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Effect of Stoichiometry on the Structure and Polarization of BaTiO₃

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Barium titanate (BaTiO₃) is a material of interest for photonic device applications due to its strong optical non-linearity. However, BaTiO₃-based devices have not found widespread adoption, in part due to the challenges associated with synthesizing high quality thin-films. Here, high-resolution scanning transmission electron microscope (STEM) imaging is used to investigate the atomic structure of both on- and off-stoichiometric BaTiO₃ synthesized by molecular beam epitaxy (MBE). This investigation reveals an asymmetry in the way the BaTiO₃ atomic lattice accommodates off-stoichiometry growth and unveils features beyond what is expected from diffraction or surface characterization techniques. Excess titanium incorporates into the BaTiO₃ lattice to form pervasive defects despite films appearing high-quality diffraction with low surface roughness. Excess barium forms a rough, water-soluble surface layer but does not significantly impact the quality of the BaTiO₃ lattice. We use STEM to map titanium atom displacement in real-space and find an average displacement distance of 30-60 pm in the strained thin-films, higher than the < 20 pm displacement in bulk BaTiO₃. We also find that the titanium atom displacement direction deviates from the *c*-axis of the unit cell, which may have implications for the material's electro-optic tensor and thus for electro-optic device design.

I. INTRODUCTION

1 In recent years, thin film barium titanate (BaTiO₃) has been gaining interest as a platform for integrated photonic devices, in large part due to its record high Pockels coefficient [1, 2]. There have been several experimental realizations of BaTiO₃-based integrated photonic devices, including waveguides, Mach-Zehnder interferometers, and ring resonators [3–10]. It is clear from these devices that the crystalline quality of the BaTiO₃ thin film is critical for the device performance. The process of fabricating integrated photonic devices from thin-film BaTiO₃ is markedly different from LiNbO₃, which is used more commonly in electro-optical devices [11]. Thin film LiNbO₃ can be commercially fabricated using a top-down approach; using the Smart-Cut process, thin films can be bonded to a silicon wafer from a bulk crystal with high uniformity, low roughness, and well-aligned crystal orientation. Unfortunately, boules of bulk BaTiO₃ cannot be synthesized on the wafer-size scale, as the Curie temperature of 130°C makes bulk BaTiO₃ prone to cracking. Therefore, thin film BaTiO₃ must be directly fabricated bottom-up using thin film deposition.

2 BaTiO₃ thin films can be synthesized via several methods, including sputtering [12, 13], metal-organic

chemical vapor deposition (MOCVD) [14, 15], pulsed laser deposition (PLD) [2, 16–20], conventional molecular beam epitaxy (MBE) [21–23], and metal-organic hybrid MBE [24]. Measurements of the Pockels coefficient in BaTiO₃ thin films has varied significantly, for example from 150 pm/V [5] to over 1000 pm/V [2, 25]. Given the large variation in device performance for BaTiO₃ modulators fabricated with different methods, it is clear that understanding the local structure of the synthesized thin films is critical. Indeed, previous work growing BaTiO₃ using metal-organic MBE directly connected aspects of the films local structure to device performance, demonstrating that BaTiO₃ films with excess titanium have higher optical losses than stoichiometric films [24]. Optimizing and scaling BaTiO₃-based technology requires strict control and understanding of the defects that form in BaTiO₃ thin films.

3 Of the methods demonstrated for BaTiO₃ fabrication, MBE allows for the greatest degree of control over film composition because it is a slow and low-energy technique [26]. This careful control means that MBE is the optimal technique for studying how small variations in crystal composition affect the overall film properties. MBE studies are ideal for precisely characterizing the nature of the defects that form in off-composition films and can help inform and possibly widen the growth window for all deposition techniques.

4 Here, we investigate the effect of stoichiometry on the formation of defects in conventional MBE grown

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thin-film $\text{Ba}_{1\pm x}\text{TiO}_{3-\delta}$ using both local and macroscopic characterization techniques to probe the structural and polar properties of these films. We find that despite seemingly high-quality structures from diffraction measurements, titanium-rich films exhibit disordered polar structures throughout the film. In barium-rich films, the excess barium does not integrate into the film but causes the films to relax more readily and forms an amorphous surface that can be removed by soaking the film in deionized water. This is distinct from what is observed in SrTiO_3 , where excess strontium leads to the formation of Ruddleston-Popper planar faults [27] and potentially enables high-quality BaTiO_3 films to be realized without precise control of the stoichiometry during deposition. We also see polarization vectors in the film that are not allowed in the BaTiO_3 tetragonal $P4mm$ space group. These off-axis polarizations are stabilized across the stoichiometry series. Our work demonstrates the ways in which the thin film stabilizes defects differently from bulk BaTiO_3 , and provides an important materials science context to the use of BaTiO_3 thin films in electro-optic devices.

II. MATERIALS AND METHODS

5 A set of six $\text{Ba}_{1\pm x}\text{TiO}_{3-\delta}$ thin films across a stoichiometry range of $x = \pm 0.1$ were synthesized on (100) SrTiO_3 substrates (-2.32% compressive strain) using a Riber Compact21 oxide MBE platform. In addition to the close lattice match, SrTiO_3 does not introduce a polar catastrophe at the interface with BaTiO_3 . SrTiO_3 is also a commonly used buffer layer for integrating BaTiO_3 thin films onto silicon wafers [1]. Barium and titanium elemental material was evaporated from Knudsen effusion cells. The atomic fluxes are calibrated first with a quartz crystal microbalance (QCM), then with reflection high-energy electron diffraction (RHEED) shutter oscillations [27]. All films were synthesized by shuttering barium and titanium one monolayer at a time. The overall stoichiometry in the film is controlled by changing the elemental layer time. The overall atomic fluxes were kept constant during the series.

6 Films are synthesized and cooled to $\leq 250^\circ\text{C}$ in a distilled ozone (80% O_3 , 20% O_2) mixture at a pressure of 5×10^{-8} Torr, controlled by a piezoelectric leak valve and supplied by Heeg Vacuum Engineering. Films were deposited at a temperature of 600-630 $^\circ\text{C}$ as measured by the *in situ* thermocouple and 723-752 $^\circ\text{C}$ as measured by the *in situ* Fluke Endurance infrared pyrometer with 1 μm spectral response. The substrates were silver pasted with PELCO[®] High Performance Silver Paste to a Haynes 214 platen. The barium elemental flux was 7.9×10^{12} atoms/($\text{cm}^2 \cdot \text{s}$) and the titanium flux was 8.7×10^{12} atoms/($\text{cm}^2 \cdot \text{s}$). The films were all approximately 25 unit cells (10 nm) thick.

