O/N anion positions are shown in purple. The tolerance factors are 0.985 and 0.937, respectively. As observed for many perovskite structures, tolerance factors below unity correspond to those with octahedral tilting. The distinct tilting schemes found in the average structures of SrTaO$_2$N and CaTaO$_2$N are illustrated in Figure 6.2. Following the Glazer[39] notation introduced in Chapter 1, SrTaO$_2$N takes on the $a_0^0a_0^0c_0^c$ structure, where octahedra tilt about the $c$-axis and adjacent layers have octahedra that rotate in opposite directions. In this tetragonal cell, Ta does not displace from the center of octahedra, but the two apical anions are positioned slightly closer to Ta than the four equatorial anions. Tilting along the $c$-axis leads to a modified coordination environment around the Sr cation as well. CaTaO$_2$N takes on the $a_0^+b_0^-b_0^-$ structure, with in phase tilting along the $a$-axis and out of phase
tilting about the \( b \) and \( c \) axes. Ta does not displace from its position in the octahedra, but the tilting similarly affects the coordination environments of the cations (the \( \text{TaO}_4\text{N}_2 \) octahedra is made up of three pairs of distinct Ta-O/N bond distances).

The use of neutron diffraction is particularly appropriate for the problem of O/N ordering since these elements are well-separated in terms of their scattering lengths, at 5.803 and 9.36 fm, respectively. Still, the absence or presence of ordering of O and N in oxynitride perovskite structures remains an interesting point of contention in the field. The case of \( \text{BaTaO}_2\text{N} \) was discussed in Chapter 5. In neutron studies of the Sr and Ca analogues, Pors et al.\cite{130} and Clarke et al.\cite{133} found the equatorial position in \( \text{SrTaO}_2\text{N} \) to be slightly oxygen rich, while Günther et al. found complete ordering with N axial anion positions\cite{131}. The latter study also reported partial anion ordering in \( \text{CaTaO}_2\text{N} \), with the axial position nitrogen rich. Still, X-ray and neutron studies of many perovskite oxynitrides support completely disordered anions: for example, the structures of \( \text{LaZrO}_2\text{N} \), \( \text{NdTiO}_2\text{N} \) and \( \text{LaTiO}_2\text{N} \) reported by Clarke and co-workers.\cite{132}

Local distortions and O/N ordering in the \( \text{ATaO}_2\text{N} \) (\( A = \text{Ba}, \text{Sr}, \text{Ca} \)) family of materials may have profound effects on optical and electronic properties. Yet, previous studies using local probes (EXAFS, PDF, HRTEM, etc.) have not
Figure 6.2. (a) The SrTaO$_2$N average structure model in $I4/mcm$ and (b) the CaTaO$_2$N average structure model in $Pnma$ viewed down the $a$, $b$, and $c$ axes. Ta octahedra are drawn in blue, Sr and Ca atoms are grey, and the disordered O/N positions are shown with purple spheres. The $a_0^0d_0^0c^-_0$ tilting scheme in (a) and the $a^+_0b^-_0b^-_0$ tilting scheme in (b) are evident.
considered SrTaO$_2$N or CaTaO$_2$N. We present here the average and local crystal structures of SrTaO$_2$N and CaTaO$_2$N as determined by the combination of Rietveld and PDF refinements of time-of-flight neutron powder diffraction data. We also present preliminary DFT calculations exploring the effects of octahedral tilting, isomeric configurations, and Ta off-centering on the stability of SrTaO$_2$N and CaTaO$_2$N structures. The observed changes in local structure across the $A$ cation series ($A = \text{Ba, Sr, Ca}$) give unique insight into the dielectric properties of this family of functional materials.

6.2 Preparation

The SrTaO$_2$N and CaTaO$_2$N samples were prepared by Young-Il Kim of Professor Woodward’s group at Ohio State University, in the manner described in reference [136]. The compounds were prepared by ammonolysis of mixed ceramic powders of SrCO$_3$ (Aldrich, 99.9+%) or CaCO$_3$ (Mallinckrodt, 99.95%) and Ta$_2$O$_5$ (Cerac, 99.5%). For the SrTaO$_2$N preparation stoichiometric measures of the reactants (with respect to the cations) were mixed in acetone using an agate mortar and pestle, placed in an alumina boat, and heated in flowing anhydrous ammonia (99.99%, \(\approx 0.5\ \text{mL/sec}\)) to between 1223 K and 1273 K at a rate of 5 K/min. After holding for as long as 80 h, it was cooled down at 10 K/min. The preparation of CaTaO$_2$N was similar. However, in this
case it was necessary to react an intermediate pyrochlore phase (Ca$_2$Ta$_2$O$_7$) in a 50/50 wt % NaCl/KCl flux for 80 h to produce stoichiometric CaTaO$_2$N without phase impurities. The resulting SrTaO$_2$N powder is orange-red in color, while the CaTaO$_2$N powder is yellow in color. The X-ray structures and dielectric properties of the two compounds were reported in reference [136].

It has been presumed that differences in crystal structure with respect to anion ordering are largely due to variations in sample preparation. Particularly, results suggest complete disorder is favored in structures when materials are prepared by nitridation of pure oxide precursor at 900 to 1000 °C, or by reacting alkaline earth oxide with TaON at 1500 °C under nitrogen.[133] Full ordering has been observed when a mineralizer is used in nitridation.[131] While these assertions have not been systematically studied, we must nonetheless maintain that our experimental results may be unique only to the samples we have studied.

### 6.3 Rietveld and PDF Neutron Scattering Study

Time of flight neutron powder diffraction data were collected on the NPDF instrument at the Los Alamos National Laboratory Lujan Neutron Scattering Center[13] at room temperature. Approximately 2 g of powder were loaded
into a vanadium can, and data were collected for 12 hours for each sample.

