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# The incommensurate modulation of tetragonal tungsten bronze quantified by high resolution 4D STEM

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## Abstract

Many members of the tetragonal tungsten bronze (TTB) family of oxides display an incommensurate periodic lattice distortion, the nature of which has been the subject of some controversy. Here we present a study of this structural modulation in the relaxor ferroelectric  $\text{Ba}_5\text{SmSn}_3\text{Nb}_7\text{O}_{30}$  (BSSN) by quantitative scanning transmission electron microscopy (STEM). We characterize the modulation in BSSN by employing a fast, pixelated direct electron detector to perform high resolution phase contrast STEM imaging of the crystalline lattice. By quantitatively analyzing the images, we visualize the atomic structural correlations present in the material on both the cation and anion sublattices. This analysis reveals the incommensurate structure to have an octahedral tilting pattern and cooperative A2 site cation displacements, analogous to an *Ama2* commensurate cell. Finally, we show that the modulation is composed of a structural motif with a period of  $3 \times d_{1\bar{1}0}$  and modified by discommensurations, likely arise from frustrated octahedral tilting in the odd-valued periodicity.

## 1. Introduction

The tetragonal tungsten bronze (TTB) structure comprises a large family of complex oxides which has been shown to exhibit structural modulations across many compositions. The TTB unit cell is formed of corner shared oxygen octahedra that are typically occupied by small transition metal ions. The octahedra are linked together to form square and pentagonal cages, the A1 and A2 sites, which host the larger cations (A small triangular cage is also formed but is most often unoccupied). The basic TTB structure is highly amenable to doping or alloying, as evidenced by the wide range of compositions found in literature. Its chemical flexibility makes TTBs an attractive system in which to optimize functional properties, such as its permittivity, through compositional engineering. Recent work has demonstrated that alloying or doping schemes can enhance the recoverable energy densities and high breakdown fields of relaxor-type TTBs, achieving a useful combination of properties for energy storage capacitor applications.[1–4] It has been empirically shown that TTBs with classical ferroelectric behavior tend to possess commensurate modulations while relaxor-type ferroelectrics are generally incommensurate, the latter due, at least in part, to chemical disorder on some or all of the cation sublattices.[5,6] Incommensurate TTBs have been widely researched in the structure community, with previous work proposing conflicting models of the modulation based on X-ray and electron diffraction experiments[7–10] as well as theoretical modeling[11,12]. Reports, however, offer conflicting models of the octahedral tilting patterns, and disagree on the long range coherence of the modulation (harmonic versus slab intergrowth) as well as its symmetry (tetragonal versus orthorhombic).[7–9,13,14] Only recently, has a complete characterization of the incommensurate modulation of the oxygen sublattice been achieved by Krayzman and coworkers.[13]

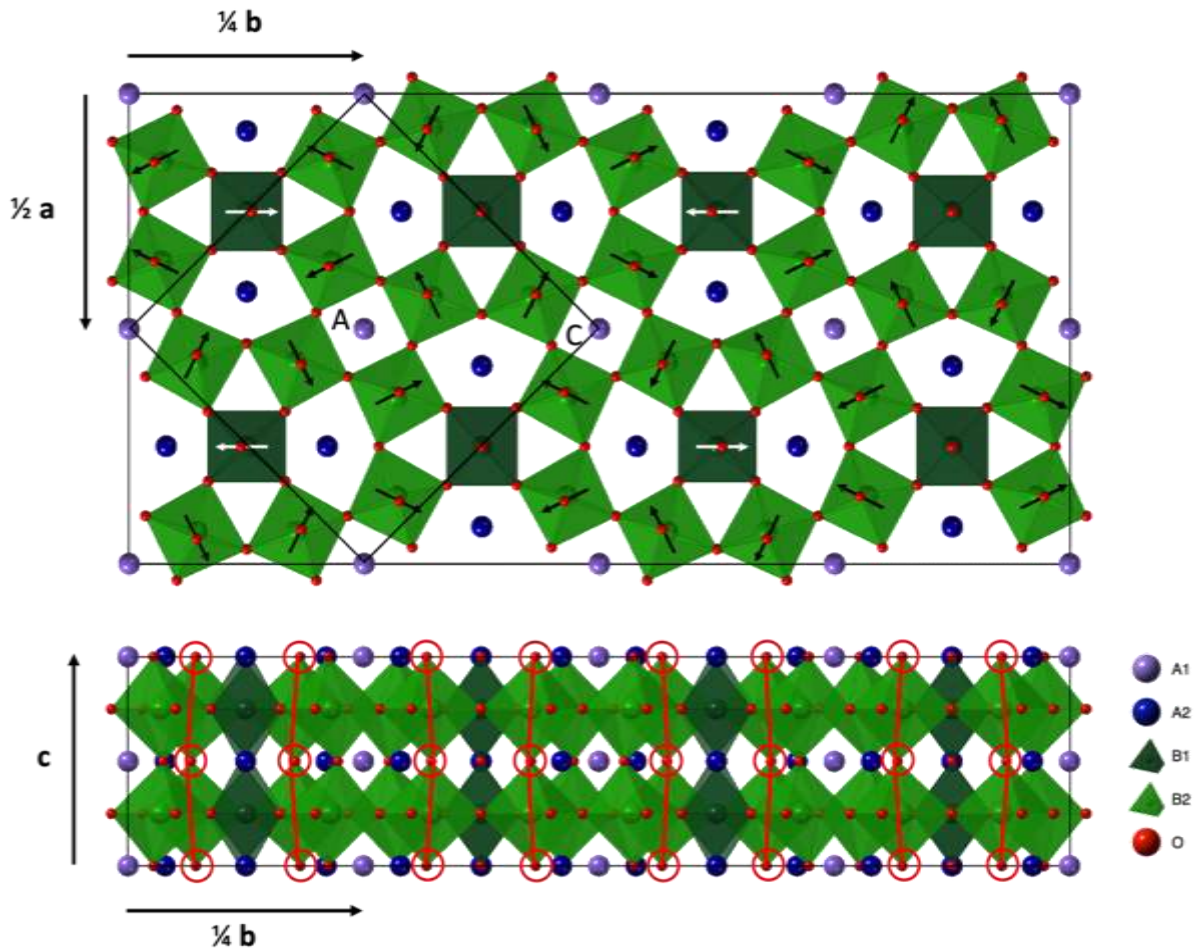
Their study incorporated several types of scattering data gathered on  $\text{Sr}_{0.61}\text{Ba}_{0.39}\text{Nb}_2\text{O}_6$ , a composition with 20% vacancies among the A-site cations (sometimes called an “unfilled” TTB). A large atomic model was refined to the data using a random Monte Carlo approach with several constraints (supported by experimental evidence) to enforce the presence and domain size of two orthorhombic orientational modulation variants. From the resulting model, the authors extracted two basic structural distortion blocks (of lengths  $3 \times$  and  $4 \times d_{1\bar{1}0}$  spacings, approximately 26.6 and 35.5 nm, respectively), which, when present together, reproduce the full set of incommensurate reflections from single crystal X-ray diffraction. While the method and findings are both reasonable and reliable, they measure the structure indirectly via the Monte Carlo generated model. Here we examine the modulation in the incommensurate TTB,  $\text{Ba}_5\text{SmSn}_3\text{Nb}_7\text{O}_{30}$  (BSSN), directly probing the atomic structure of both the cation and anion sublattices through quantitative analysis of differential phase contrast (DPC) scanning transmission electron microscope (STEM) images.