7 The single-crystal substrates were prepared by cleaning with Micro 90 alkaline cleaner, DI water, ace-

tone, then isopropanol for 5 minutes each, then etching in DI water held at 60 $^\circ\text{C}$ for 30 minutes, and finally annealing in air at 1000 $^\circ\text{C}$ for 4 hours. This produces SrTiO_3 substrates with atomically smooth surfaces with unit cell step height terraces.

8 All six films were grown sequentially within a period of 24 hours without cooling the elemental sources. The XRD measurements were performed with a Malvern Panalytical Empyrean diffractometer using $\text{Cu K}\alpha_1$ radiation. Atomic force microscopy (AFM) images are taken in tapping mode with the Oxford Instruments MFP3D.

9 The 10% barium-rich film, 10% titanium-rich film, and the stoichiometric film were further investigated using STEM imaging. Cross-sectional transmission electron microscope (TEM) samples were prepared using a FEI Helios 660 focused ion beam (FIB). The films were sputter-coated with a 10 nm layer of a Pt/Pd alloy to protect the film surface during FIB preparation. The FIB was operated at 30 keV, except for the final thinning step, which was done at 2 keV.

10 High-resolution STEM imaging was performed using a Thermo Fisher Scientific Themis Z G3 aberration-corrected microscope at an accelerating voltage of 200 kV, a convergence semi-angle of 18.3 mrad, and a probe current of 50 mA. High-angle annular dark-field (HAADF) images were taken at a collection angle ranging from 64 – 200 mrad. Up to 50 successive images were collected at each location. These stacks of images were cross-correlated and averaged to reduce drift effects. We also collected low-angle annular dark field (LAADF) images of the titanium-rich sample with a JEOL ARM 200F aberration-corrected STEM operating at 200V. These LAADF images were collected with collection angles ranging from 45 - 180 mrad. Corresponding HAADF-STEM images of the same location were collected with collection angles ranging from 68 - 280 mrad.

11 A Gaussian fitting method was used to identify the atom positions in the HAADF-STEM images [28]. This method works by identifying the brightest pixels in each image and fitting a two-dimensional Gaussian peak around each of those pixels. The brightest pixels were those of the barium atoms, so this method was able to accurately measure the position of the barium sub-lattice. This barium sub-lattice was then subtracted from the image and the procedure was repeated to construct the titanium sub-lattice (Fig. S9). By constructing the full BaTiO_3 lattice in this way, we could precisely measure atomic spacing in each image [29–32]. In particular, this enabled mapping the polar domain structure of the films because when BaTiO_3 is polarized, the central titanium atom in each unit cell is displaced. Previous work has measured this displacement to be as high as 16 pm in relaxed BaTiO_3 [33], and it is known that strain enhances the ferroelectric polarization in BaTiO_3 [31, 32]. Therefore, by measuring titanium atom displacement from the nominal center of mass of each unit cell, we were able to construct a map of ferroelectric polarization for each

image.

12 Electron energy loss spectroscopy (EELS) was also performed on the 10% titanium-rich sample, using dual-range EELS with a dispersion of 0.3 eV and 0.01 s of exposure per pixel. Local background averaging was implemented to improve the signal-to-noise ratio when subtracting the background signal [34]. We mapped the Ti- $L_{2,3}$ edge, O- K edge, and Ba- M edge to investigate variations in the elemental composition of this film.

13 X-ray Absorption Spectroscopy (XAS) experiments were conducted on the 10% titanium-rich, stoichiometric, and 10% barium-rich samples at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory, utilizing Beamline 6.3.1. Spectra were collected at 300 K in electron yield. A fixed linear horizontal photon polarization was used throughout the experiment. The sample orientations were adjusted to enable measurements at two geometries: normal incidence (I_x), where the beam was directed perpendicular to the sample surface, and grazing incidence (I_z) at 30° , where the beam intersects the sample plane at a lower angle. Furthermore, due to geometric effects, distortions arise at grazing incidence causing signal variations. To mitigate this a geometric correction was applied to the acquired grazing incidence data [35]. All acquired X-ray absorption spectra were normalized to the incident photon flux. The final spectra, presented here, have been offset vertically for clarity at their respective absorption edges.

14 XPS data is collected using a Thermo Scientific K-Alpha+ with an Al K-alpha micro-focused monochromator source with an energy of 1486.7 eV and a 180° double focusing hemispherical analyzer with 128-channel detector. Measurements were taken in location on each sample, at least 1 mm away from the edges of the sample, with a spot size of $400\ \mu\text{m}$. To reduce charging, all samples were wrapped in foil with a 1-2 mm hole for the beam. Surface measurements of the barium-rich films nevertheless showed charging of 10s of eV, up to 200 eV in one case. All samples were cleaned by sputtering for 240 seconds using the Ar ion beam source in cluster mode with a cluster size of 1000 atoms and a total energy of 8000 eV. This cleaning procedure significantly reduced the carbon signal on all samples. For the depth profile on the 5% barium-rich sample, we use a monatomic Ar ion beam source. Etching was done by repeating a pattern of 60 seconds etch and 30 seconds pause to reduce charging. The sample was etched for 10 minutes at 500 eV, 10 minutes at 1000 eV, and 1 minute at 2000 eV, all with the ‘low current’ setting (‘film interior’ measurement), for a further 9 minutes at 2000 eV low current and 3 minutes at 2000 eV with high current (‘interface’), then for a further 3 minutes at 2000 eV high current (‘substrate’).

15 Analysis was conducted using the Advantage software. Atomic percentages were found by comparing area under the Ba- $3d_{5/2}$, Ti- $2p$, O- $1s$, Sr- $3d$, and C- $1s$ peaks in a survey spectrum with 0.5 eV energy resolution. Back-