The diffraction data were analyzed with the Rietveld method as embodied in the GSAS-EXPGUI[16, 17] suite of programs. Backgrounds, scale factor, lattice parameters, isotropic displacement parameters, profile parameters, atom positions, and anion site occupancies were refined. The results of the refinements are given in Figure 6.3 and Table 6.1 and are consistent with results from similar studies.

A preliminary investigation of possible perovskite tilt systems for SrTaO$_2$N supported refinement in the tetragonal $I4/mcm$ model. Refinements were carried out for fully ordered (N in apical anion position), fully disordered, and for partially ordered (refined occupancy) anionic arrangements. The fully ordered model gave the poorest fit, but a better agreement was achieved with a partially ordered model than with a completely disordered model. In the refinement N accounted for 56(3)% of the occupancy of the axial position, and only 22(2)% of the occupancy of the equatorial position.

CaTaO$_2$N data was refined in the $Pnma$ structure. Fully disordered, fully ordered (N in apical position only) and refined O/N anion occupancies were investigated. The results support slightly N-rich apical positions regardless of starting values. N was found to occupy 40(1)% of axial position and 29.8(6)% of the equatorial position, close to the 1/3 occupancies expected for fully dis-
Figure 6.3. (a) SrTaO$_2$N and (b) CaTaO$_2$N Rietveld refinement results for the time-of-flight neutron diffraction data (145° detector bank). Data are given as circles and the solid lines are fits using the $I4/mcm$ and $Pnma$ structures, respectively. Difference curves are displayed below the data. Expected peak positions for the two crystal structures are displayed in panels above each of the fits.
ordered anions. Models with full anion disorder were nearly as sufficient. In our analysis, if anisotropic atomic displacement parameters were used, the refinement tended to full disorder. This distinction may influence some of the observed controversy in the literature regarding anion site order. Regardless, the use of a mineralizer in the preparation of CaTaO$_2$N here did not result in an ordered anion arrangement, as was found for SrTaO$_2$N by others.[131] This may indicate a difference in thermodynamic stability of ordered anion arrangements in the compounds.

Similar to what is seen in Figure 5.1 for BaTaO$_2$N, the largest $d$-spacing peak in Figure 6.3 for (a) SrTaO$_2$N and (b) CaTaO$_2$N is poorly fit by average structure models. As discussed previously, this may reflect poor characterization of O/N disorder in the models or the neutron absorption of Ta. In Table 6.1 the Sr/Ca site isotropic atomic displacements are high with respect to the O/N site displacements, providing further evidence for structural disorder. In a good structural model, the displacement factors refined for lighter elements should be higher than those refined for heavier elements. This is the case reflected in Table 5.1 where the refined atomic displacement parameter for Ba in the Rietveld analysis of BaTaO$_2$N is more reasonable. In this case, it is the Ta atomic displacement parameter that is higher than expected. This is rationalized in considering the results of the local structure analysis: the parame-
Table 6.1. Lattice parameters and atomic positions from SrTaO$_2$N and CaTaO$_2$N Rietveld refinements. Refined parameters are shown with error.

SrTaO$_2$N in $I4/\text{mcm}$: $a = 5.6960(1)$ Å, $c = 8.0718(3)$ Å, $R_w = 2.64$

<table>
<thead>
<tr>
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<th>$z$</th>
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<tr>
<td>Sr</td>
<td>4$b$</td>
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<td>0</td>
<td>0.5</td>
<td>0.25</td>
<td>0.0107(1)</td>
</tr>
<tr>
<td>Ta</td>
<td>4$c$</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0082(2)</td>
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<tr>
<td>O1/N1</td>
<td>4$a$</td>
<td>0.44/0.56(3)</td>
<td>0</td>
<td>0</td>
<td>0.25</td>
<td>0.025(1)</td>
</tr>
<tr>
<td>O2/N2</td>
<td>8$h$</td>
<td>0.78/0.22(2)</td>
<td>0.2676(2)</td>
<td>0.7676(2)</td>
<td>0</td>
<td>0.0145(9)</td>
</tr>
</tbody>
</table>

CaTaO$_2$N in $Pnma$: $a = 5.61773(9)$ Å, $b = 7.8917(1)$ Å, $c = 5.54685(8)$ Å, $R_w = 1.78$

<table>
<thead>
<tr>
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<th>Frac.</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$U_{iso}$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>4$c$</td>
<td>1</td>
<td>0.0317(2)</td>
<td>0.25</td>
<td>0.9944(4)</td>
<td>0.0154(2)</td>
</tr>
<tr>
<td>Ta</td>
<td>4$b$</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>0.0070(1)</td>
</tr>
<tr>
<td>O1/N1</td>
<td>4$c$</td>
<td>0.60/0.40(1)</td>
<td>0.4818(2)</td>
<td>0.25</td>
<td>0.0756(2)</td>
<td>0.0149(3)</td>
</tr>
<tr>
<td>O2/N2</td>
<td>8$d$</td>
<td>0.702/0.298(6)</td>
<td>0.2915(1)</td>
<td>0.0402(1)</td>
<td>0.7092(1)</td>
<td>0.0103(2)</td>
</tr>
</tbody>
</table>
ters become more reasonable using local structure models that incorporate Ta
displacements. The questions of anion ordering and possible cation displace-
ments lead us to consider the local structures of SrTaO$_2$N and CaTaO$_2$N.

