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ABSTRACT

We use dark-field x-ray microscopy to reveal evidence of subtle structural heterogeneity in BaTiO3 single crystals at temperatures of 150 °C—well above the Curie temperature of 125 °C. The heterogeneity exhibits domain-like ordering on the scale of several micrometers, pronounced curvature, and a preference for (110) lattice directions. Complementary high-resolution x-ray reciprocal space measurements suggest that the features originate from point defects (most likely oxygen vacancies) that coalesce along pre-existing domain walls during aging. A simple thermodynamic model suggests that the weak elastic strains associated with the heterogeneity are likely to locally raise the Curie temperature in their vicinity, creating nucleation sites for the ferroelectric phase upon cooling through the ferroelectric phase transition.

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Structural heterogeneity is crucial to many of the macroscopic functional properties of ferroelectric materials. Local variations to the lattice can have marked effects on local polarization and electronic structure, as well as serving as pinning centers for mobile interfaces or nucleation sites for new phases. In complex oxide ferroelectrics, the typical sources of structural heterogeneity range from oxygen vacancies, dislocations, domain walls, interphase and grain boundaries, and inclusions and pores. These defects and their associated electric and elastic fields create lattice distortions at nearly every relevant length scale, from the atomic to the scale of entire grains (and potentially beyond). Correspondingly, defects have the potential to influence—and even define—the macroscopic functionality of ferroelectric materials and devices. For example, the dynamic formation and distribution of vacancy dipoles can enhance the recoverable energy density and strain via domain wall pinning and, at larger scales, homogeneities can be unpredictably and catastrophically affected by long-range clamping strains from grain boundaries and dislocations. Whether such heterogeneities improve or diminish the final macroscopic properties of a ferroelectric material depends entirely on the complex interplay between the type of defects present, their interactions, and their distribution.

Heterogeneity is also believed to be critical to the phase transition between the paraelectric and ferroelectric states, where the electric and elastic fields created by defects influence the nucleation and growth of domains, and can significantly affect the resulting domain morphology. Even in relatively "pure" ferroelectrics, such as BaTiO3, polar heterogeneity can be inferred from dielectric spectroscopy and x-ray scattering measurements well above the Curie temperature (Tc). While it is speculated that this heterogeneity may seed the formation of polar domains at the transition, it has not been directly observed. It is also likely that domains nucleate from defects with long-ranging strain fields, such as dislocations. Reliably predicting nucleation from such long-ranging heterogeneities, however, is a significant challenge that requires a coherent simulation framework spanning multiple length scales. Such models require either an exceptionally large grid size (which is computationally intensive) or an amalgamation of different models (which is complex and seldom robust). Furthermore, multi-scale data do not exist for guiding and validating such multi-scale models. As such, the role of structural heterogeneity is not typically accounted for in many theoretical and simulated treatments of phase transitions in ferroelectrics.

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To date, experimental investigations into the role of defects in the ferroelectric phase transition have been limited to either individual length scales or to the surfaces of samples. For example, surface imaging techniques, such as second harmonic generation (SHG) microscopy,\textsuperscript{7} piezoresponse force microscope (PFM),\textsuperscript{13,18} scanning x-ray diffraction microscopy,\textsuperscript{19} and x-ray photoelectron emission microscopy (X-PEEM),\textsuperscript{16} are prevalent for studying the morphology and structure of the emerging ferroelectric phase. However, the biaxial strain state at the surfaces of samples means that the measurements of both the defects and the phase transition itself may not be representative of the bulk material.\textsuperscript{17} Macroscopic properties and average structural measurements, such as of the dielectric response and large-signal polarization and strain hysteresis,\textsuperscript{17} provide direct insight into the functional and property changes associated with the phase transition, while high-energy powder x-ray diffraction provides a direct correlation with structural changes.\textsuperscript{5,6,21} Though sensitive to the bulk material, such macroscopic and average measurements cannot correlate the transition and morphology to specific defects and their local vicinity, however. Ultimately, we require the ability to visualize the structure and morphology \textit{in situ} around individual embedded defects during the ferroelectric phase transition.

