

# Incommensurate Modulation and Competing Ferroelectric/ Antiferroelectric Modes in Tetragonal Tungsten Bronzes

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<b>ABSTRACT:</b> The nanoscale structure of $Sr_{0.61}Ba_{0.39}Nb_2O_{67}$ a classic uniaxial relaxor ferroelectric crystallizing with the tetragonal tungsten bronze (TTB) structure and exhibiting an incommensurate modulation, has been determined by atomistic refinements using combined data from variable-temperature neutron total scattering, extended X-ray absorption fine structure, and three- dimensional single-crystal diffuse scattering. We found the modulation to arise from the intergrowth of structural slabs featuring distinct types of octahedral rotations directed to	3d <sub>110t</sub>



demonstrated the coexistence of competing polar  $\Gamma_3^-$  and antipolar  $\Gamma_2^-$  modes for off-centering of Nb above the nominal ferroelectric transition temperature of 350 K. The nanoscale-correlated antipolar distortions, which exhibit their largest amplitudes at 425 K, are suppressed below the transition. We identified coupling between the polar off-centering of Nb on its two symmetrically distinct sites as a fundamental characteristic controlling the ferroelectric-to-relaxor crossover in TTBs. We then used it to propose a simple microscopic interpretation for the previously established empirical trend that links crystal-chemical parameters in these systems to their polar response.

### INTRODUCTION

A fundamental understanding of the origins of dielectric relaxation and ways to control the relaxor-to-ferroelectric crossover in tetragonal tungsten bronzes (TTBs) continues to attract the interest of the materials science and physics communities. Despite decades of research, the exact nature of structural distortions in these systems and the mechanisms of their dielectric and polar responses remain uncertain.<sup>1-3</sup> The TTB structure, A1A22B1B24O15, differs from the more widely studied and exploited perovskites by the connectivity of oxygen octahedra, as depicted in Figure 1, which results in a tetragonal archetypical unit cell.<sup>4</sup> The tiling of octahedra in the  $\{ab\}$ layers creates 12-fold (A1) and 15-fold (A2) oxygen coordination environments available to the A cations (the triangular channels typically remain empty). The octahedral B sites acquire two distinct symmetries being coordinated by 4A2 (B1) and 2A1 and 4A2 sites (B2) (Figure 1). Many known TTB structures at ambient temperature exhibit incommensurate displacive modulations attributable to rotations of oxygen octahedra.<sup>5,6</sup> The types of octahedral rotations and the origins of the incommensurate periodicity have not been established.

minimize octahedral deformations. This modulation involves

displacements of the A cations (Sr and Ba) but exerts no significant effect on the polar displacements of Nb. Our results

Zhu et al.<sup>6</sup> used the data for various TTB systems to propose crystal-chemical criteria for predicting the type of tilting modulation and the accompanying polar response (relaxor or classic ferroelectric). Their empirical model assumed that the larger A cations support larger octahedral volumes, which

promote cooperative polar displacements of the B cations, a mechanism similar to that in perovskites. As the average ionic radius of the A cations is reduced, a ferroelectric response changes into a relaxor. At the same time, the substitution of sufficiently small cations on the A2 sites favors commensurate octahedral rotations that promote a ferroelectric response.<sup>6</sup>, The principal significance of the commensurability here is not in the periodicity per se but in the distinct tilting pattern in the reported commensurate structures requiring deformations of octahedra, which appear to induce stronger coupling among the polar B-cation displacements.

A large body of research into the structure and properties of TTBs concentrated on Sr<sub>x</sub>Ba<sub>1-x</sub>Nb<sub>2</sub>O<sub>6</sub> (SBN) solid solutions  $(0.33 \le x \le 0.82)$ , which exhibit electrooptic and piezoelectric properties of practical interest, with the polar response changing from ferroelectric to a relaxor as the Sr/Ba ratio (x) increases to  $\geq 0.6$ .<sup>1</sup> Additionally, SBN has been used as a model system for fundamental studies of structure-property

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**Figure 1.** (a) Schematic drawing of the tetragonal tungsten bronze structure viewed along the *c*-axis. Labels mark the symmetrically distinct A- and B-cation sites. The unit cell of a prototype tetragonal P4/mbm structure is outlined with a square. (b and c) Schematic depictions of the coordination environments for the B1 and B2 octahedral sites, respectively.

relations in TTBs. Like many other members of this structural class, SBN compositions display an incommensurate modulation.<sup>5</sup> Earlier transmission electron microscopy (TEM) work by Bursill and Lin<sup>8</sup> suggested this modulation was onedimensional, with its coherence length limited to <10 nm. The material appeared as an assemblage of nanoscale domain variants featuring orthogonal directions of the modulation vector. The same authors used simulations of electron diffraction data to propose a model that attributes the incommensurate periodicity to a sequence of structural blocks and/or slabs featuring distinct patterns of displacements for the apical oxygen atoms. These intergrown slabs were attributed to two closely related and competing structures having similar energies. Subsequent attempts to determine the exact nature of the modulation by refining atomic positions against X-ray or neutron scattering data ignored the TEM results, describing it instead as two-dimensional sinusoidal and using a superspacegroup formalism.<sup>9,10</sup> Such refinements suggested the modulation was associated with octahedral tilting, but the topology of the underlying octahedral rotations remained unclear.

Recently, several studies considered not only the average structure of SBN<sup>11,12</sup> but also its local atomic order.<sup>13,14</sup> Pasćiak et al.<sup>13</sup> employed molecular dynamics (MD) simulations validated by qualitative comparison with the experimental atomic pair distribution function (PDF) obtained from neutron total scattering to investigate local structural distortions. Static and dynamic effects were separated by averaging multiple MD snapshots. The primary result was dissimilar displacive behavior on the Nb1 and Nb2 sites (Figure 1b,c), which was also noted in previous experimental structural refinement studies,<sup>15</sup> with the former sites exhibiting a considerably larger off-centering along the polar tetragonal axis. Nb2 cations displayed an additional off-centering in the  $\{ab\}$  plane, and their displacements appeared to be much more dynamic than those of Nb1. A coexistence of the two Nb subsystems with the distinct dynamics of polar displacements as a function of temperature has been proposed to play a major role in the observed dielectric relaxation. The MD simulations

also produced octahedral tilting with a pattern of rotations that required significant deformations of octahedra, although the size of atomic configurations was insufficient to accommodate the incommensurate modulation. A correlation between the local A-cation chemistry and the magnitudes of octahedral rotations has been observed.