To look at the local structure in real space, the experimental PDF was ex-
tacted from the total scattering data using the program PDFGetN.[20] Back-
ground contributions were subtracted and the data were corrected for detector
deadtime, absorption, multiple scattering, inelasticity effects, and normalized
by the incident flux and total sample scattering cross-section. The $Q$ vector
used for extraction of the $G(r)s$ was 30 Å$^{-1}$. PDF refinements were carried out
in the program PDFfit2 and PDFgui.[24] PDF refinement included the scale
factor, lattice parameters, quadratic peak sharpening, and isotropic atomic cor-
relation factors.

Real-space refinements of SrTaO$_2$N and CaTaO$_2$N began using the average
structures as models: refining a scale factor, sample broadening, lattice pa-
rameters, the positions of atoms and atomic displacement parameters. In both
cases refinement of occupancy in the anion position was tried but the values
changed negligibly and therefore were held constant (fixed to the values re-
fined in the Rietveld analysis). Figure 6.4 shows the PDF fits to 10 Å in $r$ for
(a) SrTaO$_2$N and (b) CaTaO$_2$N. In both cases the fit is fairly good at high-$r$,
but poor for describing the Ta-O/N and Ca/Sr-O/N nearest neighbors in the
Figure 6.4. 10 Å (a) SrTaO$_2$N and (b) CaTaO$_2$N PDF refinements using the average structure models from Rietveld analysis. The pair distribution function is given in circles, fits are given as solid orange lines, and the difference curves are displayed below the data.
experimental $G(r)$s. The results from 10 Å PDF refinement using the average $I4/mcm$ and $Pnma$ structures as models are given in Table 6.2.

PDF refinement results (over 20, 10, and 4.5 Å in $r$) using the average structure $I4/mcm$ and $Pnma$ models are summarized in Tables 6.3 and 6.4 for SrTaO$_2$N and CaTaO$_2$N, respectively. The results convey the Ta-O/N bond lengths, Ta-O/N-Ta bond angles and the goodness-of fit factors over the various refinement ranges explored. The values are conveyed to emphasize the sensitivity of the PDF method to local bond distances rather than to specific crystallographic descriptions of structure over short refinement ranges. Rietveld refinement results are given in both tables for comparison.

Table 6.3 shows that the average $I4/mcm$ model does a poor job at describing the low-$r$ SrTaO$_2$N PDF but a fair job at describing the high-$r$ PDF ($R_w$ is 9.35% for the 20 Å refinement and 16.2% for the 4.5 Å refinement). This is analogous to the situation observed for BaTaO$_2$N in Chapter 5, and provides evidence for local structure correlation missing from the average structure model. Nonetheless, the analysis shows an increased difference between the axial and equatorial Ta-O/N atom-atom distances and a corresponding increase in bending of Ta-O/N-Ta angles for lower-$r$ refinements. This is modelled in $I4/mcm$ through the refinement of the 8$h$ equatorial anion position, and supports a local structure with increased octahedral tilting compared to
Table 6.2. Lattice parameters and atomic positions from 10 Å SrTaO$_2$N and CaTaO$_2$N PDF refinements. Refined parameters are shown with error.

**SrTaO$_2$N in $I4/mcm$:** $a = 5.70(1)$ Å, $c = 8.09(2)$ Å, $R_w = 13.6\%$

<table>
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<th>$y$</th>
<th>$z$</th>
<th>$U_{iso}$ (Å$^2$)</th>
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<tr>
<td>Sr</td>
<td>4$b$</td>
<td>1</td>
<td>0</td>
<td>0.5</td>
<td>0.25</td>
<td>0.007(1)</td>
</tr>
<tr>
<td>Ta</td>
<td>4$c$</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.007(1)</td>
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<tr>
<td>O1/N1</td>
<td>4$a$</td>
<td>0.44/0.56</td>
<td>0</td>
<td>0</td>
<td>0.25</td>
<td>0.020(4)</td>
</tr>
<tr>
<td>O2/N2</td>
<td>8$h$</td>
<td>0.78/0.22</td>
<td>0.271(2)</td>
<td>0.771(2)</td>
<td>0</td>
<td>0.010(2)</td>
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</table>

**CaTaO$_2$N in $Pnma$:** $a = 5.59(2)$ Å, $b = 7.90(2)$ Å, $c = 5.58(2)$ Å, $R_w = 16.2\%$

<table>
<thead>
<tr>
<th>atom</th>
<th>Wyck.</th>
<th>Frac.</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$U_{iso}$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>4$c$</td>
<td>1</td>
<td>0.0317</td>
<td>0.25</td>
<td>0.9944</td>
<td>0.017(4)</td>
</tr>
<tr>
<td>Ta</td>
<td>4$b$</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>0.008(1)</td>
</tr>
<tr>
<td>O1/N1</td>
<td>4$c$</td>
<td>0.60/0.40</td>
<td>0.473(3)</td>
<td>0.25</td>
<td>0.077(3)</td>
<td>0.007(2)</td>
</tr>
<tr>
<td>O2/N2</td>
<td>8$d$</td>
<td>0.702/0.298</td>
<td>0.290(3)</td>
<td>0.041(2)</td>
<td>0.709(3)</td>
<td>0.008(1)</td>
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Table 6.3. Ta-O/N bond lengths and Ta-O/N-Ta angles from SrTaO$_2$N Rietveld and 20, 10 and 4.5 Å PDF structure refinements using the $I4/mcm$ model. The lattice parameters, atomic displacement parameters and the equatorial ($8h$) O/N position were refined in the 20 and 10 Å PDF refinements. The lattice parameters were fixed for the 4.5 Å refinement.