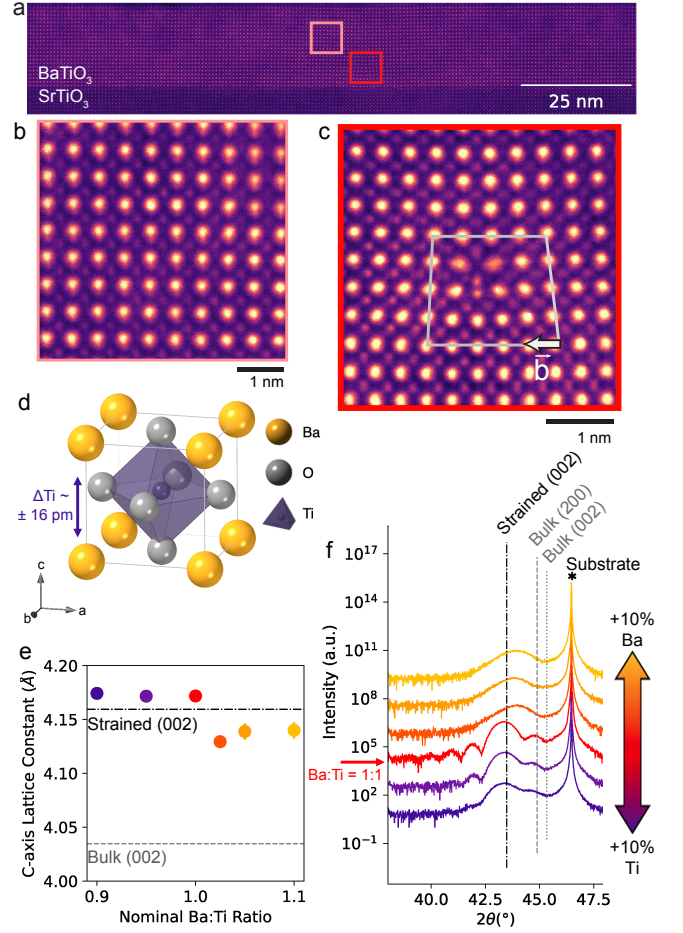


Figure 1. (a) Low magnification high-angle annular dark field (HAADF) scanning transmission electron microscope (STEM) image of the stoichiometric film. A single edge dislocation is observed in the center of the region imaged. (b) High magnification HAADF-STEM image of the stoichiometric film. The BaTiO_3 unit cell structure can be clearly observed. (c) High magnification HAADF-STEM image of an edge dislocation in the stoichiometric film. (d) Schematic of the BaTiO_3 unit cell. BaTiO_3 has a centro-symmetric tetragonal unit cell, with the central titanium atoms displaced along the c -axis approximately 16 pm, created a polarization vector. (e) c -axis lattice constant fits extracted from X-ray diffraction data. The titanium-rich and stoichiometric films have lattice constant consistent with a unit cell fully strained to the SrTiO_3 substrate, while the barium-rich films have a slightly lower lattice constant. (f) X-ray diffraction scan of the (002) peak of the six films.

ground subtraction was done with a modified version of the Shirley algorithm. We assume an instrument error of 0.5% for each atomic percentage. For the purposes of error propagation in the barium to titanium ratio we assume this error is independent for barium and titanium.

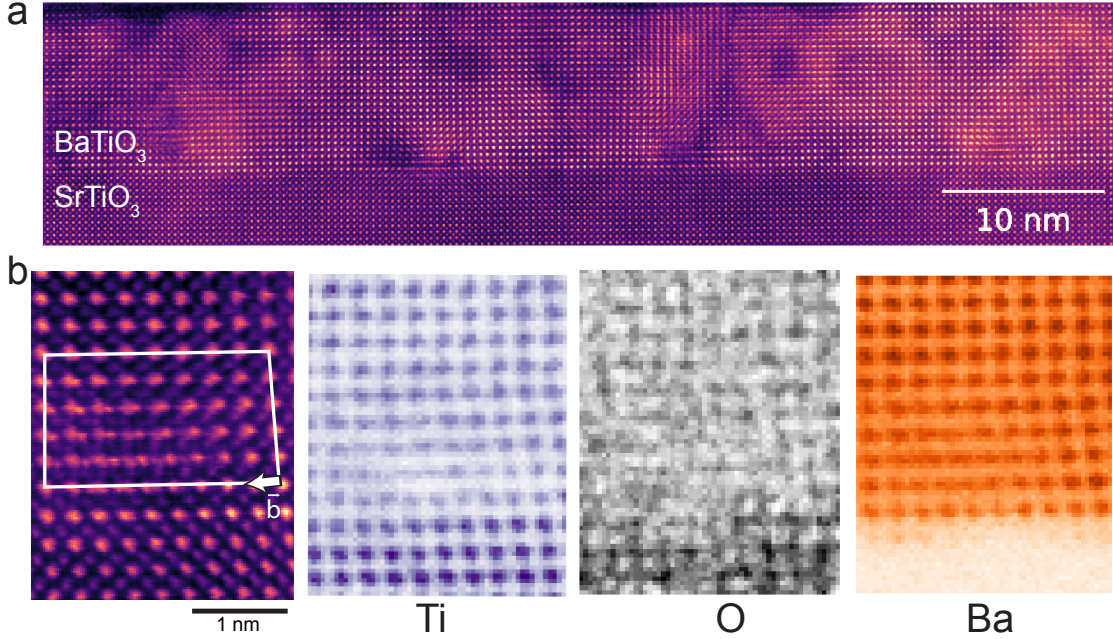


Figure 2. (a) Atomic resolution HAADF-STEM image of the 10% titanium-rich film. The film exhibits a high concentration of defects. (b) Electron energy loss spectroscopy (EELS) of one such defect at the $\text{Ba}_{1\pm x}\text{TiO}_{3-\delta}/\text{SrTiO}_3$ interface, shown in the HAADF image on the right. EELS maps of the Ti- $L_{2,3}$, O- K , and Ba- M edges indicate a uniform distribution of barium and titanium and do not show titanium-stuffing in the defect or the presence an additional phase.

III. RESULTS

16 We present HAADF-STEM images of the stoichiometric film in Fig. 1a, and high-magnification images in Fig. 1b-c. The film is single-phase with an abrupt interface between the $\text{BaTiO}_{3-\delta}$ film and the SrTiO_3 substrate. In the high-magnification image shown in Fig. 1b, we observe the perovskite structure (Fig. 1d) with the highly scattering barium atoms appearing yellow and the lighter titanium atoms appearing purple. While most of the film is coherent to the substrate, we observe a single edge dislocation (Fig. 1b) in the approximately 125 nm wide region imaged in Fig. 1a. This is consistent with prior studies which have found edge dislocations emerge above ~ 2 nm critical film thickness due to the high compressive strain between the $\text{BaTiO}_{3-\delta}$ film and SrTiO_3 substrate [36].

17 Following the synthesis of high-quality stoichiometric BaTiO_3 , we now intentionally vary the composition of the film from 10% titanium excess to 10% barium excess. The composition of the films is independently measured with XPS (Fig. S6). *In situ* reflection high energy electron diffraction (RHEED) during the MBE deposition (Suppl. Fig. S2a) and atomic force microscopy (AFM; Suppl. Fig. S2b) indicate that the surfaces of the stoichiometric and titanium-rich films are comparably smooth with visible terraces from the underlying substrate. In contrast, the barium-rich film has 10 nm islands on the surface and a RHEED pattern consistent with the forma-

tion of 3-D islands. Even the 2.5% barium-rich sample shows characteristic spottiness in RHEED that indicates some island-growth mode. The stoichiometric and 5% titanium-rich samples are very similar in RHEED, both with 1/2 order streaks along the (100) azimuth, while the 10% titanium-rich film has a 1/3 order surface reconstruction.