Dark field x-ray microscopy (DFXM) is a synchrotron-based technique that can probe a defined volume in a bulk material, where both the elastic distortions around individual defects and the nucleating domains can be imaged directly and in real-time during heating, cooling, or the application of electric fields.\textsuperscript{5,6,21} In this paper, we report the presence of subtle, ordered microscale structures in BaTiO\textsubscript{3} single crystals at temperatures >25 K above \(T_C\). Based on both DFXM images and high-resolution x-ray reciprocal space maps (RSMs), we show that the structures likely originate from the agglomeration of point defects around pre-existing domain walls. We speculate that this may influence the repeatability of the domain structure upon successive heating and cooling cycles.

Single crystals of BaTiO\textsubscript{3} were purchased commercially (Crystal GmbH, Germany) with dimensions of \(5 \times 5 \times 0.5 \text{ mm}^3\) and ground and polished to a final thickness of 0.15 mm. To remove any residual strains imparted during polishing, the crystals were subsequently annealed at 400 °C for two hours with a heating and a cooling rate of 1 K/min. Silver electrodes with approximate dimensions of \(4 \times 4 \text{ mm}^2\) were hand-painted onto the opposing \(5 \times 0.5 \text{ mm}^2\) faces. In addition to the application of electric fields to the sample, the silver electrodes also act as a charge sink to avoid charge build-up during the synchrotron x-ray experiments.

The DFXM and RSM measurements were carried out at the hard x-ray microscope located on beamline ID06 at the European Synchrotron Radiation Facility (ESRF). The sample was mounted using a dedicated sample environment\textsuperscript{17} and heated using a hot gas blower (Cyberstar, France). A photon energy of 17 keV (\(AE/E = 10^{-5}\)) was used such that the crystal could be imaged in transmission geometry through the 0.15 mm direction with an attenuation of approximately 75%. The 200 Bragg reflection was used for both the DFXM and RSM measurements, at a scattering angle of \(2\theta \approx 20.92°\). The measurements sampled a 400 × 0.5 mm\textsuperscript{2} section through the sample, generated using line-profile illumination from a one-dimensionally focusing compound refractive lens (CRL) positioned approximately 500 mm upstream of the sample. The DFXM setup utilized an objective CRL with a 250 mm focal length, placed between the sample and CCD-based x-ray imaging detector, along the path of the 200 Bragg reflection. This resulted in a geometrical magnification of 19× and a nominal spatial resolution of 70 and 183 nm/pixel in the horizontal and vertical directions, respectively. Acquiring images while scanning the tilt of the sample around the two axes orthogonal to the scattering vector then permitted the reconstruction of quantitative maps of the local lattice misorientation within the selected scattering volume.\textsuperscript{22}

Figure 1 shows DFXM intensity images obtained (a) at room temperature and (b) at 150 °C—approximately 25 K above the \(T_C\) for BaTiO\textsubscript{3}. The room temperature image shows the periodic stripe-like features in the intensity contrast one would expect from a ferroelectric single crystal with domains along \{110\} lattice planes. This corresponds well with both previous DFXM images of BaTiO\textsubscript{3} using the 200/002 reflection\textsuperscript{5} as well as images obtained using comparable techniques, such as electron microscopy.\textsuperscript{18} We note that, for the room temperature image (a), the angular deviations between the domains in the central region and the top and bottom regions are an artifact due to the projection of the surface domain structure from the finite thickness of the illuminating x-ray beam.

We initially hypothesized that, upon heating the crystal above \(T_C\), the stripe-like intensity contrast from the domains should completely disappear as the sample transformed from the ferroelastic tetragonal phase to the paraelectric cubic phase (which cannot contain crystallographic twins). The DFXM intensity image of the paraelectric crystal should, therefore, be a flat representation of the sample with no discernable intensity contrast. Instead, the DFXM images we acquired revealed clear stripes, with a periodicity of approximately 3–10 μm. The stripes alternate in light and dark intensity, are approximately oriented at the same angle as the room temperature domains, but have a fourfold to fivefold increase in width. Most strikingly, the boundaries between the stripes exhibit significant curvature reminiscent of those seen in improper ferroelectrics.\textsuperscript{18} Structural features resembling those in Fig. 1(b) have not been reported in the literature; however, we note that the DFXM intensity images correspond to an extremely small region of reciprocal space\textsuperscript{25} and, as such, it is possible that these features are blurred when imaged by more conventional diffraction-based techniques with larger angular bandwidth.