An experimental study of the local structure in SBN by Li et al.<sup>14</sup> employed a combination of Rietveld and both small- and large-box refinements from neutron total scattering data. These analyses also highlighted significant differences for the displacements of Nb1 and Nb2, with the former decreasing gradually upon heating and the latter remaining constant, which appears to contradict the trends obtained in the MD simulations. The ferroelectric-to-relaxor crossover with an increasing Sr:Ba ratio has been attributed to the effects of the chemical disorder on the pentagonal A2 sites, which modifies displacements of the neighboring oxygen atoms. Both local-structure studies suggested the existence of local polarization well above the perceived Curie temperature, supporting previous inferences from other measurements.<sup>16</sup>

Other works targeting the local atomic order utilized diffuse X-ray scattering from single crystals of SBN.<sup>17-21</sup> These studies revealed (00L) sheets of diffuse intensity attributed to correlations among the Nb displacements along the *c*-axis octahedral chains. Recent measurements performed over a large volume of reciprocal space suggested different temperature dependencies for the diffuse intensity in the vicinity of the H0L Bragg peaks with H = 2n and H = 2n + 1.<sup>19,20</sup> The latter set is forbidden by P4bm space-group symmetry. The diffuse intensity near the H = 2n reflections peaked around 350 K, whereas that around the H = 2n + 1 locations, upon heating, increases steeply to a maximum at  $\approx$ 425 K, followed by a plateau-like behavior at higher temperatures. Such distinct trends for the diffuse scattering near the two sets of Bragg peaks have been ascribed to the coexistence of ferroelectric (polar) and antiferroelectric (antipolar) displacements.

Local-structure studies of SBN have provided insights into the behavior of atomic displacements and the effects of local chemistry. However, many key questions remained unanswered, including the nature of the incommensurate modulation, the role of correlated polar versus antipolar displacements, and the exact structural mechanisms underlying the empirical trend identified by Zhu et al.<sup>6</sup> Here, we aim to close this knowledge gap by performing in-depth analyses of the local and nanoscale structures in SBN. Recently, we developed the ability to refine large atomic configurations representing structural snapshots while simultaneously fitting X-ray/neutron total scattering data from powders and threedimensional (3D) distributions of X-ray diffuse scattering intensity from single crystals. This approach has already been applied to determine the nanoscale structure of the prototype perovskite relaxor ferroelectric PbMg<sub>1/3</sub>Nb<sub>2/3</sub>O<sub>3</sub>, with several significant new features of atomic order uncovered.<sup>22</sup> Notably, the refined atomic arrangements accounted for a number of nontrivial experimental results not included in the fit, which attested to the model fidelity. In this work, we extended this method to TTBs, which feature unit cells significantly larger than those of perovskites and exhibit an incommensurate modulation yielding nanoscale twin domains.

# EXPERIMENTAL SECTION

Synthesis and Characterization.  $Sr_{0.61}Ba_{0.39}Nb_2O_6$  ceramics were prepared using conventional solid-state synthesis.  $BaCO_3$ 

(99.99%), SrCO<sub>3</sub> (99.994%), and Nb<sub>2</sub>O<sub>5</sub> (99.9985%) were mixed and ball-milled in isopropanol in a planetary mill using yttria-stabilized zirconia as grinding media. The dried powders were pelletized and calcined at 1300 °C. After a second ball milling, powders were pelletized and sintered at 1350 °C. X-ray diffraction with Cu K $\alpha_1$  radiation was used to confirm phase purity.

TEM samples were prepared by mechanical polishing of sinterered pellets, followed by ion thinning at -100 °C until perforation. The samples were coated with a thin carbon layer to improve their electrical conductivity. Electron diffraction and TEM imaging were performed in a transmission electron microscope operated at 300 kV. Atomic-resolution high-angle annular dark field (HAADF) images were collected also at 300 kV in a scanning transmission electron microscope (STEM) equipped with a monochromator and a probe aberration corrector. HAADF image simulations were performed using the Dr Probe software.<sup>a</sup>

Neutron scattering measurements were performed in POLARIS time-of-flight powder diffractometer at ISIS. The samples were placed in vanadium containers, 6 mm in diameter. Temperature control was achieved using a high-temperature furnace. Data suitable for Rietveld refinements were collected at a series of temperatures between 300 and 850 K. Total scattering data, which required significantly longer counting times, were recorded at 300, 350, 425, and 500 K (this set of temperatures was selected to match those used for single-crystal X-ray diffraction measurements). The total scattering data were further processed using the GUDRUN software to obtain a scattering function, S(Q), and its Fourier transform, which represents a PDF. Extended X-ray absorption fine-structure (EXAFS) data were collected at the NIST 6-BM beamline at NSLS-II (Brookhaven National Laboratory) for the Sr K and Ba L<sub>3</sub> absorption edges. The EXAFS data were reduced using the Athena software. Initial analysis of these data using fits of parametrized models of the Sr and Ba coordination was performed in the Artemis software,<sup>23</sup> with FEFF8<sup>24</sup> used to calculate amplitudes and phases for photoelectron scattering.

The Sr<sub>0.61</sub>Ba<sub>0.39</sub>Nb<sub>2</sub>O<sub>6</sub> single crystal was provided by Altechna (Vilnius, Lithuania). Measurements of diffuse X-ray scattering were performed at beamline ID28 of ESRF using incident radiation with a wavelength  $\lambda$  of 0.784 Å (to avoid Sr fluorescence) and a PILATUS3 1M detector. Temperature control was achieved using a heat blower. The CrysAlis software package was used to refine the orientation matrix; the final reciprocal-space reconstructions of 3D diffuse intensity distributions were accomplished with locally developed custom software.

Rietveld refinements were performed using TOPAS<sup>25</sup> (see the Supporting Information for details). Atomistic structural refinements were carried out using the development version of the RMCProfile software<sup>22,26-29</sup> against the following experimental data sets: (1) neutron scattering function, S(Q), (2) its corresponding PDF in D(r)form, (3) the neutron Bragg profile, (4) Sr EXAFS, and (5) Ba EXAFS and the 3D distribution of X-ray diffuse scattering intensity measured on a single crystal. The EXAFS data provide chemically specific information required to determine the coordination environments of Sr and Ba that share the pentagonal sites. For neutron total scattering, the instrumental resolution function was explicitly accounted for.<sup>28,29</sup> In addition to the experimental data, we imposed two types of restraints on the atomic coordinates: The first type<sup>30</sup> added a penalty term for deviations of bond valence sums<sup>31</sup> for the constituent species from the respective ideal values (i.e., 2 for Ba and Sr, 5 for Nb, and 2 for oxygen). The second type promoted smooth profiles for peaks describing distributions of near-neighbor distances in partial pair distribution functions by limiting the magnitudes of their second derivatives; this restraint helps to regularize refined configurations. The weights assigned to the individual data sets and restraints were adjusted automatically during fits using a statistical analysis of changes in the total residual and its individual components after a series of atomic moves, a procedure described elsewhere.<sup>22,29</sup> The refinements were performed sequentially using the configuration obtained for one temperature as the starting point for refining the structure at the next higher temperature.