18 Despite the observation of island growth in the RHEED of the barium excess film, the XRD spectra of all samples show a single crystalline phase consistent with BaTiO_3 (Fig. S1). The out-of-plane lattice constants extracted from a Nelson-Reilly fit of the XRD data are shown in Fig. 1e [37]. For comparison, we also show the c -axis lattice constant of single-crystal BaTiO_3 and the c -axis lattice constant of BaTiO_3 fully strained to SrTiO_3 , assuming a BaTiO_3 Poisson ratio of 0.4 [38]. The stoichiometric and titanium-rich films show an out-of-plane lattice constant consistent with films fully strained to the SrTiO_3 substrate. The barium-rich films have a lower lattice constant that falls between the fully strained and fully relaxed values. The lack of clear peaks at the bulk (200) 2θ value indicates that all films are majority c -axis oriented (Fig. 1f). Reciprocal space mapping and rocking curves (Fig. S3) show similar results. Although all films are mostly strained to the substrate, the stoichiometric film has the highest crystalline quality, evidenced by the sharpest diffraction peak in Fig. 1f, while the barium-rich films show a degradation of the diffraction peak and the greatest relaxation in reciprocal space mapping (Fig. S3).

19 We now consider the local structure of these off-

composition films with HAADF-STEM. Figure 2 shows a detailed analysis of the 10% titanium-rich film. Despite the smooth surface in AFM and crystallinity in the *in situ* RHEED and XRD spectra, the resulting local structure in HAADF-STEM looks distinct from that of the stoichiometric film. As shown in Fig 2a, the 10% titanium-rich film shows a high concentration of localized defects. There appear to be uniformly distributed defects, consistent in appearance with screw dislocations, that do not appear in any of the other films (Fig. 2b). These screw defects were further investigated with electron energy loss spectroscopy (EELS) spectroscopic imaging of the interface (Fig. 2b). The EELS spectroscopic image shows an atomically abrupt interface between the SrTiO_3 and $\text{Ba}_{1\pm x}\text{TiO}_{3-\delta}$, manifest in the barium elemental map. EELS measurements do not show an excess of titanium in the defect areas, so it is likely that the excess titanium atoms incorporate as point defects through the film. Notably, we do not observe the formation of any distinct secondary phase such as TiO_x .

20 Figure 3 shows a detailed analysis of the barium-rich film. In contrast to the titanium-rich film, HAADF-STEM images of the 10% barium-rich film exhibit the ordered perovskite structure more similar to that of stoichiometric BaTiO_3 (Fig. 3a). The concentration of edge dislocations is higher than in the stoichiometric film (Fig. 3b), and these edge dislocations do not occur solely at the $\text{BaTiO}_{3-\delta}/\text{SrTiO}_3$ interface, but instead appear in the middle of the film as well as highlighted in circles in Fig. 4a. Despite the presence of a spotty RHEED pattern during synthesis and a rough AFM surface (Fig. S2b), no secondary phase is observed in the HAADF-STEM images.

21 Instead, we find that the top few nanometers of the barium-rich film appear amorphous in STEM imaging (Fig. S7). This is not observed in the titanium-rich sample or the stoichiometric sample. Additionally, some areas of the barium-rich film are susceptible to beam damage and amorphization on the order of 5 minutes (Fig. S7). Soaking the as-grown films in room-temperature deionized water for approximately 72 hours significantly modifies the surface and a smoother film surface can be recovered (Fig. 3d). The XRD pattern before (as-grown) and after the water treatment is unchanged (Fig. S8). This suggests the amorphous region observed in the HAADF-STEM image is water soluble and can be readily removed.

22 We use XPS to provide a complimentary view of barium-rich films in Fig. S6. Surface measurements on all as-grown barium-rich films show a >10% barium-rich composition regardless of the nominal composition. However, a depth profile of the 5% barium-rich sample shows that while the film surface is barium-rich, the film interior has an elemental ratio that matches the stoichiometric film. This indicates that the barium-rich films are not compositionally uniform throughout the thickness.

23 We now analyze the polar domain structure of all three $\text{BaTiO}_{3-\delta}$ thin films. Figure 4 shows maps of the

titanium atom displacement, corresponding to ferroelectric polarization, for the barium-rich (Fig. 4a), stoichiometric (Fig. 4b), and titanium-rich films (Fig. 4c). To validate this method, we also show the titanium atom displacement of the non-polar SrTiO_3 substrate (Fig. 4d), which shows the resolution of this measurement to be around 10 pm, much less than the net polarizations shown in the $\text{BaTiO}_{3-\delta}$ films. Polar histograms of the titanium displacement magnitude and direction are shown to the right of each corresponding image. In all cases, the polarization of the films is greater than that of the bulk crystals. In the stoichiometric and barium-rich films, we observe a titanium atom displacement ranging from approximately 20 pm to 60 pm. In the stoichiometric film, the imaged region contains two domains that are both at least 20 nm wide. In the barium-rich film, the imaged region contains a single domain that is approximately 100 nm wide. The titanium-rich film contains domains on the order of 10 nm wide or less with a variety of orientations.

24 The histograms in Fig. 4 demonstrate that the direction of titanium displacement is not limited to the tetragonal c -axis. Indeed we see a variety of titanium-displacement directions. To further compare the direction of displacement with the orientation of the unit cells locally, we consider small areas of each of the films in more depth. Here we simultaneously analyze the polarization polarization direction (Fig. S10a) as well as the local c/a ratio (Fig. S10b). Notably, in both the stoichiometric and off-stoichiometry films, we observe areas where the titanium atoms show in-plane displacement in unit cells where the c -axis is oriented out-of-plane—that is, we observe titanium atoms that are displaced perpendicular to the c -axis of the unit cell. This is in contrast to the $P4mm$ space group, where the titanium displacement is restricted to the c -axis of the tetragonal unit cell.

Finally, we note that in addition to cation off-stoichiometry, titanate films are highly susceptible to forming oxygen vacancies which can impact the electrical, optical and structural properties. We perform x-ray absorption spectroscopy at the O- K and Ti- $L_{2,3}$ edges as shown in Fig. S11. Comparing the $\text{Ba}_{1\pm x}\text{TiO}_{3-\delta}$ Ti- $L_{2,3}$ edge lineshapes to those reported on a series of $\text{SrTiO}_{3-\delta}$ oxygen-deficient films[39] using EELS spectroscopy, we find all samples are consistent with $\delta \leq 0.1$. We also perform I-V measurements on all samples, demonstrating $\sim G\Omega$ - $T\Omega$ resistance in the films, with the highest conductivity in the most titanium-rich films. The high resistance also suggests minimal oxygen vacancies. To further probe the possibility of enhanced oxygen-vacancies in the 10% titanium-rich film, we performed additional low-angle annular dark field (LAADF) STEM imaging of this film (Fig. S12). The LAADF-STEM image shows enhanced contrast which could indicate localized oxygen defect structures.