In discussing the origin of these features, we first consider whether they could arise as an artifact of the DFXM technique. Similar to other diffraction imaging methods like dark-field TEM or x-ray section topography, DFXM is susceptible to artifacts from dynamical scattering, which appear as alternating bright and dark sinusoidal fringes parallel to the incident surface of the scattering volume.\textsuperscript{22} In the present case, however, the regions are clearly oblique to the surface of the crystal (which is parallel to the bottom of the image frame), and the intensity variations have relatively sharp boundaries that do not resemble sinusoids (see the supplementary material A). Furthermore, the bright boundaries that we observe vary in thickness and intensity, most noticeably around their regions of highest curvature. Since this is observed in the bulk of a single crystal, we conclude that the wavy domain-like features depict true structural heterogeneities within the crystal. As such, another possible explanation for the wavy, stripe-like features is that the crystal was not sufficiently beyond the \(T_C\) to be completely paraelectric, and the features are simply ferroelastic domains of the room-temperature tetragonal symmetry. However, the mechanical compatibility requirements for ferroelastic domains dictate that the walls lie on well-defined lattice planes (e.g., [110]), meaning...
that this cannot explain the pronounced curvature of the boundaries that we observe. We note that, while local strains may cause domain wall curvature, such strains would be clearly visible in the DFXM images and, due to their required magnitude, would certainly obscure the stripe-like features altogether. Purely ferroelectric domain walls (i.e., 180°) do not have the same elastic compatibility requirements and, as such, may be curved. However, the intensity contrast in DFXM images of 180° domain walls is entirely phase contrast and, as such, cannot account for the large difference in the average intensity of the alternating stripes that we observe.

Excluding the possibility of instrument artifacts or domain walls, we employed high-resolution x-ray reciprocal space mapping to provide more detailed insight into the crystallographic irregularities within the sampling volume of the crystal. As the RSMs were measured using the same experimental setting and geometry as the DFXM images (i.e., by simply removing the objective lens), the maps correspond to the same volume of material probed in Fig. 1.

Figure 2 shows integrated projections through each of the three orthogonal reciprocal space dimensions, detailing the extent of the structural heterogeneity. The reciprocal space intensity distribution can be summarized as two plate-like features, each with slightly different positions and orientations. The separation between the plates is readily shown in Fig. 2(c) and quantified accordingly (see the supplementary material B); however, the orthogonal perspectives, shown in Figs. 2(a) and 2(b), do not show such separation. Nonetheless, the plate-like intensity distributions exhibit a fine structure that deviates from the smooth, ellipsoidal Gaussian that one would expect from an ideal (i.e., homogenous and un-strained) cubic crystal. We, therefore, conclude that our diffracting volume predominantly contains two discrete [200] lattice vectors and, thus, the crystalline distortions necessary to rotate the relatively large volumes of the material defined by the wavy stripe-like features.

The small rotations in the lattice vector seen in the RSMs can be directly correlated with the stripe-like features in the DFXM images by studying the maps of lattice mosaicity reconstructed from DFXM images acquired under different sample tilt angles (Fig. 3). Here, the map represents the average local lattice tilt (misorientation) around the rotational axis concentric with the azimuthal axis of the x-ray scattering. Assuming a coherent lattice (i.e., no dislocations), this misorientation must arise only from small, local lattice strains.

In general, the stripe-like features have a relatively constant lattice orientation that are separated by much larger changes in orientation at their boundaries. This is exemplified in the line plot in Fig. 3(b), where an angular deviation of -0.0023° is observed at the boundary between two adjacent stripes. Furthermore, the local intensity-angle reciprocal space maps (extracted from the raw DFXM datasets) for each

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**FIG. 1.** DFXM intensity images of the BaTiO3 single crystal, acquired using the (200) Bragg reflection. (a) Room-temperature image characterized by straight domain walls through the entirety of the bulk. (b) High-temperature (150 °C) image above Tc (Tc = 125 °C) exhibiting wavy features across the entire field of view. (c) Close-up region of interest of the high-temperature image showing visible fringe patterns between the different areas with low and high intensity. Note that for all images, the sample surfaces are located at the top and bottom extremes of the image and are parallel to the incident x-ray wave-front. We note that the intensity scale is identical for all three images.