BSSN is in the paraelectric state at room temperature, however, it exhibits relaxor behavior, with a  $T_m$  of approximately 175 K and a maximum relative permittivity of 220 at 1kHz.[15] In previous work, we have shown that: 1) BSSN has a modulation vector of  $\mathbf{q} = 0.314(\mathbf{a}^* \pm \mathbf{b}^*) + 0.5\mathbf{c}^*$ ; 2) of the cation sublattices, only the A2 sublattice exhibits the modulative displacements and 3) short-range polar correlations are present on the B1 sublattice at room temperature, consistent with the diffuse relaxor-to-paraelectric transition.[14] To uncover the nature of the modulation in BSSN, we apply the vector pair correlation function (vPCF) [14] to quantitatively visualize the pattern of structural distortions, despite a high degree of disorder. In doing so, we extend our previous work

to include the modulation of the oxygen octahedra and the cooperative character of the cation displacements. We compare the resulting vPCFs to two competing models representing commensurate approximations of the octahedral tilting, explained in detail below.

**1.1. *Amm2 model*:** Bursill and Lin proposed an “intergrowth” model from their structural refinement of the incommensurate modulation in unfilled  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Nb}_2\text{O}_6$ .<sup>[9]</sup> Their model consists of blocks of two different orthorhombic unit cells. Both block types contain distortions of the B2 octahedra (comprising the square cage around the A1 site) characterized by displacements of the apical oxygen atoms in clockwise (C) and counterclockwise (A) rotations about their near neighbor A1 sites. The ordering of the C/A rotations differs between the two cells with *Amm2* having ...CAAC... ordering and *Cmm2* having ...AC... ordering. While the C/A rotation ordering is different for the two