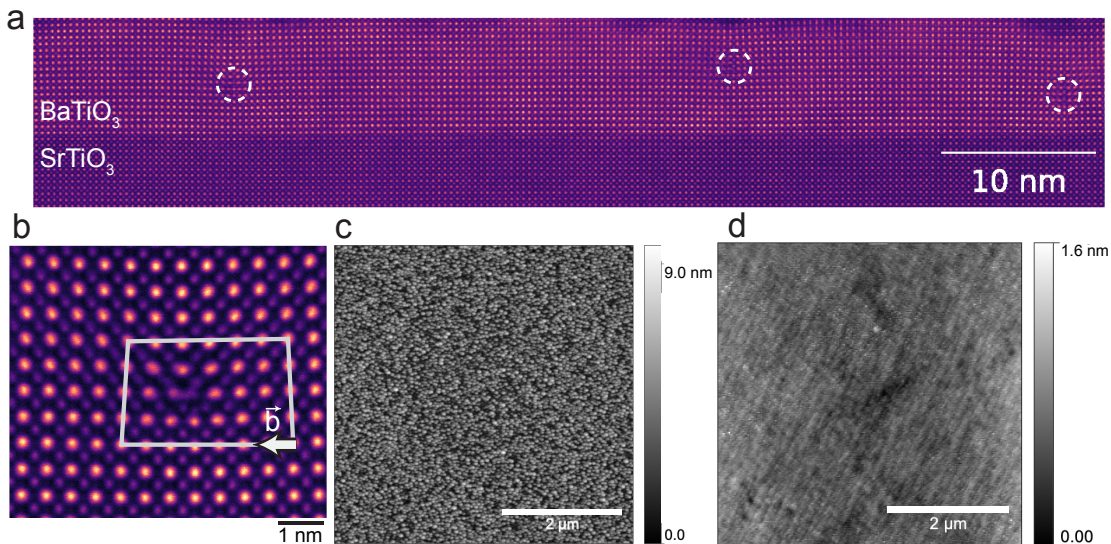


Figure 3. (a) Low magnification and (b) high magnification HAADF images of the 10% barium-rich film. The film has an ordered perovskite structure with few defects, similar to that of stoichiometric BaTiO_3 . Defects are consistent with edge dislocations. (c) Atomic force microscope (AFM) image of the film's surface before (as-grown) and (d) after treatment with deionized water. The surface of the film is dramatically smoother following the water treatment.

IV. DISCUSSION

25 Using MBE, we synthesize a high-quality stoichiometric thin film of $\text{BaTiO}_{3-\delta}$ as demonstrated by XRD, STEM, AFM, and RHEED characterization. Our high-resolution HAADF-STEM imaging shows a coherent film with an abrupt interface to the substrate. As the film is compressively strained to the SrTiO_3 substrate ($\epsilon = -2.1\%$), we observe a much higher titanium displacement than has been reported for relaxed BaTiO_3 [33]. This increased titanium atom displacement correlates with stronger polarization, which has been observed in electrical measurements of strained thin films [31], but our work provides the first atomic-scale real-space measurement of this enhanced displacement.

26 In addition to the synthesis of stoichiometric $\text{BaTiO}_{3-\delta}$ films, we also intentionally synthesize films with a varying barium to titanium ratio. First, we note that titanium-rich films appear initially to be high-quality based on macroscopic measurements: the RHEED looks very similar to the stoichiometric film until around 10% excess, the lattice constant remains similar to that of the stoichiometric films, and the surface remains smooth in AFM measurements. However there are pronounced differences in the local structure. Screw dislocations form throughout the film, as do regions of local disorder that may be caused by pervasive point defects. These structural characteristics are very similar to titanium-rich SrTiO_3 films [27], as well as other similar materials [40–42]. While the picoscale identification of a single excess titanium atom is below the resolution limit of electron microscopy, there have also been previous studies using cathodoluminescence spectroscopy

which suggest that excess titanium incorporates into the SrTiO_3 lattice as interstitial atoms[43], along with corresponding oxygen vacancies. In our polar analysis, we find small, disordered polar domains in the as-grown films. Taken together, we conclude that although the titanium-rich films may initially appear to be high-quality, there is significant structural disorder present. Prior work has indicated that titanium-rich films have poor optical properties compared to more stoichiometric films [24] which could be related to the nanoscale disorder observed.

27 In contrast barium excess causes a degradation of the X-ray diffraction peak intensity, a rough surface in AFM, and a high concentration of barium at the film surface, as measured by XPS. However, we observe a highly ordered film interior with sparse edge dislocations in STEM and a stoichiometric film interior with XPS. We do observe edge dislocations both near the film-substrate interface and in the middle of the film, and we anticipate that these defects would continue to form with the growth of a thicker film. The presence of these defects corresponds to a partial relaxation of the film (supplementary Fig. S5). The areas around these defects also seem to become amorphous under the electron beam, indicating that they are not very energetically stable (see supplementary Fig. S7). However, despite the relaxation and electron beam sensitivity, 100 nm-scale polar domains are observed.

28 We also note that there are marked differences in how thin films incorporate defects compared to bulk BaTiO_3 . In the bulk phase diagram, BaTiO_3 is a line compound below temperatures of around 700°C and excess titanium or barium incorporates in secondary phases: excess titanium forms BaTi_2O_5 and excess ex-