**Construction of Atomistic Models for Refinements.** Our electron diffraction patterns confirmed the presence of incommensurate reflections with the modulation vector  $\mathbf{q} \approx 0.31(\mathbf{a}_t^* \pm \mathbf{b}_t^*) + 0.5\mathbf{c}_t^*$ , where  $\mathbf{a}_t^*$ ,  $\mathbf{b}_t^*$ , and  $\mathbf{c}_t^*$  are the reciprocal-lattice vectors corresponding to the prototype TTB unit cell with  $a_t \approx 12.45$  Å and  $c_t \approx 3.94$  Å. TEM dark field images (Figure 2) recorded using such



**Figure 2.** (a) Dark field TEM image recorded with one of incommensurate reflections strongly excited near the  $[110]_t$  zone-axis orientation. (b) Zone-axis selected area  $[110]_t$  electron diffraction pattern from the imaged area. (c) Magnified view of the region outlined in panel a. The contrast is consistent with the presence of two orientational variants of the incommensurately modulated phase with orthogonal directions of the incommensurate component of the modulation vector so that only one of these variants (imaged as bright regions) contributes in a given  $[110]_t$  orientation.

incommensurate reflections were similar to those reported by Bursill and Lin.<sup>8</sup> As mentioned in the Introduction, these results suggest that the modulation is one-dimensional and that the sample consists of twin domains, <10 nm in size, having the incommensurate component of **q** aligned with the  $[110]_t$  and  $[\overline{110}]_t$  tetragonal directions. Such domain assemblages were modeled using an atomic configuration of  $12 \times 12 \times 20$  unit cells, each having lattice parameters  $\sqrt{2a_t \times c_v}$  which consisted of four domains representing two variants of the incommensurately modulated structure as illustrated in Figure 3. Atoms residing in each of these domains were labeled using different markers. The overall size of the configuration was approximately 21.2 nm × 21.2 nm × 7.8 nm with a total of  $\approx$ 260000 atoms, which is much larger than configurations used in the reported MD simulations and RMC refinements from total scattering. We tried two starting models: one with all atoms located at the ideal positions and another with the oxygen atoms in



**Figure 3.** Schematic drawing illustrating the domain model assumed for the atomic configurations used in the RMC refinements. Here, a labeling system was introduced to distinguish atoms belonging to different domains, which represent two orientational variants of the incommensurately modulated structure. During fits, atoms from variant I were allowed to contribute to only the diffuse intensity in the slabs with *L* half-integer depicted in panels c and d of Figure 4, whereas atoms from variant II contributed to only the slabs in panels e and f of Figure 4. All of the atoms contributed to the scattering in the slabs of reciprocal space centered on planes with *L* integer.



**Figure 4.** (a and b) Experimental diffuse scattering in the *HK*0.5 and *HK*1.5 sections of reciprocal space, respectively. The indices correspond to a unit cell with dimensions of  $\sqrt{2a_t} \times \sqrt{2a_t} \times c$ , which has *a*- and *b*-axes rotated by 45° relative to the prototype structure (Figure 1). The red circles and yellow squares indicate examples of reflection sets belonging to variants I and II, respectively. (c and d) The same sections as in panels a and *b*, respectively, but having one set of the incommensurate reflections replaced with the background intensity expected for a single orientational variant of the modulated structure. (e and f) Similar to panels c and d, respectively, but for variant II. The modified diffuse intensity distributions were used as input to RMCProfile.

each variant displaced to mimic the oxygen shifts and the incommensurate periodicity suggested in ref 8. Given the lack of evidence for short-range ordering of the A-site species in our TEM/STEM data, we assumed a random distribution. The A1 and A2 sites were populated per their occupancies estimated from the Rietveld analyses: A1 – 0.74Sr, A2 – 0.39Sr + 0.486Ba. This distribution of the A-site species was kept fixed during the RMC refinements.

Treatment of Single-Crystal Diffuse Scattering. According to the TEM results, reflections associated with the incommensurate modulation in the single-crystal X-ray diffuse scattering data form two subsets, each associated with one of the two modulation variants having orthogonal directions of the incommensurate component of the modulation vector (Figure 4). The nanoscale size of the modulated domains as revealed by the TEM images is too small for detection by single-crystal X-ray diffraction. Suppose now that all atoms in the configuration during fitting contribute to the entire set of the satellite reflections. Then, the RMC procedure will attempt to build a two-dimensional modulation rather than spatially distinct domains modulated along different directions. We addressed this refinement problem by sectioning the 3D diffuse scattering data sets into slabs centered on HKL layers with L half-integer and integer (Figure S2). The half-integer slabs contain first-order satellite spots associated with the incommensurate modulation, but no fundamental reflections. The integer slabs include the fundamental Bragg peaks and high-order incommensurate satellites, which are weaker than the those of first order and are masked by the (00L) diffuse scattering sheets. For each half-integer slab (Figure 4a,b), we generated two versions corresponding to domains with the modulation vector directed along the  $[110]_t$  (Figure 4c,d) or  $[1\overline{1}10]_t$  (Figure 4e,f) direction. In these slabs, the intensity under the satellite reflections of the second variant was equated with the surrounding background. Then, during the fit, only atoms from a single variant, I or II (Figure 3), were allowed to contribute to the half-integer slabs, a constraint consistent with the recovery of a one-dimensional modulation. All atoms were allowed to contribute to the integer slabs. A single

intensity scale factor was used to reproduce the entire 3D diffuse scattering data set.

For the fit, we defined the diffuse intensity distribution in the  $[110]_{tr}$   $[1\overline{10}]_{tr}$   $[001]_{t}$  basis over the reciprocal-space volume delimited by HKLs  $330_{\nu}$   $3\overline{3}0_{\nu}$  and  $002.5_{\nu}$  respectively. The intensity was mapped onto a Q-space grid of  $121 \times 121 \times 69$  voxels distributed uniformly along  $[110]_t$  and  $[1\overline{10}]_t$  and nonuniformly along  $[001]_t$ with a higher number density of voxels near the (00L) planes (L)integer and half-integer). This number of voxels was selected as a trade-off between a sufficient number of points across the intensity profiles and practical computing times. The distribution of the diffuse intensity along the *c*-direction is considerably narrower than in the {*ab*} plane. Modeling such a width (Figure S3) would require atomic configurations with sizes prohibitively large for the current version of RMCProfile. Therefore, before comparison with the calculated signal, the experimental diffuse scattering data were convolved with a Gaussian function reflecting the size of the configuration box along the [001] direction (Figure 5 and Figure S3).

**Tracing the Origins of Diffuse Scattering via the Inverse Fourier Transform.** Diffuse scattering calculated from atomic coordinates that were refined against experimental data encodes contributions from different types of correlations among the existing atomic displacements. We employed the inverse Fourier transform (IFT) of a complex X-ray scattering amplitude<sup>22</sup> to identify correlated displacements giving rise to specific diffuse scattering features. While inaccessible in experimental measurements, which yield only intensities, such a complex amplitude can be readily calculated from a given set of atomic coordinates obtained from RMC refinements. Here, we were interested in the IFT of the diffuse scattering amplitude, which in RMCProfile is determined as the difference between the total and average amplitudes according to the formalism described in ref 32.