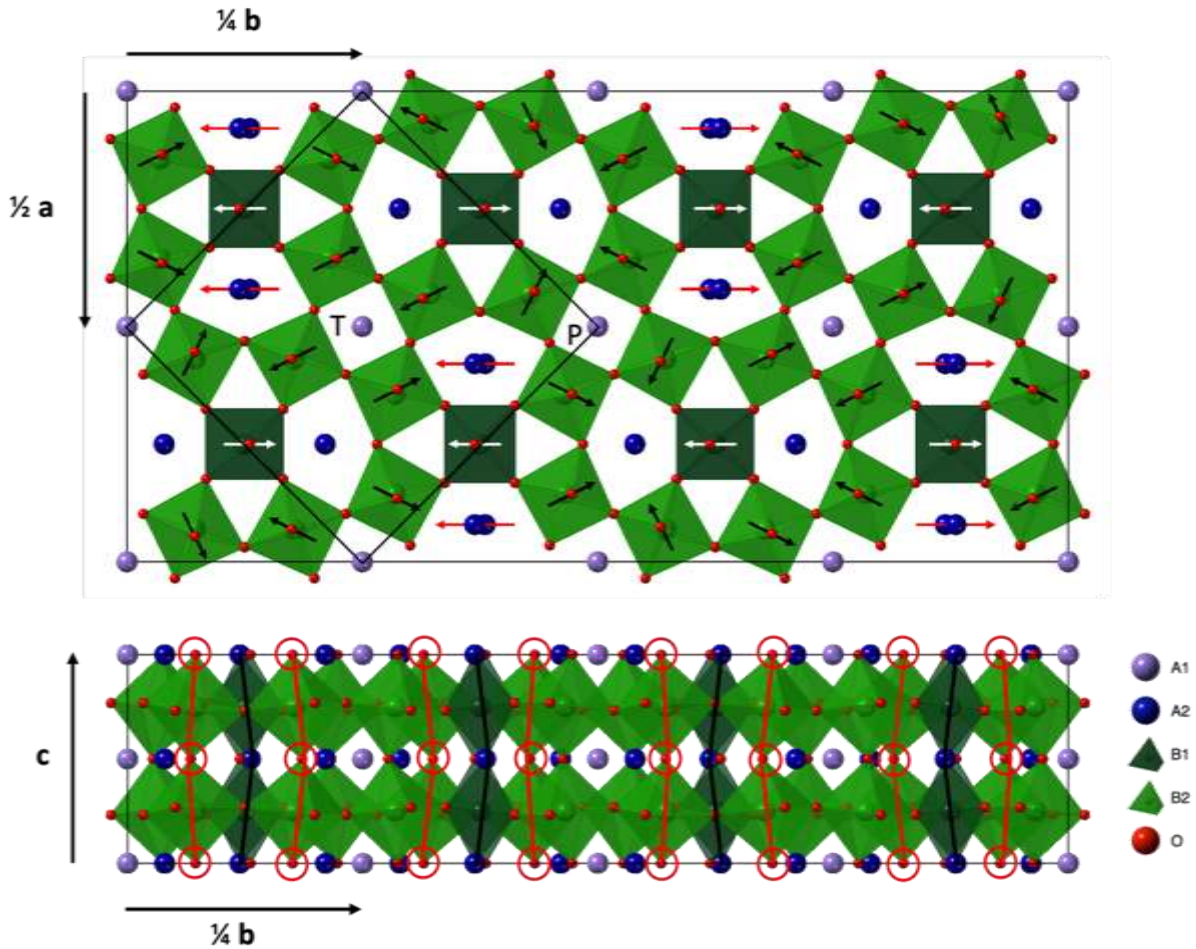
cell types, both result in the same types of projected displacements when viewed along the  $[110]_{\text{TTB}}$  zone axis (which corresponds to the  $[100]$  zone axis for the unit cells of both blocks). The Amm2 structure is illustrated in **Figure 1**. To understand the observations expected for this model in our study, we focus on the pairs of oxygen columns visible by DPC STEM imaging, illustrated in **Figure 1** (circled in the lower



**Figure 1:** Amm2 commensurate model of the incommensurate modulation shown along the  $[001]$  zone axis (top) and  $[100]$  zone axis (bottom). The black square in the top view indicates the basic TTB cell relative to the Ama2 cell. Arrows in  $[001]$  projection indicate the displacement of the respective atomic positions at the top/bottom plane of the cell; atoms at the mid-plane along  $[001]$  have the opposite displacement. In the  $[100]$  projection, red circles indicate the oxygen positions observable in DPC STEM images and the heavy red lines the tilting of the octahedra.

panel). These oxygen columns occupy the apical positions of the B2 octahedra. Regardless of the ordering of C and A rotations, the projected structural distortions produced by this type of octahedral tilting pattern result in pairs of oxygen columns on either side of any A1 column having opposite displacement directions (i.e. their displacements are anticorrelated). For simplicity, we will consider the  $Amm2$  cell to represent this type of tilting pattern.