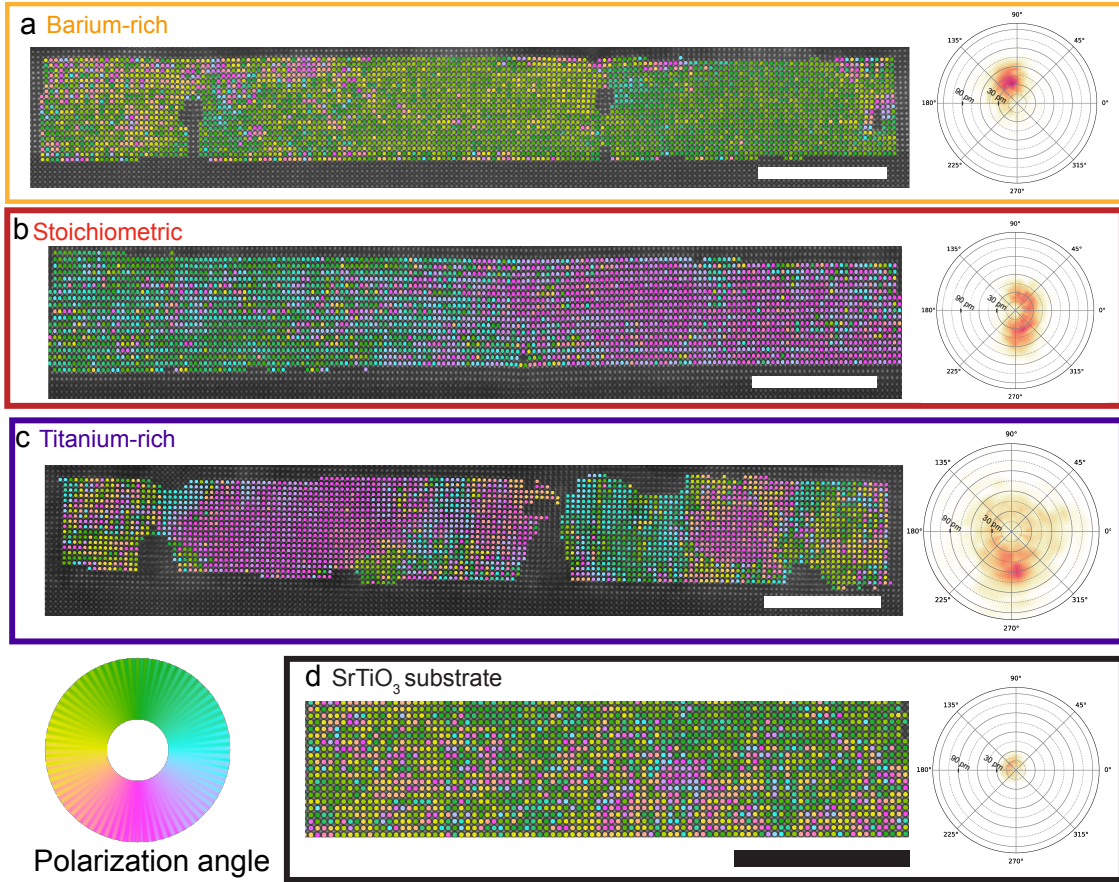


Figure 4. Polar domain mapping of the (a) 10% barium-rich film, (b) stoichiometric film, and (c) 10% titanium-rich film. The color scale indicates the direction of titanium atom displacement and the scale bar is 10 nm for all three images. Polar histograms of the titanium displacement are shown to the right of each corresponding image. The spacing on these plots is 20 pm. Both the barium-rich and stoichiometric films exhibit large, out-of-plane polar domains, whereas the titanium-rich film has many small, disordered domains. (d) Polar domain mapping on the non-polar SrTiO₃ substrate, to demonstrate the resolution of this measurement.

cess barium creates Ba₂TiO₄. In our films, no secondary phases (such as TiO_x, BaTi₂O₅, Ba₂TiO₄ or BaO) are observed. The excess titanium appears to be uniformly incorporated throughout the film, resulting in the formation of point defects. Barium-rich films deviate from the behavior observed in both bulk BaTiO₃ as well as in SrTiO₃. In bulk BaTiO₃, excess barium creates the secondary phase Ba₂TiO₄ and in SrTiO₃, Ruddlesden-Popper-type defects form rock-salt layers [27]. We do not observe either of these phases in any of our measurements.

29 The excess barium supplied during growth appears to remain on the surface, a phenomenon shown in the compositional difference between XPS surface and film interior measurements. The segregation of BaO is consistent with observations of ion segregation observed in solid oxide fuel cells [44]. Based on the spotty RHEED pattern, the barium excess appears to form a crystalline compound. Because we do not observe any evidence of a crystalline compound in XRD or STEM, we posit

that the compound is water sensitive and becomes amorphous upon exposure to atmosphere [45]. Furthermore, the surface roughness observed with AFM is removed after treating the film with deionized water. This suggests that excess barium supplied during film deposition did not incorporate into the BaTiO_{3-δ} lattice, but instead formed a crystalline, water-sensitive, barium oxide-based compound on the film surface while preserving pristine BaTiO₃ beneath it. Treating barium-rich films with water may be a promising avenue to recover relatively high quality films and this path should be further studied on thicker films.

30 Our high-resolution HAADF-STEM imaging also reports a titanium atomic displacement that appears to deviate from the P4mm space group. In Ba_{1±x}TiO_{3-δ} thin films of all stoichiometries, the titanium atomic displacement is not strictly confined to the *c*-axis of the tetragonal unit cell. Prior work on bulk BaTiO₃ has observed contrasting local and long-range space group structure [31, 33, 46]. Recent studies

have shown that, at higher temperatures, highly crystalline BaTiO₃ can exhibit metastable phases with a different space group and titanium displacements in the [111] and crystallographically equivalent directions, in line with the order-disorder polarization model [2, 47]. This is further supported by *ab initio* computational work, which finds that using a purely P4mm description of BaTiO₃ yields results that do not agree with experimental measurements of the electro-optic response of BaTiO₃, while using an average of these lower-symmetry structures produces results that agree with experiment [48]. Because a material's symmetry sets the allowed values of its electro-optic tensor, understanding the nature of the titanium displacement and thus the crystal symmetry of the BaTiO₃ in thin film form is important for electro-optic device design.

V. CONCLUSIONS

31 This study provides a comprehensive understanding of how the and local atomic and polar structure of barium titanate thin films is affected by the stoichiometric variation that may occur with different growth methods, growth conditions, and calibration schemes. Using a combination of atomically-precise MBE, macroscopic diffraction characterization and picoscale STEM imaging, we explore a series of Ba_{1±x}TiO_{3-δ} films with varying Ba:Ti ratio. We find significant nanoscale disorder in the titanium-rich films, despite the coherent diffraction measurements and smooth film surface. The films do not incorporate significant excess barium into the film structure; rather this excess barium forms a surface layer which can be removed with water. We thus find that synthesizing slightly barium-rich materials may be a promising pathway to achieving high-quality materials with a larger synthesis window. In all of our materials, we see a ferroelectric polarization which is not clamped to the *c*-axis of the P4mm space group. These results suggest it is critical to characterize BaTiO₃ films used in photonic devices in the microscale: local variations in the atomic-

structure, crystal symmetry and polarization could dramatically impact the electro-optic tensor of the material, measurements of electro-optic properties and device performance.

Author Contributions: Synthesis of films by MBE was performed by L.B.L., with assistance from D.R.B., C.M.B. and J.A.M. XRD analysis was performed by L.B.L., A.B. and C.M.B. AFM was performed by L.B.L. XPS was performed by L.B.L. in discussion with H.G.L. XAS was performed by N.K.T. with assistance from A.T.N. and J.A.M. Transport was performed by A.E.C. TEM imaging and analysis was performed by A.E.C. and Y.Z., with assistance from J.G., I.E.B. and R.M.W. A.E.C., L.B.L. and J.A.M. wrote the paper, with input from all authors. R.M.W. and J.A.M. conceived of and guided the study.