First, we used a stand-alone program to calculate a 3D distribution of the complex amplitude of diffuse scattering for the refined atomic configurations. The number of reciprocal-space points used in these



**Figure 5.** (a) Experimental diffuse scattering in the H00 section at 300 K. (b) Same as panel a but convolved with a Gaussian function reflecting the size of the atomic configuration along the *c*-axis. While this convolution broadens the initially narrow *c*-axis distribution of the diffuse intensity in sections with *L* integer, the character of the much broader features, such as the diffuse intensity distribution around reflection 002, is retained. (c) Same as panel b but with the number of pixels reduced to a sparser grid to ensure reasonable computing times. (d) Calculated for a refined configuration after simultaneous fitting of powder and single-crystal data. Note that all of the experimental diffuse scattering features are reproduced.

calculations must be selected to provide sufficient sampling of the rapidly varying real and imaginary parts of the amplitude. We then calculated the IFT by integrating the calculated scattering amplitude over reciprocal-space volumes encompassing the diffuse features of interest. The resulting IFT signal, which is a real function, displays positive and negative peaks flanking the atomic positions. Extensive tests confirmed that for atoms exhibiting the largest magnitude of the IFT, a vector linking these peaks reflects the direction of a displacement component, which contributes the most to the selected diffuse scattering feature. In principle, the length of this vector is related to the displacement magnitude. The scattering vectors for the diffuse scattering included in the IFT must be sufficiently large to provide an adequate resolution for atomic displacements in real space; that is, recovering smaller displacement components requires larger reciprocal-space coverage. In practice, obtaining the actual displacement magnitudes in SBN via the IFT would require scattering vectors that are prohibitively large. Therefore, at present, we could only reliably recover directions of displacements responsible for diffuse scattering.

# RESULTS

Figure 6 and Figure S4 summarize the experimental and calculated signals at 300 and 550 K. Overall, the agreement is satisfactory given the approximations and assumptions involved. Similar-quality fits were obtained for 350 and 425 K. The distributions of the diffuse scattering intensity calculated separately for the Ba, Sr, Nb, and O species in the refined configurations demonstrated that the incommensurate reflections arise primarily from correlations involving O, Ba, and Sr. In contrast, the prominent (00L) (L integer) diffuse scattering sheets are associated mainly with Nb. These results

agree with previous suggestions and are supported by our STEM images of SBN, Fourier-filtered using the incommensurate reflections (Figure S5). The contrast in such images is modulated only in the (001) planes containing Ba and Sr columns. Recent, more elaborate analyses of the STEM contrast for another TTB compound, also exhibiting a similar incommensurate modulation, reached the same conclusion.<sup>33</sup>

The refined atomic coordinates were analyzed to extract octahedral rotations, polyhedral distortions, and cation displacements. Octahedral rotation angles and distortions were determined using the GASP software.<sup>34</sup> In the following, we distinguish cation displacements from their average positions and those from the geometric centers of the oxygen polyhedra hosting these cations. The former displacements define instantaneous atomic positions described by atomic probability density distributions (PDDs). The off-center shifts, also termed off-centering, depend on both cation and oxygen displacements, yielding electric dipoles that contribute to polarization.

**Octahedral Rotations.** In the individual twin domains of the refined configuration (Figure 3), octahedral rotations exhibit a clear preference for a regular pattern that minimizes distortions of the octahedra; the same trend was obtained for both starting models. Ignoring some inevitable disorder and imperfections (e.g., our models represent instantaneous structures, and the RMC procedure favors disorder), the regularized observed tilting pattern for domain D1 (variant I) is illustrated in Figure 7. Maps of the actual octahedral rotations are shown in Figure S6. The two domains of the



**Figure 6.** Experimental and calculated signals for SBN at 300 K, representing the RMCProfile fits. (a) Neutron Bragg profile, (b) neutron scattering function F(Q), (c) neutron PDF, (d) magnified view of the local range in panel c, (e) Ba EXAFS, and (f) Sr EXAFS. The experimental and calculated traces are indicated using black and red lines, respectively. The residual traces are colored green. (g-j) X-ray diffuse scattering intensity in the *HKL* sections of reciprocal space with *L* half-integer and integer. The values of *L* are indicated in the figures. In each figure, the left and right halves represent the experimental (Exp) and calculated (Fit) intensities, respectively. The sections with *L* half-integer correspond to variant I. A similar-quality fit was obtained for the sections representing variant II. Note that the diffuse intensity was fitted on a 3D grid, with only planar sections shown here for the sake of convenience.

same modulation variant (i.e., D1 and D3 for variant I or D2 and D4 for variant II) feature a sequence of slabs A and B having thicknesses of  $2\sqrt{2a_t}$  and  $1.5\sqrt{2a_t}$  (or  $3\sqrt{2a_t}$ ), respectively, which appear to yield an incommensurate periodicity; the stacking directions in the two variants are orthogonal to each other.

The TEM/STEM/HRTEM images (Figure 2 and Figures S5 and S7) suggest that the domain size along the modulation direction is limited to  $\approx 10\sqrt{2a_t}$  spacings, indicating that the sequence of slabs in each of these domains is short and varies from domain to domain. That is, the overall incommensurate periodicity reflects an average over several such regions that diffract coherently. In our configuration, the incommensurate peaks correspond to an average over the two domains for each variant, with the slab sequence being rather irregular,

consistent with the patchy appearance of the modulation contrast in the FFT-filtered HRTEM/STEM images (Figures S5 and S7). In the adjacent octahedral layers along the *c*-axis, the rotations occur in opposite directions yielding a doubled periodicity and periodically corrugated  $[001]_t$  octahedral chains.

The tilting within slabs A is the same as in the quasicommensurate phase of Ba<sub>2</sub>NaNb<sub>2</sub>O<sub>15</sub> where it yields Ama2 symmetry with lattice parameters of  $2\sqrt{2a_t} \times \sqrt{2a_t} \times 2c_t$ .<sup>35</sup> The pattern for slabs B has not been reported. A commensurate modulation with this pattern would result in a lattice periodicity of  $3\sqrt{2a_t}$ . While tilting pattern A does not require octahedral distortions, pattern B involves deformations in certain linkages labeled in Figure 7 using dashed circles; however, overall, the extent of such distortions is relatively



**Figure 7.** Schematic rendering of a (001) octahedral layer illustrating patterns of octahedral tilts in a single modulation variant in the refined configurations. This drawing provides a regularized representation of the actual tilts, which are shown in Figure S5, ignoring deviations and imperfections associated with the nature of the models, which incorporate thermal fluctuations, and also with a randomizing tendency of the RMC procedure (Figure S5). The modulation direction is horizontal. We obtained similar-character tilting patterns for the second variant but with the modulation vector in the orthogonal direction. Red arrows indicate the directions of octahedral tilts, whereas the semitransparent yellow and magenta disks highlight characteristic fragments of the rotation patterns to guide the eye and facilitate the comparison with the actual tilting directions in Figure S5. Magenta disks represent all octahedra forming a pentagonal channel tilted outward. Yellow disks represent all octahedra forming a pentagonal channel tilted inward. The A and B slabs forming the incommensurate sequence are marked using vertical black lines. The slab thicknesses along the horizontal direction are indicated in the figure. Labels 1 and 2 mark octahedra that exhibit predominant rotations around the *x*- and *y*-axes, respectively; these labels are referenced in Figure 8. Dashed black circles mark linkages in slabs B that require deformations of the octahedra. As mentioned in the text, rotations of octahedra in adjacent (001) layers occur in opposite directions leading to a doubled periodicity along the *c*-axis.

small and likely mitigated by reduced rotation angles at the strained locations.

In each of the four domains, the differences in the statistical distributions of the tilting angles around the x- and y-axes for the distinctly oriented octahedra in the average unit cell (i.e., labeled 1 and 2 in Figure 7) were consistent with the changes in the modulation direction. Given the highly symmetric and largely deformation-free character of octahedral tilts obtained in our refinements without any constraints other than the experimental data, we consider this result, which provides an explicit picture of the modulation, as reliable.