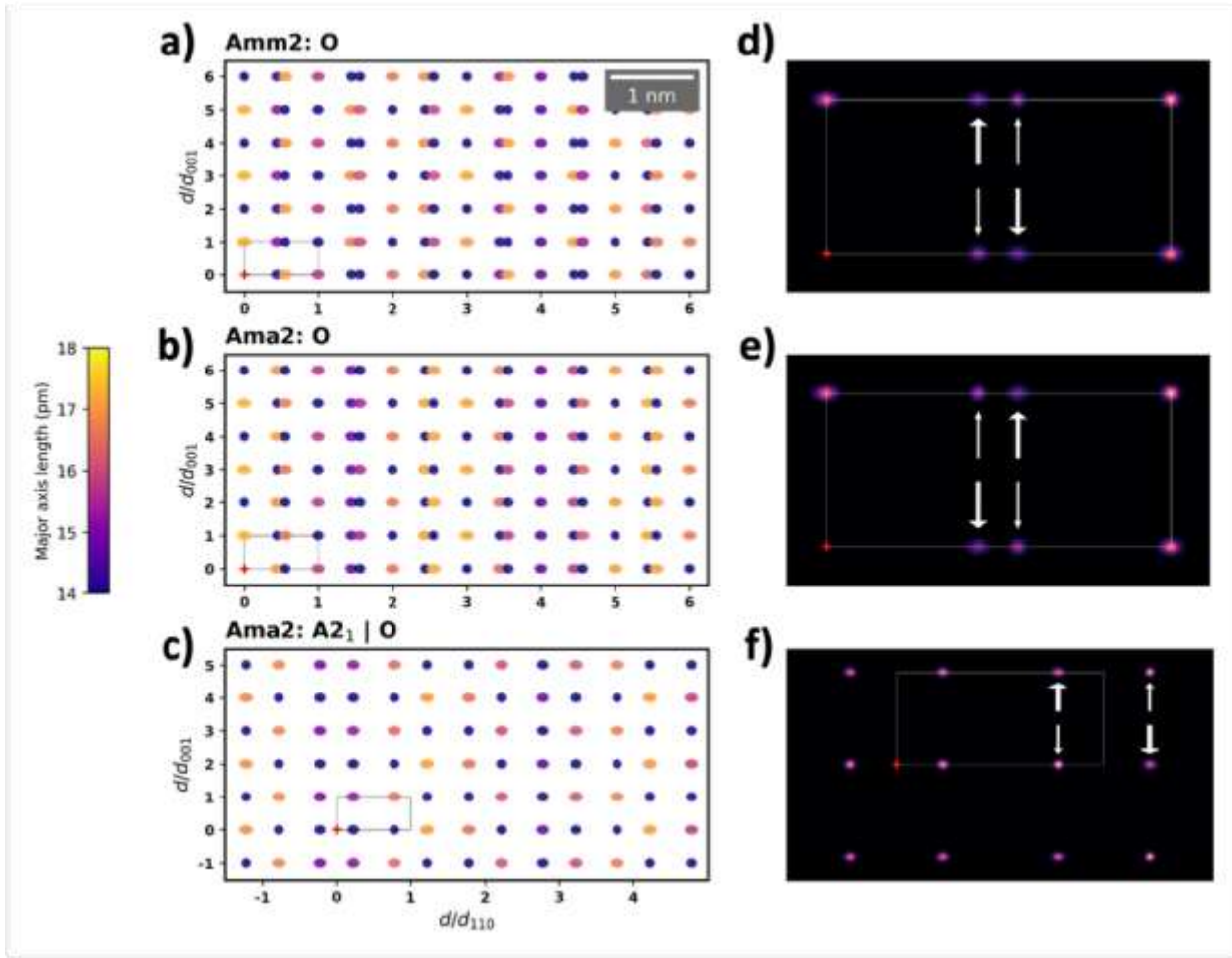
**1.2. Ama2 model:** A second model approximating the incommensurate tilting modulation is the Ama2 unit cell. It has the same orientation relationship to the basic tetragonal cell as that of the Amm2 model discussed above. The Ama2 model was first introduced by Labbe and co-workers[7] as a structural refinement for the nearly commensurate  $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$  (BNN) and included as one of the two structural blocks inferred for SBN by Krayzman, et al.[13] Significantly, this model represents a tilt configuration compatible with only rigid-body rotations of the octahedra in the TTB



**Figure 2:** Ama2 commensurate model of the incommensurate modulation shown along the [001] zone axis (top) and [100] zone axis (bottom). The black square in the top view indicates the basic TTB cell relative to the Ama2 cell. Red circles and heavy red lines carry the same meaning as **Figure 1**. Additionally, heavy black lines highlight the shifts of the  $\text{A2}_1$  positions.

structure, requiring no octahedral distortions which are likely to be energetically unfavorable.[6,13] The model, as well, can be described by the tilting patterns around the A1 site, in a similar manner to the Amm2 model but with different tilting schemes. In contrast to the C and A rotational tilt pattern of the Amm2 model, A1 nearest-neighbor octahedra in the Ama2 cell have either a “pinched” or a “transverse” scheme, as shown in **Figure 2**. Viewed along the [100] zone axis, the “pinched” tilts produce anti-correlated displacements of the apical B2 oxygen column pairs on either side of the A1 sites. The “transverse” arrangement gives correlated displacements in projection. Additionally, this structure solution for BNN indicates displacements on the half of the A2 sites with their long pentagonal axis parallel to the long axis of the unit cell.[7] The Ama2 model used here is based on the average BSSN structure,[15] with displacements like those found by Labbe and coworkers.

Considering the two models as viewed along their [100] zone axes, the projected displacements in each are characterized by unique correlations that can be used to distinguish them. From experimental STEM data, we can quantify the observed correlations by vPCFs. To understand how the two models are expected to manifest in the vPCFs, we first generate incommensurate lattice models for both structures, adjusting the modulation vector of the commensurate models to match that reported



**Figure 3:** Model vPCFs representing those expected from STEM imaging along the  $[110]_{\text{TTB}}$  zone axis for the two octahedral tilting models. **a) – c)** show the equivalent ellipse measured for each peak. **d) – f)** are the intensities of the corresponding vPCF for the peaks near the origin. Wide and narrow arrows point to wider and narrower peak distributions in each vPCF. The red “+” indicates the origin of the vPCFs and the black or white boxes indicate the basic TTB cell with dimensions  $\sim 8.9\text{\AA} \times 3.9\text{\AA}$ , corresponding to the  $d_{110}$  and  $d_{001}$  plane spacings, respectively.