<table>
<thead>
<tr>
<th></th>
<th>Rietveld</th>
<th>20 Å PDF</th>
<th>10 Å PDF</th>
<th>4.5 Å PDF</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{Ta-O/N}$ (Å)</td>
<td>(2×) 2.01796(8)</td>
<td>(2×) 2.02(1)</td>
<td>(2×) 2.021(7)</td>
<td>2.0190(4)</td>
</tr>
<tr>
<td></td>
<td>(4×) 2.0188(1)</td>
<td>(4×) 2.014(3)</td>
<td>(4×) 2.02(2)</td>
<td>2.03(2)</td>
</tr>
<tr>
<td>$\angle_{Ta-O/N-Ta}$ (°)</td>
<td>171.96(9)</td>
<td>172.18(3)</td>
<td>170.23(6)</td>
<td>166.8(1)</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>180</td>
<td>180</td>
<td>180</td>
</tr>
<tr>
<td>$R_w$ (%)</td>
<td>2.64</td>
<td>9.35</td>
<td>13.6</td>
<td>16.2</td>
</tr>
</tbody>
</table>

the long-range crystal structure.

For CaTaO$_2$N there is also an increasing trend in asymmetry in the TaO$_4$N$_2$ polyhedra for lower refinement ranges. However, Table 6.4 shows the average $Pnma$ model is nearly as sufficient at describing the 10 Å PDF ($R_w = 16.2\%$) as the 20 Å PDF ($R_w = 15.7\%$). The low-$r$ CaTaO$_2$N data is well-fit by the $Pnma$ model ($R_w = 12.6\%$), but only with significant anion movement. Figure 6.5 compares the 4.5 Å PDF refinement result using (a) the atomic positions from the average structure Rietveld refinement and (b) refined anion positions. The average structure atomic positions poorly model the Ta-O/N and Ca-O/N nearest neighbor correlations, but the local structure model captures the peak

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Table 6.4. Ta-O/N bond lengths and Ta-O/N-Ta angles from CaTaO$_2$N Rietveld and short-range PDF structural refinements using the $Pnma$ structure. The lattice parameters, atomic displacement parameters and the O/N positions were refined in the 20 and 10 Å PDF refinements. The lattice parameters were fixed for the 4.5 Å refinement.

<table>
<thead>
<tr>
<th></th>
<th>Rietveld</th>
<th>20 Å PDF</th>
<th>10 Å PDF</th>
<th>4.5 Å PDF</th>
</tr>
</thead>
<tbody>
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<td>$d_{Ta-O/N}$ (Å)</td>
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<td>(2×) 2.020(5)</td>
<td>(2×) 2.02(3)</td>
<td>(2×) 1.93(2)</td>
</tr>
<tr>
<td></td>
<td>(2×) 2.0186(7)</td>
<td>(2×) 2.02(2)</td>
<td>(2×) 2.03(3)</td>
<td>(2×) 2.027(4)</td>
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<tr>
<td>$\angle_{Ta-O/N-Ta}$ (°)</td>
<td>155.33(7)</td>
<td>153.6(2)</td>
<td>154.0(4)</td>
<td>153.3(3)</td>
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<td></td>
<td>154.08(4)</td>
<td>155.17(6)</td>
<td>154.1(1)</td>
<td>153.58(5)</td>
</tr>
<tr>
<td>$R_w$ (%)</td>
<td>1.78</td>
<td>15.7</td>
<td>16.2</td>
<td>12.6</td>
</tr>
</tbody>
</table>
Figure 6.5. A comparison of the CaTaO$_2$N PDF fits to the first few Å of real space data using (a) the average structure model and (b) the model with anion positions refined and thus increased octahedral tilting. Black circles correspond to the experimental PDF and the fits are given as orange and cyan lines through the data. The difference curves lie below in black. Ta-O/N bond distances corresponding to each model are given to the right of the respective fits.
shapes well. $R_w$ for the refinement in (a) was 20.1 % and $R_w$ for the refinement in (b) was 12.6 %. The distinct Ta-O/N bond distances corresponding to each fit are shown at the right of the figure. In the $Pnma$ perovskite structure both the axial ($4c$) anion position and the equatorial ($8d$) anion positions can be refined. The movement of these anion positions had a significant impact on the quality of fit and the increased tilting and bond distortion observed. The quality of the low-$r$ fit for CaTaO$_2$N reflects the flexibility of the lower symmetry model employed, and is not necessarily an indication of less local distortion compared with SrTaO$_2$N.

To model the discrepancy between observed local structure and that of the $I4/mcm$ model in SrTaO$_2$N, we considered several variations of the perovskite structure incorporating displacements of Ta, cis and trans bond alternation, and increased octahedral tilting.

The construction of suitable supercells began with ordering anion positions on the $I4/mcm$ lattice and then applying Ta displacements in specific directions. The crystallographic descriptions of these structures were generated by explicitly inputting atoms into the program Isotropy.[144] As discussed in the previous chapter, the models considered can be divided using several general classifications. Cis models are those where the 2 N on corners of the TaO$_4$N$_2$ octahedra share a common edge and trans models are those where the 2 N
Figure 6.6. The local models used in the PDF analysis of SrTaO$_2$N: Unit cells are delineated in black, Ta octahedra are shown in blue, Sr ions are grey, small blue spheres represent N and small orange spheres represent O. The top half of the figure shows an $I4cm$ polar trans model of SrTaO$_2$N down [001] at left and down [010] at right. In the bottom half of the figure an antipolar cis structure in $Ima2$ is displayed. The [001] views at left display the tilting schemes in common with the average structure $I4/mcm$ model. Displacements have been exaggerated in the figures for clarity. Coordinates for these models are given in Table 6.5.
occupy positions on either side of an octahedron, forming near linear N-Ta-N bonds. These two configurations were displayed in Figure 5.2. ‘Polar’ models are those that have net Ta displacements and ‘antipolar’ models describe those where the displacement of Ta ions cancel out.