The magnitude of octahedral rotations decreases weakly but monotonically as the temperature increases (Figure 8). The reversal in the relative magnitudes of rotation angles around the x- and y-axes for the distinct octahedra in the domains representing variants I and II attests to the regularity of the tilting patterns. This reversal is also reflected in the PDDs calculated for the oxygen atoms in the refined configuration (Figures S8 and S9). Overall, our results support the original interpretation of the incommensurate modulation by Bursill and Lin<sup>8</sup> as arising from the intergrowths of slabs representing distinct but closely related structures. However, the octahedral rotations and their patterns identified here bear no resemblance to the modulation by displacements of apical oxygen atoms as proposed in their work and assumed in one of our starting models. Similar to perovskites, octahedral tilting in TTBs is driven by the chemical bonding requirements of the A cations and is accompanied by A-cation off-centering. The



**Figure 8.** Average tilting angle (about the in-plane axes) as a function of temperature for variant I, D1 (Figure 3). The red circles and blue squares refer to the rotations around the *x*- and *y*-axes, respectively, in Figure 7: (a)  $[(Nb1)O_6]$  and (b)  $[(Nb2)O_6]$ . For Nb2, the filled and empty symbols correspond to the types of  $[(Nb2)O_6]$  octahedra labeled as 1 and 2 in Figure 7. The relative magnitudes of rotation angles for these octahedral types are reversed for variant II, consistent with the tilting pattern depicted in Figure 7.

mixture of distinct tilting patterns leading to the incommensurate structure presumably represents a compromise between satisfying such requirements for Ba and Sr, which exhibit dissimilar ionic radii (in 12-fold coordination,  $R_{Ba}^{2*} = 1.61$  Å, and  $R_{Sr}^{2*} = 1.44$  Å), while maintaining minimal deformations for the oxygen octahedra. The presence of vacant A sites is also expected to affect the energetic balance.

In the commensurately tilted structure with a unit cell of  $2\sqrt{2a_t} \times \sqrt{2a_t} \times 2c_t$  and Ama2 symmetry,<sup>35</sup> half of the A2 cations [A2(1) in Figure S10] undergo off-center shifts preferentially along the a-axis, with opposite directions of the displacements in successive c-layers (Figure S10). This half corresponds to A2 sites with the long dimensions of their pentagonal channels oriented parallel to the a-axis, which represents the direction of the modulation. Symmetry restricts shifts of the other half of the A2 cations [i.e., A2(2)] as well as the A1 cations to the c-axis. The A-cation PDDs obtained by folding our refined configurations separately for each domain (D1 to D4) onto the  $\sqrt{2a_t} \times \sqrt{2a_t} \times c_t$  unit cell reveal highly anisotropic displacements of Ba and Sr on A2 sites. The PDDs for the A2 sites labeled A2(1) and A2(2) exhibit the largest displacements along the x- and y-axes, respectively, consistent with the orthogonal orientations of the pentagonal channels hosting these sites (Figure S10). Importantly, in D1, representing variant I, the x-axis displacements for site A2(1)are significantly larger than the y-axis displacements for site A2(2), whereas in D2 of variant II, this relationship is reversed. Such differences in the A-cation PDDs conform to expectations for the tilted structure as depicted in Figure 7. We used the IFT of the calculated incommensurate reflections to confirm that the A-cation displacement components, which contribute to the modulation, are antiparallel in the neighboring c-layers. As expected from crystal-chemical considerations, the magnitude of the Sr off-centering within the A2 sites exhibits a negative correlation with the average rotation angle for the adjacent octahedra; that is, larger rotations result in smaller Sr off-centering. Thus, the A-cation displacements are part of the modulation, with their directions and magnitudes coupled to the tilting patterns.

Nb Off-Centering. As in previous reports,<sup>13,14</sup> the average magnitudes of vectors describing the local Nb off-centering,  $\Delta_{\rm Nb'}$  are larger for Nb1 sites. A PDD for the angle between  $\Delta_{
m Nb1}$  and the *c*-axis (Figure 9c), calculated per steradian, peaks at zero, whereas a similar PDD for  $\Delta_{
m Nb2}$  reveals significant  $(15-30^{\circ})$  deviations of these vectors from the *c*-direction, with larger inclinations observed at higher temperatures. Such a difference in the directions of the off-centering on the two Nb sites agrees with the MD simulations.<sup>13</sup> Upon heating, the average moduli of the *c*-axis projections,  $\langle |\Delta_{Nb}^z| \rangle$ , for both Nb1 and Nb2 decrease monotonically, with  $\langle |\Delta^{z}_{Nb1}| \rangle$  changing more slowly across the transition at 350 K. These trends are also reflected in the nearest-neighbor Nb1-O and Nb2-O distance distributions calculated separately for the apical and planar oxygen atoms at 300 and 550 K (Figure 10). Our results agree with those of Li et al.,<sup>14</sup> suggesting a reduction in the *c*axis component of  $\Delta_{\mathrm{Nb}_{1}}$  on heating much more significant than that predicted by MD.

The average projections of  $\Delta_{\rm Nb}$  onto the *c*-axis,  $\langle \Delta_{\rm Nb}^z \rangle$ , are much smaller than the corresponding average magnitudes,  $\langle |\Delta_{\rm Nb}^z| \rangle$  (Figure 9a,b). Also, on heating,  $\langle \Delta_{\rm Nb}^z \rangle$  decays faster than  $\langle |\Delta_{\rm Nb}^z| \rangle$ , reflecting more equal fractions of positive and negative dipoles at higher temperatures, which can be regarded as a sign of the increasing dynamic disorder for the Nb1 and Nb2 sites. For a *P4/mbm*  $\leftrightarrow$  *P4bm* ferroelectric transition occurring at 350 K,  $\langle \Delta_{\rm Nb}^z \rangle$  is expected to go to zero above this temperature, which contrasts with the dependence presented in Figure 9. Rietveld refinements in the polar *P4bm* space group consistently produced non-zero polarization even at 550



**Figure 9.** (a) Temperature dependence of the average (over the configuration) magnitude of the local Nb off-centering,  $\Delta_{\rm Nb}$ . Solid lines with circles depict data for Nb1, and dashed lines with squares Nb2. Red indicates the total magnitude, blue the *c*-axis component, and green the in-plane component. (b) Temperature dependence of the average *c*-axis component of  $\Delta_{\rm Nb}$ ,  $\langle \Delta^z_{\rm Nb} \rangle$ . Squares depict data for Nb1, filled circles data for Nb2, and empty circles the average for Nb. (c) PDD for angle  $\theta$  between  $\Delta_{\rm Nb}$  and the *c*-axis calculated per steradian, as illustrated in the schematic drawing (inset). Black and red lines correspond to 300 and 550 K, respectively. Solid and dashed lines refer to Nb1 and Nb2, respectively. The maximum probability is at  $\theta = 0^{\circ}$  for 300 K but gradually shifts to larger angles as the temperature increases. Error bars reflect single standard deviations estimated from the three configurations refined from different starting models.