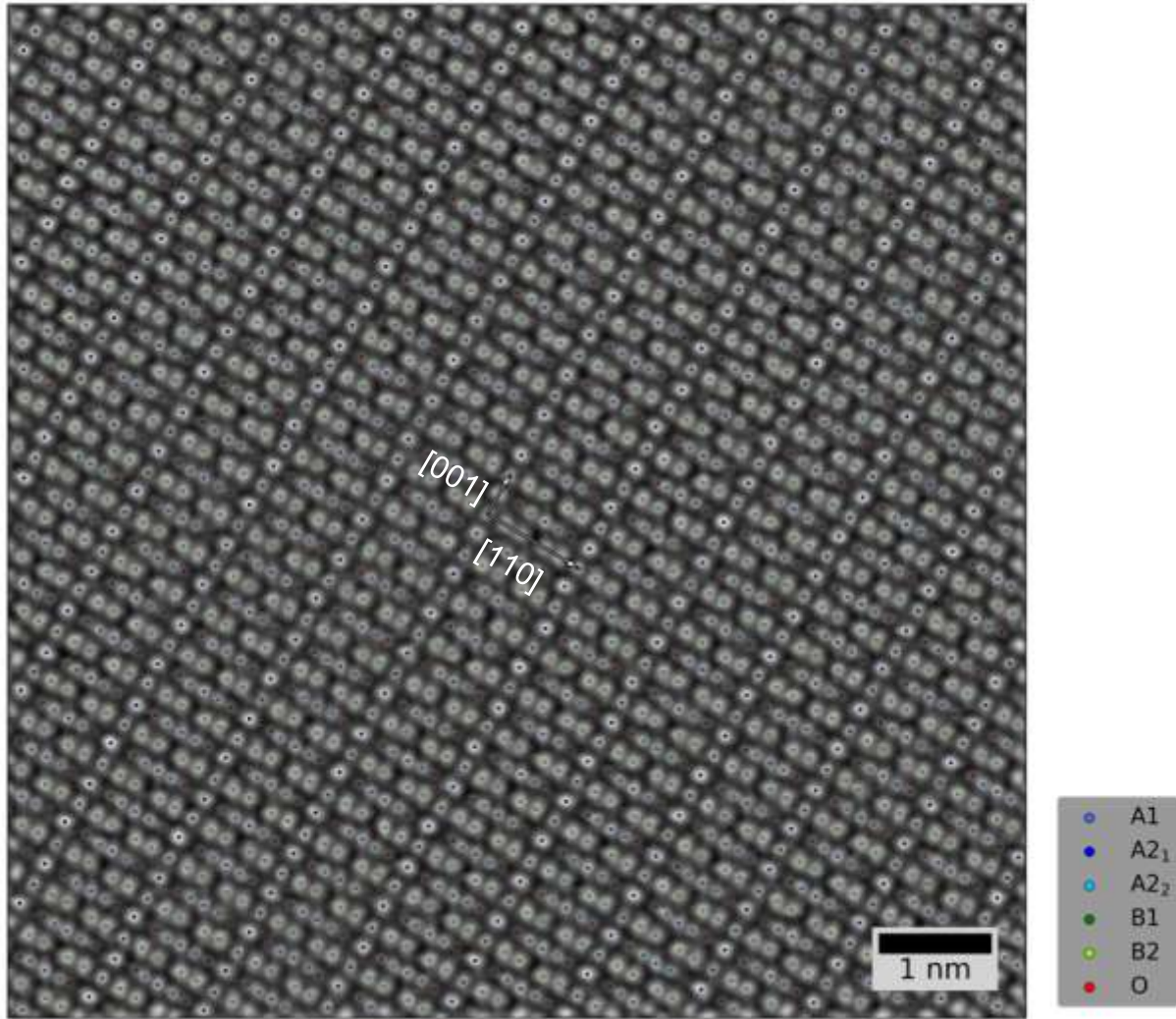
previously for BSSN.[14] The process used to create the model vPCFs for the two structures is described in the **Supplementary Information** and the final model vPCFs are shown in **Figure 3**, illustrating the peak width patterns expected for the two models. Note the alternating wide/narrow widths of the pairs of peaks near  $0.5d_{110}$  in the O | O vPCFs, as indicated by the white arrows in **Figure 3d-e**. The pattern of distribution widths are almost identically opposite between the two models. Additionally, the O | A2<sub>1</sub> partial vPCF from the Ama2 model has a specific ordering of wide and narrow peaks (**Figure 3c, f**).

## 2. Experimental and data analysis methods

TEM samples are prepared from ceramic pellets of BSSN. The ceramic processing method was reported previously.[15] Samples are cut from the pellets on a low-speed diamond saw, mechanically wedge polished (Allied Multiprep) using diamond lapping films down to  $1\mu\text{m}$  and final polished with a  $0.01\mu\text{m}$  silica lapping film. Finally, the wedge samples are ion milled (Gatan PIPSII) with a final beam voltage of 0.2 kV to remove surface damage.