A number of trans polar, trans antipolar and cis antipolar models were considered in the analysis of the local structure of SrTaO$_2$N. As before, larger mixed models, such as those containing cis and trans, or variations of TaO$_{6-x}$N$_x$ with $x=0,1,2,3$, calculated by Fang et. al contain too many atoms for the kind of PDF analysis used here and were not considered. Two of the most illustrative models are presented in Figure 6.6. The top half of the figure shows an $I4cm$ polar trans model of SrTaO$_2$N down [001] at left and down [010] at right. The [001] view conveys the tilting scheme held common with the average structure model displayed in Figure 6.1. The [010] view at right displays Ta displacements in the $+z$ direction. The $I4cm$ model therefore has the classification $a_0^0a_0^0c_+^+$ in modified Glazer notation. In the bottom half of the figure an antipolar cis structure in $Ima2$ is displayed. The [001] view at left again displays the tilting scheme common with the average structure $I4/mcm$ model. The view at [100] on the right more clearly reveals the cis ordering of the N ions. Ta atoms are seen to move in the $y$ and $-y$ directions, towards N containing edges of octahedra, in both views. Thus adjacent octahedra have Ta
Table 6.5. Starting structures corresponding to the PDF models used in the SrTaO$_2$N analysis.

(a) $I4cm$, polar $trans$

$a = 5.695 \text{ Å}, c = 8.069 \text{ Å}$

<table>
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<tr>
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<th>$y$</th>
<th>$z$</th>
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<td>0.75</td>
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<td>Ta</td>
<td>$2a$</td>
<td>0</td>
<td>0</td>
<td>0.98</td>
</tr>
<tr>
<td>N</td>
<td>$2a$</td>
<td>0</td>
<td>0</td>
<td>0.75</td>
</tr>
<tr>
<td>O</td>
<td>$4c$</td>
<td>0.27</td>
<td>0.77</td>
<td>0</td>
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</tbody>
</table>

(b) $Ima2$, antipolar $cis$

$a=8.069 \text{ Å}, b=5.695 \text{ Å}$

<table>
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<tr>
<th>atom</th>
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<th>$y$</th>
<th>$z$</th>
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</thead>
<tbody>
<tr>
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<td>$2a$</td>
<td>0.25</td>
<td>0.5</td>
<td>0.25</td>
</tr>
<tr>
<td>Ta</td>
<td>$2b$</td>
<td>0.25</td>
<td>0.27</td>
<td>0.98</td>
</tr>
<tr>
<td>N</td>
<td>$2b$</td>
<td>0.75</td>
<td>0.23</td>
<td>0.02</td>
</tr>
<tr>
<td>O</td>
<td>$2b$</td>
<td>0</td>
<td>0</td>
<td>0.75</td>
</tr>
<tr>
<td>O</td>
<td>$2b$</td>
<td>0</td>
<td>0</td>
<td>0.75</td>
</tr>
</tbody>
</table>
Table 6.6. Ta-O and Ta-N bond lengths and goodness of fit parameters over 4.5 Å PDF refinement for the local SrTaO$_2$N models tried in the current study.

<table>
<thead>
<tr>
<th>Isomeric config.</th>
<th>$I4/mcm$</th>
<th>$I4cm$</th>
<th>$Ima2$</th>
<th>$Ima2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{Ta-O}$ (Å)</td>
<td>(fixed)</td>
<td>(4×) 2.03(2)</td>
<td>(fixed)</td>
<td>(1×)2.0(1)</td>
</tr>
<tr>
<td>$d_{Ta-N}$ (Å)</td>
<td>(2×) 2.023</td>
<td>(1×) 1.95(8)</td>
<td>(1×) 2.13(8)</td>
<td></td>
</tr>
<tr>
<td>$R_w$ (%)</td>
<td>17.9</td>
<td>16.8</td>
<td>15.4</td>
<td>12.7</td>
</tr>
</tbody>
</table>

that displace in opposite directions, analogous to the Pbmm model used in the analysis of the local structure of BaTaO$_2$N. The Ima2 model can be described with the modified Glazer notation $a_0^0 b_0^{+} b_0^{-}$. Crystallographic descriptions of the models are given in Table 6.5.

The models above were tried with and without Ta displacements (without Ta displacements the local $I4cm$ model is equivalent to the trans ordered $I4/mcm$ model). Ta did not move significantly from the center of octahedra in any of the refinements tried, and were thus fixed to their positions from the average structure analysis. Table 6.6 shows resulting Ta-O and Ta-N bond lengths and $R_w$ values from 4.5 Å PDF refinements using the local models de-
Figure 6.7. A comparison of the SrTaO$_2$N PDF fits to the first few Å of real space data using (a) the average structure $I4/mcm$ model with disordered anions, (b) the trans $I4cm$ model with anion positions refined and (c) the cis $Ima2$ model with anion positions refined. Black circles correspond to the experimental PDF and the fits are given as colored lines through the data. The difference curves lie below in black.
scribed. Recall the fit using the $I4/mcm$ model with disordered anions gave $R_w = 16.2\%$. When the anion positions were fixed to the values from this refinement and ordered anion arrangements were considered alone, the data revealed a clear preference. When the N are trans ordered (in the trans $I4/mcm$ model), the fit becomes worse than the disordered anion model: $R_w = 17.9\%$. Interestingly, the fit improves to 15.4\% when the N are cis ordered (in the $Ima2$ model with fixed positions). This finding agrees with the conclusion in Chapter 5 that local cis arrangements of N are preferred in the BaTaO$_2$N structure.