K, suggesting that the powder diffraction data have limited sensitivity to the loss of inversion symmetry in the average structure. In principle, given the diffuse nature of the transition for x = 0.61, the existence of a small macroscopic polarization above  $T_c$  can be real. However, our sequential approach to RMC refinements, in which the starting models for higher temperatures carried the polarization from lower temperatures, introduced a bias, which we believe is at least partly responsible for the non-zero values of  $\langle \Delta^z_{\rm Nb} \rangle$  above 350 K observed here. Nevertheless, the benefits of the sequential refinement approach, which significantly shortened the time to convergence and facilitated the comparison of configurations for different temperatures, outweighed the mostly negligible effects of this potential artifact on the interpretations of results.

The Nb off-center shifts along the *c*-axis are strongly correlated within the octahedral chains parallel to this direction. Such correlations, which give rise to the (00L, L) integer) sheets of diffuse intensity, are long-range, extending over the entire distance range spanned by the configuration. These correlations are weakly affected by temperature and remain significant at 550 K for both Nb1 and Nb2. Strong interchain correlations also exist at room temperature (Figure 11), yielding nanoscale domains with positive and negative



**Figure 10.** Partial PDFs displaying nearest-neighbor distance distributions for the Nb–O (a) apical O1 and (b) planar O2, (c) Sr(A1)–O, and (d) Sr(A2)–O and Ba–O pairs. The Nb–O partials are presented for 300 K (solid lines) and 550 K (dashed lines), with those for the Nb1–O and Nb2–O pairs colored red and blue, respectively. The Sr–O (red) and Ba–O (blue) distributions are shown for only 300 K because no significant changes occur at higher temperatures. (e) Schematic drawing of the coordination of Nb with the apical O1 and planar O2 atoms indicated. The *c*-axis direction is indicated. The levels of statistical uncertainty for the Nb1–O and Nb–O2 partials are exemplified using the uncertainty band (gray) for the Nb–O1 partial at 300 K. For the Sr–O and Ba–O partials (c and d), such uncertainty levels are within the line thickness.



**Figure 11.** (a and b) Distance dependence of a parameter describing the transverse spatial correlations among the *c*-axis Nb off-centering (i.e.,  $\Delta_{Nb}$ ) for the Nb1–Nb1 and Nb2–Nb2 pairs, respectively. Different symbols and colors refer to the four temperatures: black filled circles, 300 K; red squares, 350 K; blue triangles, 425 K; green empty circles, 550 K. (c) Temperature dependence of the correlation parameter for the *c*-axis components of  $\Delta_{Nb}$  for the nearest-neighbor Nb1–Nb1, Nb2–Nb2, and Nb1–Nb2 pairs. Empty symbols with solid lines are along the Nb1 (red circles) and Nb2 (blue triangles) *c*axis chains. Filled symbols with dashed lines are perpendicular to the chains for Nb1–Nb2 (green squares), Nb1–Nb1 (red circles), and Nb2–Nb2 (blue triangles) pairs.

directions of the Nb off-centering, respectively (Figure 12). The domain volumes are unequal, producing a finite net polarization over the configuration, consistent with the polar



**Figure 12.** Sections of the refined configurations at (a) 300, (b) 350, (c) 425, and (d) 550 K with dots representing the  $[NbO_6]$  octahedra. The color scale encodes values of the Nb off-centering along the *c*-axis, where dark blue and red limits denote the positive and negative directions, respectively. At 300 K, the presence of two nanoscale domains with Nb off-centered in opposite directions is observed. These domains are barely visible at 350 K and disappear at higher temperatures even though the distribution of the positive and negative values still exhibits clustering. The domains observed at 300 K are three-dimensional.

macroscopic structure. The interchain correlations decay rapidly upon heating (Figure 11) with a critical dependence across the ferroelectric transition temperature. Such diminishing transverse correlations reflect changes in the appearance of the diffuse intensity distributions within the (00L) sheets from segmented (centered on the Bragg peaks) at room temperature to relatively continuous at 550 K. A spatial distribution of the local polarization becomes increasingly disordered at higher temperatures, but noticeable nanoscale clustering of the Nb [001] chains carrying positive and negative electric dipoles is maintained even at 550 K. Our observation of the nanoscale ferroelectric domains and their gradual disappearance on heating across the transition is consistent with the results of PFM measurements.<sup>36,37</sup> Figure S11 displays a schematic illustrating the mutual arrangement of the nanoscale polar (i.e., red and blue in Figure 12) and tilting domains (D1–D4 in Figure 3) at room temperature, as well as the plot showing how the local polarization evolves into the average for the RMC-refined configuration.

As expected, the Nb off-centering is affected by the local chemistry (Figure 13). Vacant A sites around Nb enhance  $\Delta_{Nb}$ ,



**Figure 13.** Dependence of the average magnitude of Nb off-centering on the number of (a and b) A-site vacancies and (c and d) Sr cations in the first A-site coordination sphere of Nb (Figure 1b,c). These values were determined by surveying the  $[(Nb1O_6)A1_4]$  and  $[(Nb2O_6)A1_4A2_2]$  coordination environments in the refined configurations. Here, no distinction is made between the A1 and A2 sites. (a and c) Nb1 and (b and d) Nb2. Red for total and blue for the *c*-axis component,  $\Delta^z_{Nb}$ . Green for the in-plane component. The Sr content primarily affects the in-plane component of the Nb offcentering.

consistent with predictions of the MD simulations.<sup>13</sup> The presence of Sr also amplifies  $\Delta_{Nb'}$  despite the contraction of octahedral volumes as the local Sr:Ba ratio increases. Such an enhancement, which reflects interactions between the Nb and A cations through their shared oxygen neighbors, occurs primarily via the increase of the in-plane components of the Nb displacements, whereas changes in the *c*-axis projections are relatively small. Therefore,  $\Delta_{Nb}$  deviates more strongly from the average polar axis as the number of Sr cations around Nb increases (Figure 14); this effect is particularly significant for Nb2. The amplifying effect of Sr on  $\Delta_{Nb}$  resembles a trend observed in perovskites, such as in Ca-substituted BaTiO<sub>3</sub>, where off-center displacements of the small A-site species support those of the B cations.<sup>38</sup>

**Polar versus Antipolar Modes for Nb.** HOL (*L* integer) reflections with H = 2n + 1 (and the equivalent OKL reflections) are extinct in the *P4bm* structure but appear in the



**Figure 14.** Average modulus of angle  $\theta$  between  $\Delta_{Nb}$  and the *c*-axis (see the inset of Figure 9c) as a function of the number of Sr on the A sites. These angle values were determined by surveying the  $[(Nb1O_6)A1_4]$  and  $[(Nb2O_6)A1_4A2_2]$  coordination environments in the refined configurations: red for Nb1, black for Nb2, and blue for the average for Nb.

experimental diffuse scattering data, suggesting a violation of the *b*-glide symmetry, at least locally. Moreover, the diffuse scattering intensities near *H0L* reflections with H = 2n + 1 and H = 2n exhibit distinctly different temperature dependencies (Figure 15a,b).<sup>20</sup> Our calculated diffuse scattering reproduces such differences (Figure 15c,d). Previously, the diffuse scattering near the *H0L*: H = 2n + 1 reflections has been attributed to antiferroelectric fluctuations.<sup>20</sup> We used the IFT approach to test this hypothesis as discussed below. We considered the diffuse scattering to be caused exclusively by



**Figure 15.** Temperature dependence of the X-ray diffuse scattering intensity near the (a and c) H01: H = 2n and (b and d) H01: H = 2n + 1 loci for (a and b) experimental data and (c and d) data calculated for the RMC-refined configurations. In each case, the diffuse intensity was calculated as an integral over a spherical shell centered on the corresponding H0L reflection. The intensity near the H01: H = 2n reflections exhibits a sharp peak at 350 K, whereas that for the H01: H = 2n + 1 loci increases to a maximum at 425 K, decreasing somewhat upon further heating to 550 K. For the latter set of reflections, as shown in ref 20, the actual dependence about 425 K is plateau-like, with a steady decay toward 550 K; the broad peak appearance of this trend here exists because only two temperature points were used. The statistical uncertainties in these intensities are smaller than the symbol size.

the off-center shifts of Nb, which were calculated for the refined configurations by replacing the coordinates of Nb with the  $\{xyz\}$  components of  $\Delta_{Nb}$  and omitting all other atoms.