Four dimensional (4D) STEM datasets are collected with a pixelated direct-electron detector (the “4D Camera”) installed on the TEAM 0.5 microscope at the National Center for Electron Microscopy, Molecular Foundry, Lawrence Berkeley National Laboratory.[16] In the 4D STEM technique, a 2-dimensional (2D) electron scattering pattern is collected at each pixel in a 2D raster scan of the STEM probe, yielding a 4D dataset. The increased information from such a dataset enables higher quality differential phase contrast images as compared to standard quadrant detectors. The 4D Camera operates at a frame rate of 87kHz, equating to a dwell time of  $11\mu\text{s}$  per probe

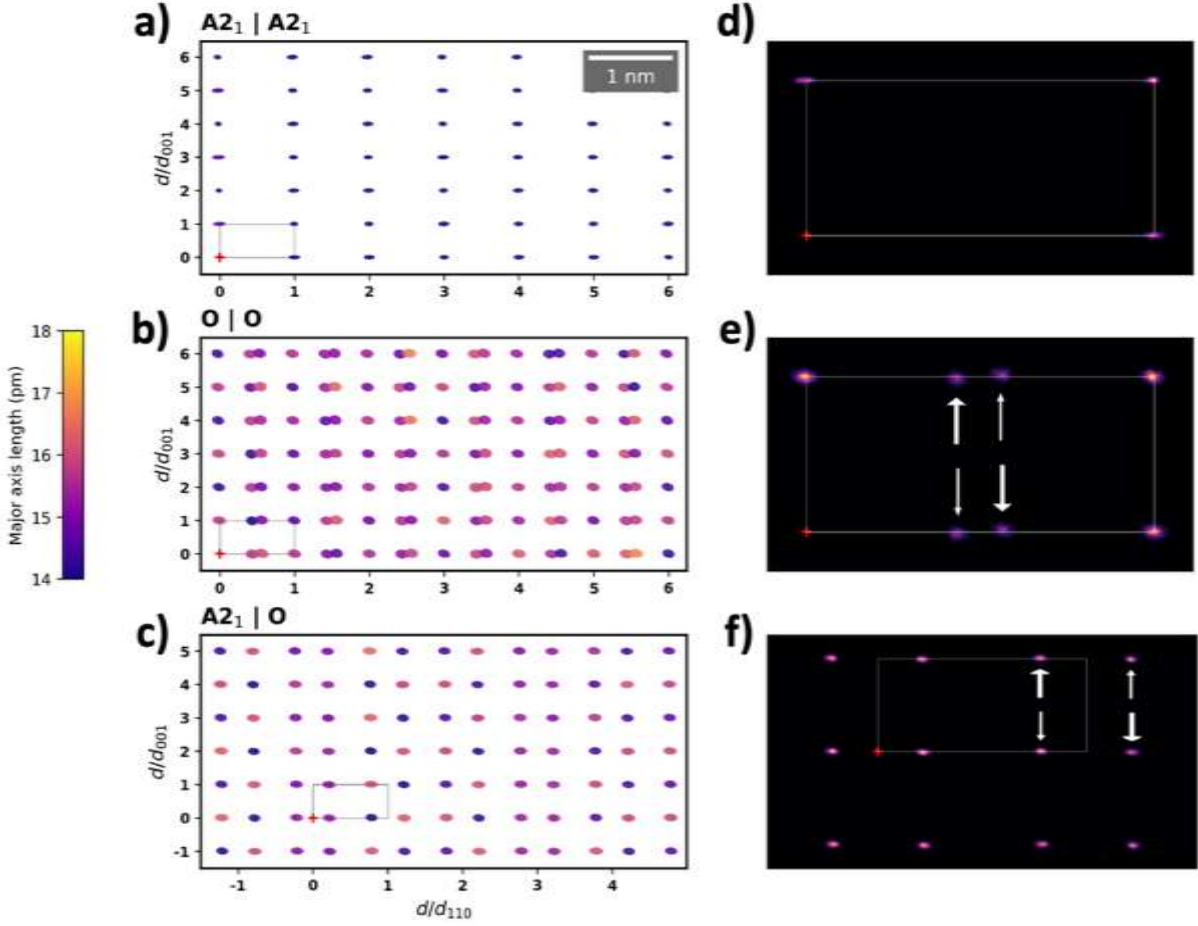
position which is comparable to typical acquisition speeds used for conventional STEM imaging. The camera is an active pixel sensor and electron counting is performed by an algorithm on each raw pattern after the scan is complete. This strategy for direct-electron detection means that for a single frame, each detector pixel can have an electron count of either 0 or 1. Therefore, care must be taken to avoid oversaturating the detector to prevent excessive lost signal. This is generally acceptable for DPC



**Figure 4:** Atom column locations measured from one of the DPC-STEM images and used in the subsequent analyses.

because the high convergence angle used for atomic-resolution imaging spreads the beam over a large portion of the detector and low beam currents (30 - 60 pA) are typically used to avoid sample damage. For our experiments, the microscope is operated at 300keV beam energy with a 21 mrad convergence angle and 25 pA beam current (as measured on the phosphor screen). The sample thickness is determined by comparing the position averaged convergent beam electron diffraction pattern

(PACBED; summed from the 4D STEM dataset) with simulations. We estimate the sample thickness in the imaged region to be 14nm (Supplementary Information Figure 1). Image quantification, including atom column position measurements and vPCF calculations are performed using the SingleOrigin Python package.[17] The measured atom-column positions for a representative image used in the subsequent analysis is shown in **Figure 4**. Details of the data processing and image analysis are included in the **Supplementary Information**.