**FIG. 2.** High resolution RSMs of the 200 Bragg peak measured at 150 °C (i.e., above Tc). Each panel shows an integration over different dimensions in q-space; (a) qz, (b) qy, and (c) qx. The scale bar denotes average (measured) photon count.
The order of 2.8 Å, resulting in lattice tilts of 0.13°—orders of magnitude larger than we observe here. As such, we instead posit that the distortions at the stripe boundaries are caused by local chemical heterogeneity.

It is difficult to ascertain exactly what role domain imprinting might have in the bulk of a macroscopic single crystal. One explanation is that the imprint acts as nucleation sites for the ferroelectric phase upon cooling through $T_C$. More specifically, the elastic strains around the boundaries between our domain-like features may be sufficient to locally raise the $T_C$ in the vicinity. These regions would then be the first to transform into the ferroelectric state and act as seeds for the further growth of the domain throughout the bulk.

To estimate the extent to which $T_C$ may be augmented by the residual strains imparted by oxygen vacancies, we first used density functional theory (DFT) to calculate the average volume change around a single oxygen vacancy in BaTiO$_3$. Simulating single vacancies in $2 \times 2 \times 2$ and $3 \times 3 \times 3$ supercells revealed a tetragonal distortion with a volume increase in 0.8%. Using the tabulated value for the elastic modulus of BaTiO$_3$ of 65 GPa, this results in approximate stress on the order of 400 MPa in the immediate vicinity of the defects. Following the work of Rosetti and others, compressive stress will augment the Curie temperature according to $\Delta T_C = 2\omega C(Q_1 \sigma_1 + Q_2 \sigma_2)$, which, again using tabulated values for the electrostrictive coefficients, suggests a local increase in $T_C$ on the order of 40 K (Ref. 31) (see the supplementary material C and D for further details).

Such a small and localized lattice distortions are most likely explained by the presence of oxygen vacancies, which are well known to agglomerate in complex oxide materials. The strain fields from individual vacancies generally have a fast, inverse-cube decay with distance from a point defect over the surrounding unit cells. However, it is conceivable that the agglomeration of many such vacancies would combine to produce an appreciable strain field whose average magnitude would be correlated with the average density of vacancies. This agglomeration is likely driven by aging, i.e., the accumulation of oxygen vacancies at local regions where the affinity is highest. It is well known that such regions may occur at domain walls (particularly when charged) and that these regions may be distorted by residual strains. It is, therefore, conceivable that the distortion of these high-affinity lines by long-range residual strains results in the curved boundaries that we observe.

Our interpretation of our observations would, therefore, be closely related to domain imprint. Using a photoemission electron microscopy-based methods, stripe-like features resembling domains have been observed at the surfaces of ferroelectric single crystals (including BaTiO$_3$) well above $T_C$. Similarly, the explanations of this imprint tend to be based on the accumulation of point defects (namely oxygen vacancies) at domain walls. However, while prior work concluded that domain imprint is predominantly a surface phenomenon, our results indicate that it may instead be a bulk phenomenon that occurs deep within macroscopically sized single crystals.

In summary, we used dark-field x-ray microscopy to reveal an unusual pattern of structural heterogeneity embedded within the bulk of a BaTiO$_3$ single crystal heated to 25 K the Curie temperature. The patterns, which repeat on the scale of several $\mu m$, resemble classical ferroelastic domains, but with boundaries that exhibit an unusually...
high degree of curvature. Although the lattice distortions associated with these features are small (on the order of 0.01 Å), the stresses associated with them are sufficient to locally increase the Curie temperature by tens of K. As these features exist above the TC, we speculate that features associated with them are sufficient to locally increase the Curie temperature with these features small (on the order of 0.01 Å).

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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