Analyses of distortions associated with irreducible representations of the P4bm TTB structure using the ISODISTORT software<sup>39</sup> reveal two principal antipolar modes,  $\Gamma_2^-$  and  $M_1^+M_4^+$ , depicted schematically in Figure 16. A recent study



**Figure 16.** Schematic rendering of the *c*-axis structural projection of the TTB structure illustrating the antipolar (a)  $\Gamma_2^{-}$  and (b)  $M_1^+M_4^+$  modes of Nb displacements along the *c*-axis. Filled circles and crosses mark positive and negative directions of these displacements, respectively.

identified these modes as possibly unstable for another TTB compound,  $K_2LaNb_5O_{15}$ .<sup>40</sup> We verified the sensitivity of our IFT procedure to such patterns of displacements by generating model atomic configurations that contained nanoscale clusters with the Nb atoms displaced according to the  $\Gamma_2^-$  and  $M_1^+M_4^+$  modes; these clusters were in a matrix featuring random Nb displacements (Figure S12). We then calculated the diffuse scattering for these models and applied the IFT to the diffuse *HKL* (L = 1 or 2) peaks. The results of these tests presented in the Supporting Information demonstrate a successful recovery of clusters with the given types of distortion modes (Figure S12).

Finally, we applied the IFT to the diffuse scattering calculated for our refined configurations. First, we performed the IFT for the diffuse scattering amplitude around the H0L: H = 2n + 1 (L = 1 or 2) reflections. The resulting signal reveals nanoscale regions that exhibit an IFT magnitude significantly greater than that of the rest of the configuration (Figure 17 and Figure S13). When  $T \ge 425$  K, the displacements of Nb atoms in such areas display a well-ordered antipolar pattern, which thus appears to be the origin of the diffuse intensity around the reflections forbidden by P4bm symmetry. When T < 425 K, a similar pattern is observed but with defects (Figure S13). Our IFT analyses for the simulated structures with nanoscale domains exhibiting different antipolar displacements indicate that the recovery of complete displacement patterns requires all of the reflections. Guided by these simulations, we focused on the Nb atoms in the regions with the largest magnitude of IFT for H0L: H = 2n + 1 and performed the IFT using the diffuse amplitude around all HKL (L = 0, 1, or 2) reflections. Remarkably, when  $T \ge 425$  K, the obtained pattern of displacements matches that in the antipolar  $\Gamma_2^-$  mode (Figure 17b). At lower temperatures, only the polar displacements could be observed.

When  $T \ge 425$  K, the polar  $\Gamma_3^-$  and antipolar  $\Gamma_2^-$  modes for the Nb off-centering coexist and compete with each other. The coherence lengths for these modes in the  $\{ab\}$  plane are on the



**Figure 17.** (a) Intensity map for the IFT using the diffuse intensity near the *H*0*L*: H = 2n + 1 (L = 1 or 2) reflections for a single layer of Nb in the refined configuration at 425 K. The diffuse scattering used in the IFT was calculated for the Nb off-centering. (b) Map of directions of the Nb off-centering along the *c*-axis in the region exhibiting the maximum intensity of the IFT in panel a. These directions were determined by performing the IFT for the Nb atoms in that region using the diffuse intensity for all of the *HKL* (L = 0, 1, or 2) reflections in the diffuse scattering calculated for the Nb offcentering. The red and blue colors correspond to the Nb off-centering directed parallel and antiparallel to the *c*-axis, respectively. The pattern (outlined by a rectangular) matches that for the antipolar  $\Gamma_2^-$  mode in Figure 16. The results for other temperatures are summarized in Figure S7.

order of several nanometers, whereas the clusters are much longer parallel to the *c*-axis; essentially, the nanodomains featuring well-developed antipolar order acquire cylinder-like shapes. Judging from the maps of  $\Delta^{z}_{Nb}$ , the polar distortion mode has a larger amplitude and below 425 K is decisively more favorable. A sharp peak of the diffuse intensity near *HOL*: H = 2n observed around 350 K can be attributed to the increase in the number of transverse correlations among the polarized octahedral chains on cooling, with the diffuse intensity in the {00*L*} planes being concentrated around the Bragg peaks.

**Coupling of Polar Displacements for Nb1 and Nb2.** We used structural models (all *P4bm*) for a series of SBN compositions determined by Podlozhenov et al.<sup>12</sup> to calculate various characteristics relevant to the present discussion (Figure 18). As the Sr content, *x*, increases, the c/a ratio decreases linearly with a concurrent contraction of the unit-cell and octahedral volumes. For the same composition, the volumes of  $[(Nb2)O_6]$  octahedra are significantly larger than those of  $[(Nb1)O_6]$  with this difference progressively diminishing as *x* increases. The larger volumes for the  $[(Nb2)O_6]$  octahedra are associated with in-plane expansion of their bases.

Nb1 sites are off-centered exclusively along the *c*-axis, and the magnitude of these shifts remains relatively unaffected by composition. In contrast, the *c*-axis displacements for Nb2, which at x = 0.33 are similar to those for Nb1, decrease monotonically as *x* increases. The in-plane component of the Nb2 off-centering exhibits the opposite trend so that for x = 0.82, the in-plane and *c*-axis shifts become similar. The relation between the  $\langle | \Delta^{z}_{Nb} | \rangle$  values for Nb1 and Nb2 is the opposite of what would be expected from the volumes of their respective oxygen octahedra. Presumably, the larger  $[(Nb2)O_{6}]$  octahedral bases enhance the off-axis Nb shifts while reducing the off-centering along the polar axis.

Overall, the average-structure data suggest that orientations of electric dipoles on the two Nb sites become progressively



**Figure 18.** Average-structure characteristics as a function of Sr content, *x*, calculated using atomic coordinates reported previously from refinements of the *P4bm* model against structure factors from deduced single-crystal X-ray diffraction data:<sup>12</sup> (a) c/a ratio, (b) unitcell volume,  $V_{uc}$  (c) octahedral volume (red squares for Nb1 and blue circles for Nb2), and (d) average Nb off-centering (red squares for Nb1 along the *c*-axis, blue circles for Nb2 along the *c*-axis, green for data in the {*ab*} plane, and blue half-filled circles for the total).

decoupled as the Sr content increases, which coincides with the emergence of relaxor behavior. The evolution of the diffuse intensity distributions in the (00*L*) (*L* integer) planes with an increasing *x*, which changes from being tightly condensed around Bragg reflections for x = 0.33 to continuous sheets for x = 0.82,<sup>2</sup> is another manifestation of a gradual loss of correlations between the octahedral chains hosting Nb1 and Nb2. A similar loss of correlations between these chains and the orientational decoupling of the off-center shifts for Nb1 and Nb2 also occurs for the presently studied x = 0.61compound upon heating.