**Figure 5:** Experimental vPCFs compiled from measurements of 5 DPC-STEM images of BSSN. a) – c) show the peak shapes over a 6x6 unit cell field of view. d) – f) show the underlying peaks near the first unit cell of a) – c), respectively. Arrows indicate key peaks in determining the modulation correlations, with the arrow widths indicating the wide and narrow peaks, as before. The red “+” indicates the origin of the vPCFs and the black or white boxes indicate the projected basic TTB cell corresponding to the  $d_{110}$  (horizontal) and  $d_{001}$  (vertical) plane spacings, respectively.

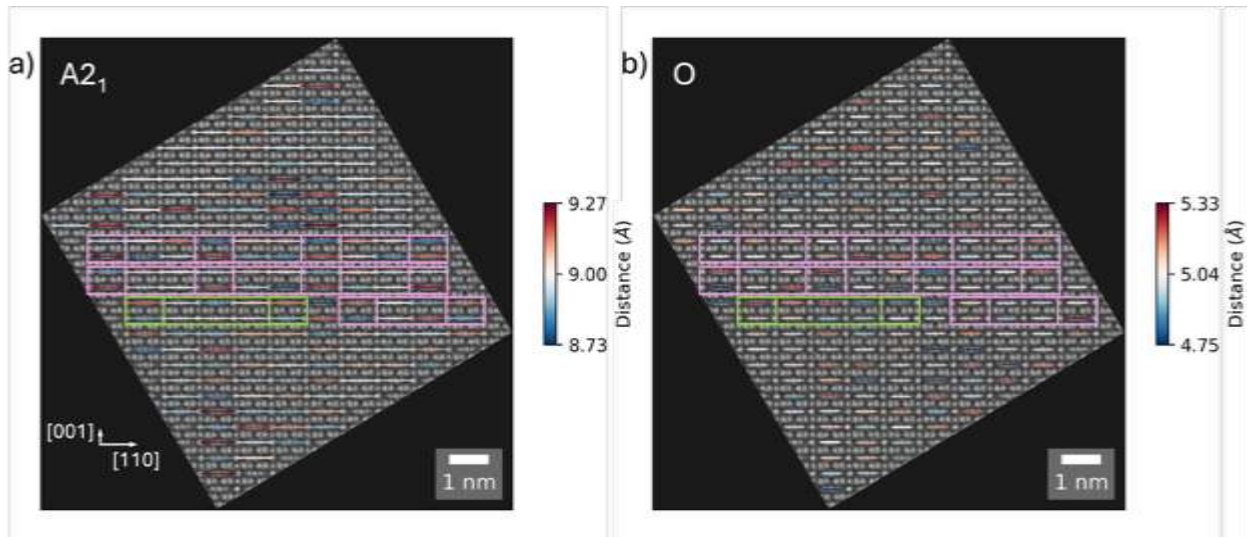
### 3. Results & Discussion

**Figure 5** shows the experimental vPCFs derived from the measured atom column positions in five DPC-STEM images. It can be seen that the peak shape pattern in the  $A2_1$  vPCF (**Figure 5a**) matches very closely with that previously reported from HAADF-STEM data,[14] confirming the  $\mathbf{q} = 0.314(\mathbf{a}^* \pm \mathbf{b}^*) + 0.5\mathbf{c}^*$  displacive modulation of Ba on the  $A2_1$  sublattice. The oxygen vPCF (**Figure 5 b & e**) exhibits wide and narrow peak

distributions in the pairs near  $0.5 \times d_{110}$ , which is nearly identical to the vPCF calculated from the incommensurate Ama2 model (**Figure 3 b & e**).

From the  $A2_1$  | O vPCF, we observe that the pairwise ordering between these two sublattices also matches the Ama2 model (compare peak shape ordering in **Figure 5 c & f** to **Figure 3 c & f**). This indicates that the  $A2_1$  Ba atoms displace according to the distortion of their oxygen coordination polyhedra. In fact, all three experimental vPCFs show good agreement with the model across the displayed range, despite the only 9.5nm field of view of the STEM images (which reduces the counting statistics, especially in peaks at longer correlation lengths).

In **Figure 6**, we map projected inter-atomic distances for the  $A2_1$  and oxygen sublattices, analyzing the same image as shown in **Figure 4**. A 2-fold periodicity is observed along the  $[001]$  direction as alternating short and long distances in both maps, though it is more evident on the cation sublattice. Colored boxes highlight a



**Figure 6:** Interatomic distances between horizontal near neighbors for the a)  $A2_1$  and b) oxygen sublattices. Boxes show segments of the sample with displacement correlations of 3 x (pink) or 4 x (green)  $d_{110}$  spacings, as observed in the  $A2_1$  sublattice. A discommensuration occurs between the 3- and 4- fold segments.

selection of periodic correlation patterns seen in the  $A2_1$  spacings along the  $[110]$  direction. The  $A2_1$  sublattice map shows a dominant periodicity of  $3 \times d_{110}$  plane spacings (pink boxes), corresponding to the modulation vector component, which is close to  $1/3$  along the  $[110]$  direction of BSSN. We note a single instance in this image where a  $4 \times d_{110}$  period (green box) can be isolated but also point out that a modulation defect (neither 3- or 4-fold periodicity) occurs to the right of this block before resuming a 3-fold pattern. Furthermore, the pattern in the the 4-fold segment can be seen as shifted right by  $1 \times d_{110}$  spacing relative to the rows above. Comparing the  $A2_1$  map with that of the oxygen sublattice, we observe that only the middle row of boxed segments shows a clear 3-fold periodicity, albeit with a defect adjacent to the end of the 4-fold segment below it. The other rows, which clearly show periodic displacements on the  $A2_1$  sublattice, do not have similar, strong correlations among the oxygen distances, including in the segment corresponding to the 4-fold block of the  $A2_1$  map.