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Effect of Stoichiometry on the Structure and Polarization of BaTiO₃

S1. X-RAY CHARACTERIZATION

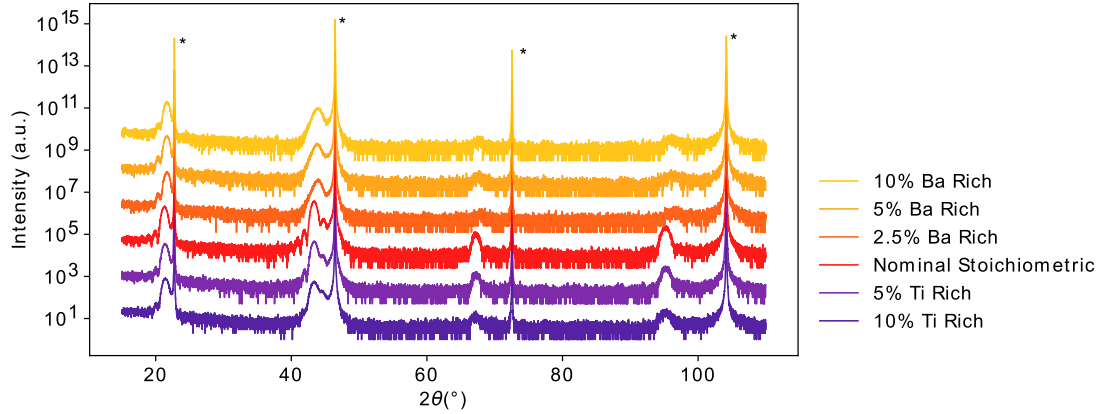


Figure S1. Full X-ray diffraction pattern from all films show single-phase films. Substrate peaks are denoted with an asterisk.

S2. SURFACE CHARACTERIZATION

In RHEED images, shown in figure S2a, the BaTiO₃ film appears as vertical streaks. The barium-rich films all exhibit additional spots, characteristic of island-mode growth. Along the $\langle 100 \rangle$ azimuth, the stoichiometric and 5% titanium-rich films had 1/2 order reconstructions, while the 10% titanium-rich film had 1/3 order reconstructions.

The surfaces of the 10% barium-rich, stoichiometric, and 10% titanium-rich films were further characterized using AFM. Images were taken of 5 μm and 10 μm areas of each film, as shown in figure S2b. Both the stoichiometric film and 10% titanium-rich film have low surface roughness and the atomic terraces of the underlying SrTiO₃ substrates are visible. The 10% barium-rich film exhibits a rough surface covered in islands that are about 10 nm in diameter. As discussed in the main text, these islands disappeared after soaking the film in deionized water for approximately 72 hours (see figure 4).

S3. STRAIN

Both the bulk and local strain states of the set of BaTiO₃ films were characterized. The bulk strain of three films of the films (10% titanium-rich, stoichiometric, and 5% barium-rich) was characterized with reciprocal space mapping (RSM). RSM allows for the extraction of both in-plane and out-of-plane lattice constants by scanning both the film and substrate in two-dimensional reciprocal space. From this data, shown in figure S3, we can see that all films are majority compressively strained to the SrTiO₃ substrate. Both off-composition films show a greater amount of relaxation compared to the stoichiometric film. The barium-rich film showed more relaxation than the titanium-rich film.

We additionally characterized the rocking curves of the films BaTiO₃ 002 peak and compared them to the substrate SrTiO₃ 002 peak, shown in Fig. S4. Full width half maximum (FWHM) values are labeled. As expected and in line with the RSM analysis, all films are strained to the substrate, but higher off-stoichiometry generally correlates with a larger FWHM of the film peak when compared to the substrate peak. Barium-rich films have a greater FWHM than titanium-rich films of the same off-composition percentage, likely corresponding to the partial relaxation observed in the HAADF-STEM imaging.

We then explored the microstructure of the strain present in these films by performing geometric phase analysis (GPA) on scanning transmission electron microscope (STEM) images. With GPA, a fast Fourier transform (FFT) is generated from a high-resolution STEM image. This FFT is used to generate a Bragg filtered image; deviations of the phase of this Bragg filtered image as compared to a calculated ideal crystal lead to a gradient which can be fit and used to calculate lattice displacement [49]. From this GPA analysis, shown in figure S5, we see that very