As noted previously and observed here, A2 cations undergo large off-center displacements directed preferentially in the  $\{ab\}$  plane, although their *c*-axis components are also significant; expectedly, the displacements of Sr on these sites are noticeably larger than those of Ba. The occupational disorder on the A2 sites creates displacive disorder around Nb, which in turn affects the directions of the Nb off-centering. Our results demonstrate that the deviations of these directions from the *c*-axis become larger as the local Sr:Ba ratio increases, similar to the trend observed for the average structure as a function of x. Likewise, we see that heating the x = 0.61structure to higher temperatures enhances deviations of the Nb off-centering from the *c*-axis, also with concurrent decay of the transverse Nb1-Nb2 correlations. Altogether, these results suggest that increasing the displacive disorder via adjustments in composition or heating weakens the coupling between Nb1 and Nb2, in agreement with the distinct dynamics of the two Nb subsystems as observed in MD simulations.<sup>13</sup>

**Microscopic Interpretation of the Crystal–Chemical Trend.** The local-chemistry dependence of the Nb offcentering identified here, together with analyses of the reported average structures for a broad range of Sr:Ba ratios, suggest a simple microscopic model for the crystal–chemical trends identified by Zhu et al.<sup>6</sup> Indeed, the unit-cell and octahedral volumes shrink monotonically with the substitution of smaller species on the A2 sites. Nevertheless, this effect per se may not be the cause of the suppression of the Nb offcentering and the emergence of dielectric relaxation.

As revealed in Figure 18, the average off-centering on the Nb1 sites remains constant despite the contraction of the hosting octahedral volumes. Likewise, for a given composition, such as x = 0.61 studied here, the local off-centering appears to be enhanced by the presence of Sr cations around Nb, despite the concurrent contraction of the oxygen octahedra. However, having a larger fraction of smaller A-site species that exhibit significant off-center displacements in the  $\{ab\}$  plane promotes displacive disorder on the Nb sites, leading to larger deviations of the Nb off-center shifts from the polar axis and weakening the Nb1–Nb2 coupling.

We propose that such weaker coupling between the two polar sublattices determines the transition from a ferroelectric response to a relaxor. The MD simulations<sup>2,13</sup> point to the same conclusion. The weaker coupling also limits the transverse correlations for the Nb chains, with the formation of nanoscale regions of opposite polarity that reduce the level of overall polarization and also contribute to the relaxor response. The type of tilting involved in the incommensurate modulation is accompanied by minimal octahedral deformations and as such does not directly affect the polar response of TTBs. However, the introduction of sufficiently small A cations, as in ref 7, can stabilize another type of rotation requiring significant deformations of octahedra. In this case, the coupling between the B1 and B2 sublattices becomes enhanced, suppressing relaxations and leading again to a classic ferroelectric response. Thus, the entire empirical trend relating the average A-cation radius and the perovskite-like tolerance factor on the A1 sites to the polar response of TTBs can be accounted for by a single fundamental characteristic, the degree of coupling between B-cation off-centering in symmetrically distinct octahedral sites.

# CONCLUSIONS

We adapted atomistic refinements using combined total scattering and EXAFS data from powders and 3D diffuse scattering data from single crystals to tetragonal tungsten bronze structures exhibiting large unit cells and nanoscale twin domains associated with an incommensurate displacive modulation. Our results revealed that this modulation is associated with a mixture of structural slabs exhibiting distinct patterns of octahedral rotations that are directed to minimize octahedral deformations. These slabs have thicknesses of  $2\sqrt{2a_t}$  and  $1.5\sqrt{2a_t}$ , respectively, and the tilting pattern in the former is the same as that observed in the commensurate superstructure of barium sodium niobate, Ba2NaNb5O15. Such a mixture likely provides an energetic compromise between the bonding requirements of Ba/Sr on the A sites and the rigidity of the [NbO<sub>6</sub>] octahedra. The resulting tilting pattern in the incommensurate modulation is such that it weakly couples to the polar displacements on Nb. For the Nb off-centering, which determines the overall polarization, we find that above the effective temperature of the paraelectric-to-ferroelectric phase transition, the competing polar  $\Gamma_3^-$  and antipolar  $\Gamma_2^$ distortion modes coexist, with the latter appearing as nanoscale fluctuations; the antipolar mode becomes unfavorable below the transition. These observations suggest the possibility of stabilizing long-range antipolar distortions in TTBs, yielding antiferroelectric structures. Recent studies report the formation

of an antiferroelectric phase in  $K_2LaNb_5O_{15}$ , although the exact nature of the double-hysteresis loops observed requires further verification.

Our results confirm distinct displacive behavior on the two symmetrically inequivalent Nb sites and suggest the dependence of their coupling on the Sr content. We use this observation to propose a simple microscopic interpretation of the previously reported empirical trend relating the geometric tolerance factor and ionic radii of the A cations to the type of polar behavior in TTBs. Substitution of smaller A cations into the 15-fold coordinated sites, which exhibit significant offcenter displacements in the  $\{ab\}$  plane, induces orientational disorder for polar off-centering on the lower-symmetry B2 sites, with weaker coupling to polar shifts of the highersymmetry B1 cations. As a result, the response changes from ferroelectric to relaxor. Introducing higher concentrations of vacancies on the A sites is thought to have a similar effect. In systems with A cations that are sufficiently small to support a change in the type of octahedral rotations from mostly deformation-free to that requiring strongly deformed octahedra, the resulting distortions enhance the coupling between the Nb networks, changing the response back to ferroelectric.

As a final remark, this work demonstrates the power of combining powder and single-crystal data in atomistic RMC refinements for uncovering highly complex nanoscale interatomic correlations. Computing speed remains a limiting factor, highlighting the need to develop much faster algorithms for calculating single-crystal diffuse scattering, making full use of modern computing power. These improvements would enable the fitting of diffuse scattering over significantly larger volumes of reciprocal space with better resolution as well as the combination of 3D data sets obtained using different radiation sources (e.g., X-rays, neutrons, and electrons). The result would be considerable advances in the applicability and fidelity of nanoscale structural models.

# ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.2c02367.

Details of Rietveld refinements, 3D rendering of the experimental single-crystal X-ray diffuse scattering, data fits for 550 K, atomic-resolution STEM and HRTEM data, figures illustrating various aspects of the RMC-refined models, results of the IFT analyses for the simulated data, and results of the IFT analyses for the RMC-refined models versus temperature (PDF)

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## Notes

The authors declare no competing financial interest.

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# ADDITIONAL NOTE

<sup>*a*</sup>The identification of any commercial product or trade name does not imply endorsement or recommendation by the National Institute of Standards and Technology.

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