A further improved refinement ($R_w = 12.7\%$) is accomplished through movement of the anions in the $Ima2$ local structure. These results again support a local picture of increased disorder in TaO$_4$N$_2$ octahedra. Figure 6.7 displays the 3 fits with anion positions refined to 4.5 Å of $r$. There was very little difference found in the quality of fit over 10 Å PDF refinements among the models considered, suggesting only a very short-range correlation.

In the CaTaO$_2$N models, a local tendency for increased octahedral tilting was accommodated (mostly) through the movement of the equatorial (8d) position. While we found the $Pnma$ model was successful at capturing local distortion present in the low-$r$ correlations of CaTaO$_2$N (Figure 6.5, we were keen to explore the effects of bond alternation (cis and trans N arrangements) on the local structure as well. Four models were tried in the analysis of CaTaO$_2$N and
are shown in Figure 6.8. In the figure, (a) and (b) show trans models and (c) and (d) display cis models. All structures have been drawn using the Pnma unit cell, but models (b-d) can be described using the lower symmetry structures (b) P2₁/m, (c) Pmc2₁, and (d) Pna2₁. The crystallographic descriptions of these structures are given in Tables 6.7 and 6.8.

Table 6.9 gives the resulting atom-atom distances and angles for the local structure CaTaO₂N models tried. The same parameters were refined in all cases, differences arise from the distinct anion orderings. There was very little distinction in the quality of fit with respect to the use of trans or cis models in the analysis: the trans Pnma model gave R_w = 13.2 %, R_w for the trans P2₁/m model was 12.6 %, and the values for the two cis models fell in between. Unlike the BaTaO₂N and SrTaO₂N local structure results, none of the local structures described here model the data better than the average structure with disordered anions. (The average structure Pnma model with disordered anions gave R_w = 12.6 %.) The main conclusion provided by the analysis is that the refined atom-atom distances are the same regardless of the particular model used, and support the local observation of increased tilting (asymmetry) in the octahedra of CaTaO₂N.

It is worth noting the implications of describing a locally disordered structure in a crystallographic manner. The PDF contains information about all of
Figure 6.8. The local models used in the PDF analysis of CaTaO$_2$N. Structures (a) and (b) have N in *trans* configurations in the Ta octahedra and structures (c) and (d) have N with *cis* positions in Ta octahedra. All structures have been drawn using the *Pnma* unit cell, but models (b-d) can be described using the lower symmetry structures (b) *P2$_1$/m*, (c) *Pmc2$_1$*, and (d) *Pna2$_1$*. The crystallographic descriptions for these structures are given in Tables 6.7 and 6.8.
Table 6.7. *Trans* local structure models used in the CaTaO$_2$N PDF analysis.

(a) *Pnma, trans*

\[ a = 5.618 \text{ Å}, \ b = 7.892 \text{ Å}, \ c = 5.547 \text{ Å} \]

<table>
<thead>
<tr>
<th>atom</th>
<th>Wyck.</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>4c</td>
<td>0.53170</td>
<td>0.25</td>
<td>0.49440</td>
</tr>
<tr>
<td>Ta</td>
<td>4b</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>N</td>
<td>4c</td>
<td>0.9818</td>
<td>0.25</td>
<td>0.57560</td>
</tr>
<tr>
<td>O</td>
<td>8d</td>
<td>0.7915</td>
<td>0.0402</td>
<td>0.2092</td>
</tr>
</tbody>
</table>

(b) *P2$_1$/m, trans*

\[ a = 5.618 \text{ Å}, \ b = 7.892 \text{ Å}, \ c = 5.547 \text{ Å} \]

<table>
<thead>
<tr>
<th>atom</th>
<th>Wyck.</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>2e</td>
<td>0.03170</td>
<td>0.25</td>
<td>0.9944</td>
</tr>
<tr>
<td>Ca</td>
<td>2e</td>
<td>0.46830</td>
<td>0.75</td>
<td>0.4944</td>
</tr>
<tr>
<td>Ta</td>
<td>2b</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ta</td>
<td>2c</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
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<td>2e</td>
<td>0.4818</td>
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<tr>
<td>O</td>
<td>2e</td>
<td>0.9818</td>
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<tr>
<td>O</td>
<td>4f</td>
<td>0.29150</td>
<td>0.0402</td>
<td>0.7092</td>
</tr>
<tr>
<td>N</td>
<td>4f</td>
<td>0.02085</td>
<td>0.9598</td>
<td>0.2092</td>
</tr>
</tbody>
</table>
Table 6.8. Cis local structure models used in the CaTaO2N PDF analysis.

(c) \( Pmc2_1, cis \)

\[ a = 7.892 \, \text{Å}, \quad b = 5.547 \, \text{Å}, \quad c = 5.618 \, \text{Å} \]

<table>
<thead>
<tr>
<th>atom</th>
<th>Wyck.</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
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</thead>
<tbody>
<tr>
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<td>0.74440</td>
<td>0.0317</td>
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<td>0.46830</td>
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<tr>
<td>Ta</td>
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<td>0.75</td>
<td>0.5</td>
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<tr>
<td>O</td>
<td>2\textit{b}</td>
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<tr>
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<td>0.01820</td>
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<tr>
<td>O</td>
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<td>0.4592</td>
<td>0.2915</td>
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<tr>
<td>N</td>
<td>4\textit{c}</td>
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<td>0.20850</td>
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</tbody>
</table>

(d) \( Pna2_1, cis \)

\[ a = 5.618 \, \text{Å}, \quad b = 5.547 \, \text{Å}, \quad c = 7.892 \, \text{Å} \]