To interpret the real-space inter-atomic distance mappings, we first point out that the modulation vector component in BSSN is much closer to  $1/3$  than the  $1/4$  associated with the Ama2 model. An approximately 80-20% mix of 3- and 4-fold blocks would be expected to yield this modulation vector. We, however, see a prevalence of 3-fold periodicity in the displacement maps without observing a significant number of 4-fold segments. This observation is also sustained by data from our previous work where no 4-fold segments can be seen on the  $A2_1$  sublattice via HAADF imaging over a much larger field of view.[14] Secondly, when undergoing an octahedral tilting modulation, a crystalline structure composed of corner-shared octahedra necessarily favors even-numbered periodicities since adjacent units tend to rotate oppositely in a gear-like

fashion. Therefore, a 3-fold modulation periodicity in TTBs necessarily involves a geometric frustration at some points of the lattice.[13] Our data, however, provides evidence for an alternative to the slab-intergrowth model [9,13] of incommensurate TTBs: a 3-fold modulation with a significant number of modulation defects, or discommensurations. This has analogy in 1T-TaS<sub>2</sub>, a well-studied layered material that hosts three distinct charge density wave modulations across a range of temperatures. At room temperature, 1T-TaS<sub>2</sub> adopts a “nearly commensurate” phase which has been shown to consist of commensurate domains separated by discommensurations.[18,19] The situation in TTBs is more complex due to orientation variants and, in many compositions, chemical (including vacancy) disorder. In **Figure 6** we see a 3-fold repeat unit with defects in the pattern along both the [110] and [001] directions. Furthermore, the identified 4-fold block and adjacent discommensuration can also be viewed as a defective group of 3-fold blocks. As additional evidence for the lack of true 4-fold blocks in our data, we point to the vPCFs (**Figure 5**). If 4-fold blocks were present, we would expect to see an increased correlation (i.e. narrower peak) at the  $4 \times d_{110}$  spacing of the vPCF, as compared to the  $1, 2$  or  $5 \times d_{110}$  peaks. Each of these peaks, however, have similar widths in both the A2<sub>1</sub> and oxygen vPCFs and are wider than peaks at multiples of  $3 \times d_{110}$ . Thus, we find the incommensurate modulation in BSSN can be described by a model with an Ama2-like 3-fold motif plus a high density of discommensurations. This model may also be applicable to other TTBs such as SBN where parts of the Monte

Carlo modeled orientational domains do not match neatly with either a 3- or 4-fold block.[13]

#### 4. Conclusions

We conclude that the incommensurate modulation in BSSN is well-described as a modification of the Ama2 model, to the exclusion of the Amm2 model or a tetragonal superlattice. Our results in a filled TTB composition with modulation vector substantially different from BNN ( $\sim 0.26c^*$  versus  $\sim 0.31c^*$ ), also point to the likelihood that the Ama2 model is generally representative of incommensurate TTBs. Specifically, in BSSN, the modulation manifests as a  $3 \times d_{110}$  repeat unit with a high density of modulation defects (discommensurations), together producing the incommensurate superlattice in diffraction. This 3-fold plus discommensuration model is a more general explanation than a 3- plus 4-fold intergrowth model and may provide a fuller description of the disorder seen in TTBs by other works.[9,13] We have shown that vPCF analysis of aberration-corrected DPC-STEM images is a powerful method to understand complex, displacive correlations via a direct, real space probe. The incommensurate TTB structure previously proved challenging to resolve with X-ray diffraction-based structure determination [8,9] and could otherwise only be unraveled by a complex combination of indirect experimental and modeling methods [13]. Furthermore, we showed that, in combination with pixelated direct-electron detectors and phase retrieval imaging methods like DPC, vPCF analysis can be extended to light elements, such as oxygen, even in structures with heavy cation sites as projected close near neighbors. Multi-slice electron ptychography, which can achieve image resolution beyond the diffraction limit, may provide even deeper understanding of incommensurate TTBs when combined with

vPCF analysis.[20] Finally, we show the vPCF method clearly reveals the order present on disordered sublattices and, we believe, our general approach should be useful for studying complex order-disorder phases in other crystal classes as well.

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### **Author Contributions:**

**Stephen Funni:** Conceptualization, Methodology, Investigation, Software, Formal Analysis, Visualization and Writing - original draft preparation. **Peter Ercius:**

Resources, Writing – review and editing. **Sebastian Calderon:** Investigation, Writing – review and editing. **Elizabeth Dickey:** Supervision, Funding acquisition, Writing – review and editing.

### **Data and Code availability:**

All data processing was completed using SingleOrigin, a Python package that includes tools for atomic resolution image quantification and vPCF analysis. The current version of SingleOrigin, is available on GitHub (<https://github.com/sdfunni/SingleOrigin>)

and the Python Package Inventory. An example notebook demonstrating the analysis in this paper is also available on GitHub.

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