<table>
<thead>
<tr>
<th>atom</th>
<th>Wyck.</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
</tr>
</thead>
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<td>0.25</td>
</tr>
<tr>
<td>Ta</td>
<td>4\textit{a}</td>
<td>0.5</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>O</td>
<td>4\textit{a}</td>
<td>0.51820</td>
<td>0.57560</td>
<td>0.25</td>
</tr>
<tr>
<td>O</td>
<td>4\textit{a}</td>
<td>0.70850</td>
<td>0.2092</td>
<td>0.0402</td>
</tr>
<tr>
<td>N</td>
<td>4\textit{a}</td>
<td>0.79150</td>
<td>0.70920</td>
<td>0.95980</td>
</tr>
</tbody>
</table>

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Table 6.9. Ta-O and Ta-N bond lengths and angles from 4.5 Å PDF refinements of CaTaO$_2$N neutron data. (The same parameters were refined in all four cases, differences arise from the anion ordering.) Note: none of the refinements show improvement over the disordered model (average structure) result, which gave $R_w = 12.6\%$.

<table>
<thead>
<tr>
<th>isomeric config.</th>
<th>$Pnma$</th>
<th>$P2_1/m$</th>
<th>$Pmc2_1$</th>
<th>$Pna2_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{Ta-X}$, Å</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(2\times)1.93(2)$</td>
<td>$(2\times)1.94(2)$</td>
<td>$(2\times)1.94(2)$</td>
<td>$(2\times)1.94(2)$</td>
<td></td>
</tr>
<tr>
<td>$(2\times)2.016(4)$</td>
<td>$(2\times)2.027(4)$</td>
<td>$(2\times)2.026(4)$</td>
<td>$(2\times)2.027(4)$</td>
<td></td>
</tr>
<tr>
<td>$(2\times)2.14(2)$</td>
<td>$(2\times)2.12(2)$</td>
<td>$(2\times)2.12(2)$</td>
<td>$(2\times)2.12(2)$</td>
<td></td>
</tr>
<tr>
<td>$\angle_{Ta-X-Ta}$ (°)</td>
<td>156.38(5)</td>
<td>153.41(5)</td>
<td>153.65(5)</td>
<td>153.39(6)</td>
</tr>
<tr>
<td></td>
<td>151.4(2)</td>
<td>153.3(3)</td>
<td>153.2(3)</td>
<td>153.3(3)</td>
</tr>
<tr>
<td>$R_w$ (4.5 Å), %</td>
<td>13.2</td>
<td>12.6</td>
<td>12.8</td>
<td>12.9</td>
</tr>
</tbody>
</table>
the pairs of atoms in our sample, yet any superstructure beyond the size of a few perovskite unit cells is too large for PDF analysis. In a study of this kind, we provide possible solutions, test them, and draw conclusions from comparing the results. We do not expect to find an absolute answer, rather we look to find the crystallographic description that best captures our observed local correlations, recognizing that the structure is, on average, disordered. Density functional theory calculations provide a way to investigate the properties of the compounds supposing they are ordered.

6.4 Density Functional Theory Calculations

Computational and experimental studies related to local O and N ordering have so far focused on BaTaO$_2$N. It is advantageous to study these short range structures computationally as calculations can predict which configurations are energetically favorable.

Density functional theory calculations were performed by Matthew Stoltzfus of the Woodward group at Ohio State University using the Cambridge Serial Total Energy Package (CASTEP) as embodied in Accelrys Materials Studio.[146] The norm-conserving non-local pseudo-potentials are generated using the Kerker scheme with a kinetic energy cutoff of 400 eV. A convergence
Table 6.10. Bond lengths and relative energies per formula unit from DFT calculations of three different SrTaO$_2$N structures. (Calculations provided by Matthew Stoltzfus.)

<table>
<thead>
<tr>
<th></th>
<th>$P4mm$</th>
<th>$I4/mcm$</th>
<th>$Pbmm$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{Ta-O}$ (Å)</td>
<td>$(4 \times), 2.037$</td>
<td>$(4 \times), 2.059$</td>
<td>$(2 \times), 2.158$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$(2 \times), 2.036$</td>
</tr>
<tr>
<td>$d_{Ta-N}$ (Å)</td>
<td>$(1 \times), 2.652$</td>
<td>$(2 \times), 2.071$</td>
<td>$(2 \times), 1.993$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$(1 \times), 1.877$</td>
</tr>
<tr>
<td>$\Delta E$ (meV)</td>
<td>$0$</td>
<td>$-85$</td>
<td>$-550$</td>
</tr>
</tbody>
</table>

criterion of 0.00002 eV was applied for the energy charge per atom, 0.001 Å for the root-mean-square displacement, and 0.05 eV Å$^{-1}$ for the root-mean-square residual force on movable atoms. Electron exchange and correlation were described using the Perdew-Wang generalized gradient approximation (GGA).[147] Geometry optimization utilized the Broyden-Fletcher-Goldfarb-Shanno Scheme[148] in a manner which permitted both the lattice parameters and atomic coordinates to be optimized.

DFT calculations on SrTaO$_2$N employ three different ordered structures including the experimentally reported one in the space group $I4/mcm$. Table 6.10 presents bond lengths from the DFT calculations with corresponding relative energies for three SrTaO$_2$N structures: trans $P4mm$, the reported trans $I4/mcm$ structure, and the cis $Pbmm$ structure which for BaTaO$_2$N is calculated.
Table 6.11. Bond lengths and relative energies per formula unit from DFT calculations of three different CaTaO$_2$N structures. (Calculations provided by Matthew Stoltzfus.)

<table>
<thead>
<tr>
<th></th>
<th>P4mm</th>
<th>Pnma</th>
<th>Pbmm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{Ta-O}$ (Å)</td>
<td>(4×) 2.03</td>
<td>(2×) 2.06</td>
<td>(2×) 2.02</td>
</tr>
<tr>
<td></td>
<td>2×) 2.06</td>
<td>(2×) 2.17</td>
<td></td>
</tr>
<tr>
<td>$d_{Ta-N}$ (Å)</td>
<td>(1×) 3.06</td>
<td>(2×) 2.06</td>
<td>(2×) 1.97</td>
</tr>
<tr>
<td></td>
<td>(1×) 1.86</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta E$ (meV)</td>
<td>−360</td>
<td>−250</td>
<td>0</td>
</tr>
</tbody>
</table>

to be most stable. For SrTaO$_2$N as well, it is this Pbmm structure, rather than the experimentally reported $I4/mcm$ trans structure that is found by DFT to be most stable. The preference for cis ordering agrees with our local structure observations for both cases. Both the $P4mm$ and the $I4/mcm$ structure are trans and the former allows short-long N-Ta-N bond alternation, while the latter allows tilting of the TaO$_4$N$_2$ polyhedra. Similar to the theoretical result observed for BaTaO$_2$N in Chapter 5, the SrTaO$_2$N $P4mm$ structure has an unusually large c parameter resulting in nearly square pyramidal Ta. Recent insights on $d^0$ oxide perovskites suggest that when a natural tendency to tilting is frustrated, strong tetragonal off-centering distortions can ensue.[123]

DFT calculations for CaTaO$_2$N were performed on three different ordered structures. Table 6.11 presents bond lengths from the DFT calculations with
corresponding relative energies for trans $P4mm$, trans $Pnma$ and cis $Pbmm$ structures. As seen in the BaTaO$_2$N and SrTaO$_2$N cases, the CaTaO$_2$N $P4mm$ structure has an unusually large $c$ parameter: here it is enhanced even further. Ignoring this unrealistic optimization, it is the trans ordered $Pnma$ that has the lowest energy for CaTaO$_2$N, supporting the importance of TaO$_4$N$_2$ tilting in the structure observed experimentally. Interestingly, the theoretical Ta-O and Ta-N distances in $Pnma$ are found to be equivalent from DFT. This contrasts with our experimental results, which support a high degree of local asymmetry in the TaO$_4$N$_2$ octahedra. In contrast to what is found in BaTaO$_2$N and SrTaO$_2$N, $Pbmm$ is the least stable structure calculated for CaTaO$_2$N. However, it is impossible to draw strong conclusions from the set of calculations presented here. The models tried contain variation in octahedral tilting, cation off-centering and O/N bond alternation, and it is challenging to separate these effects. Calculations for models distinguished only by differences in anion ordering, such as those presented in Figure 6.8, may provide more insight on the specific stabilization effects of anion ordering, and should be investigated in the future.
6.5 Summary

The analysis of total neutron scattering data for the perovskite oxynitrides SrTaO$_2$N and CaTaO$_2$N revealed several structural features that are likely important for the distinct properties of the materials. The average structure results support mixed occupancy of O and N in anion positions for both compounds and the local structure results support increased octahedral tilting and asymmetric TaO$_4$N$_2$ polyhedra in both cases. At low-$r$ SrTaO$_2$N data were best described with a model incorporating cis N in octahedra. DFT calculations support the stabilization effects of cis ordering in the compound. In our analysis of CaTaO$_2$N, the effects of cis and trans bond alternation were less clear, and perhaps support a disordered structure with respect to O and N anions. A more thorough theoretical study could be pursued to understand the effects of various perovskite structure features on the stabilization of the materials.

Table 6.12 gives the Goldschmidt tolerance factors for the family of structures studied in Chapters 5 and 6 and summarizes our findings. The relationship between the Goldschmidt tolerance factor and octahedral tilting is well established in perovskites and oxynitride perovskites. The tolerance factor of 1.043 for BaTaO$_2$N supports the likelihood of Ta off-centering in the structure, and this is what we observe locally. The tolerance factor of 0.985 for SrTaO$_2$N suggests octahedral tilting plays a larger role in the overall energy compared
Table 6.12. Calculated Goldschmidt tolerance factors for the three compounds analyzed in this study along with structural features observed.

<table>
<thead>
<tr>
<th>compound</th>
<th>$\tau$</th>
<th>structural features</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTaO$_2$N</td>
<td>1.043</td>
<td>cubic average structure</td>
</tr>
<tr>
<td></td>
<td></td>
<td>local off-centering of Ta</td>
</tr>
<tr>
<td></td>
<td></td>
<td>local $cis$ ordering of N</td>
</tr>
<tr>
<td>SrTaO$_2$N</td>
<td>0.985</td>
<td>tetragonal average structure</td>
</tr>
<tr>
<td></td>
<td></td>
<td>increased local octahedral tilting</td>
</tr>
<tr>
<td></td>
<td></td>
<td>possible local $cis$ ordering of N</td>
</tr>
<tr>
<td>CaTaO$_2$N</td>
<td>0.937</td>
<td>orthorhombic average structure</td>
</tr>
<tr>
<td></td>
<td></td>
<td>increased local octahedral tilting</td>
</tr>
<tr>
<td></td>
<td></td>
<td>no evidence for anion ordering</td>
</tr>
</tbody>
</table>

to BaTaO$_2$N, and the calculations and experiments verify this. CaTaO$_2$N has a tolerance factor of 0.937, indicating an octahedral tilting distortion is certain to be present, which is again verified by experiment and in the calculations. The structures involving tilting do not require a large Ta cation displacement, a notion supported by our results.
Bibliography


cristaux (cas du silicium, du quartz, et des pérovskites ferroélectriques.


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[131] E. Günther, R. Hagenmayer, and M. Jansen. Structural investigations