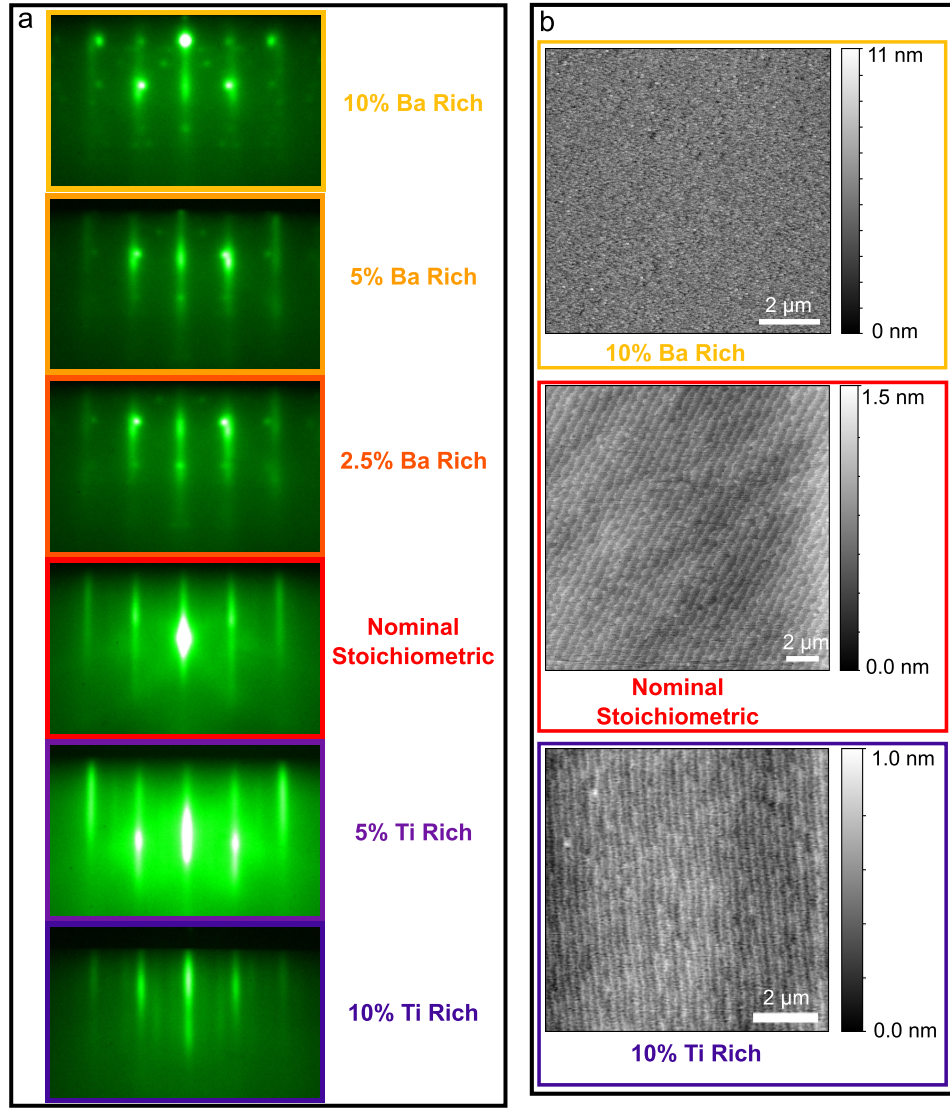


Figure S2. (a) Reflection high energy electron diffraction (RHEED) images obtained during film growth of all six films along the $\langle 100 \rangle$ azimuth. (b) Atomic force microscope (AFM) micrographs of the 10% barium-rich, stoichiometric, and 10% titanium-rich films. While the titanium-rich films are similar in roughness to the stoichiometric films, the barium-rich films are considerably rougher in both RHEED and AFM.

little in-plane strain is present in the stoichiometric and barium-rich films, except for at the locations of defects. The titanium-rich films show more local variation in the in-plane strain. All three films exhibit local out-of-plane strain variations, particularly around defects.

S4. XPS COMPOSITIONAL MEASUREMENTS

XPS results are shown in Fig. S6. All XPS data was taken on as-grown films; no water treatment was performed on the barium-rich films prior to measurements. Surface measurements of the titanium-rich and stoichiometric films show that all films are within error of their nominal composition, indicating that our MBE-shuttering scheme produces tight compositional control and our actual vs. nominal compositional error is small. Given the film uniformity in STEM, we take the surface measurements for these samples as representative of the entire film thickness.

However, the barium-rich films show very different results. The surface of all barium-rich films is 10% barium rich or higher regardless of their nominal composition. Since we know from STEM results that the barium-rich films are not uniform throughout their thickness, we etch the 5% barium-rich film and take a depth profile (Fig. S6b). We see

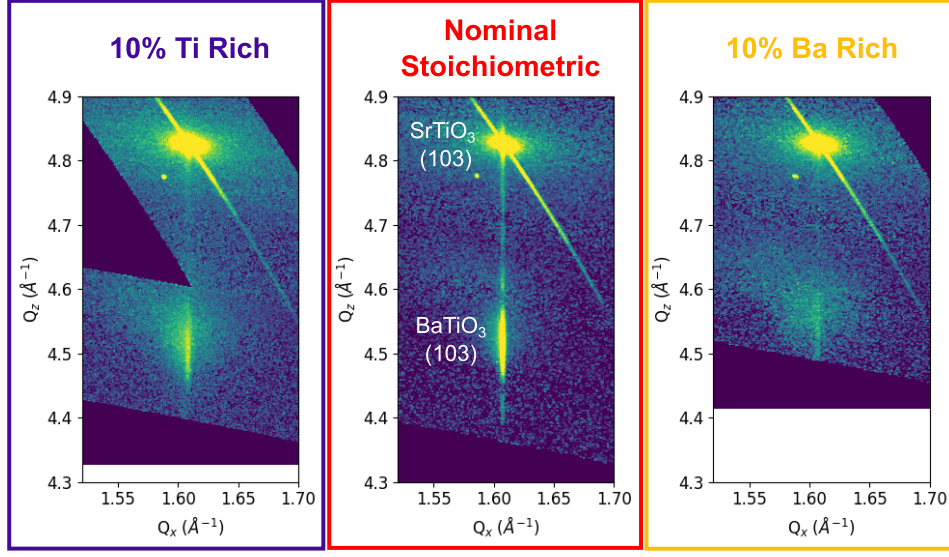


Figure S3. Reciprocal space mapping (RSM) of the [-103] film and substrate peaks for the 10% titanium-rich (left), stoichiometric (center), and 5% barium-rich films. In both the titanium-rich and stoichiometric case, the film peaks are aligned with the much brighter substrate peaks in the x-axis, indicating that the films are strained to the SrTiO_3 substrate. In the barium-rich case, the film peak is shifted slightly to the left of the substrate peak, indicating partial relaxation.

that while the film surface is indeed barium-rich, the film interior is stoichiometric. To demonstrate that the XPS etching is effective, we also show measurements taking as the etch begins to reaches the SrTiO_3 substrate (labeled ‘interface’), and after the entire film has been etched through and no barium remains (‘substrate’).

S5. AMORPHIZATION OF BARIUM-RICH FILM

While imaging the 10% barium-rich film, we observed beam damage near defects that progressed on the time-scale of minutes and caused amorphization of the film. This process is shown via images of one such defect in figure S7. Over the course of approximately four minutes, the amorphous surface appears to expand and fold down to the defect, but does not continue to grow below the defect. After some initial time period of surface amorphization during the first several minutes of imaging, the remaining film stayed stable on the time-scale of hours with no further damage. This is likely due to structural instability introduced by the presence of these defects.

S6. ATOMIC LATTICE MAPPING

We analyzed the BaTiO_3 atomic lattice using atomap, an open-source Python library [28]. Figure S9 presents a schematic depiction of the procedure. We start by identifying the brightest pixels in a selected region of a raw HAADF-STEM image. Each pixel represents the approximate center of mass of an atom of the heaviest element present in the image; in our case, these are the barium atoms. The barium atom positions are refined by fitting a 2-D Gaussian to each of those bright pixels, which allows us to construct the barium sublattice. We then subtract the barium sublattice from the image, leaving us with an image where the brightest pixels present correspond to titanium atoms. We repeat our Gaussian fitting procedure to identify the titanium sublattice. We can also subtract the titanium sublattice from the image to validate our method. Finally, we add both sublattices together to form the complete atomic lattice that can now be precisely measured.

S7. POLARIZATION AND LATTICE CONSTANT

We compare each unit cell’s in-plane and out-of-plane lattice constants to a relaxed c -axis unit cell. Smaller in-plane and larger out-of-plane lattice constants are consistent with a strained, c -axis oriented unit cell, while larger in-plane and smaller out-of-plane lattice constants are consistent with an a -axis oriented unit cell. Figure S10 shows

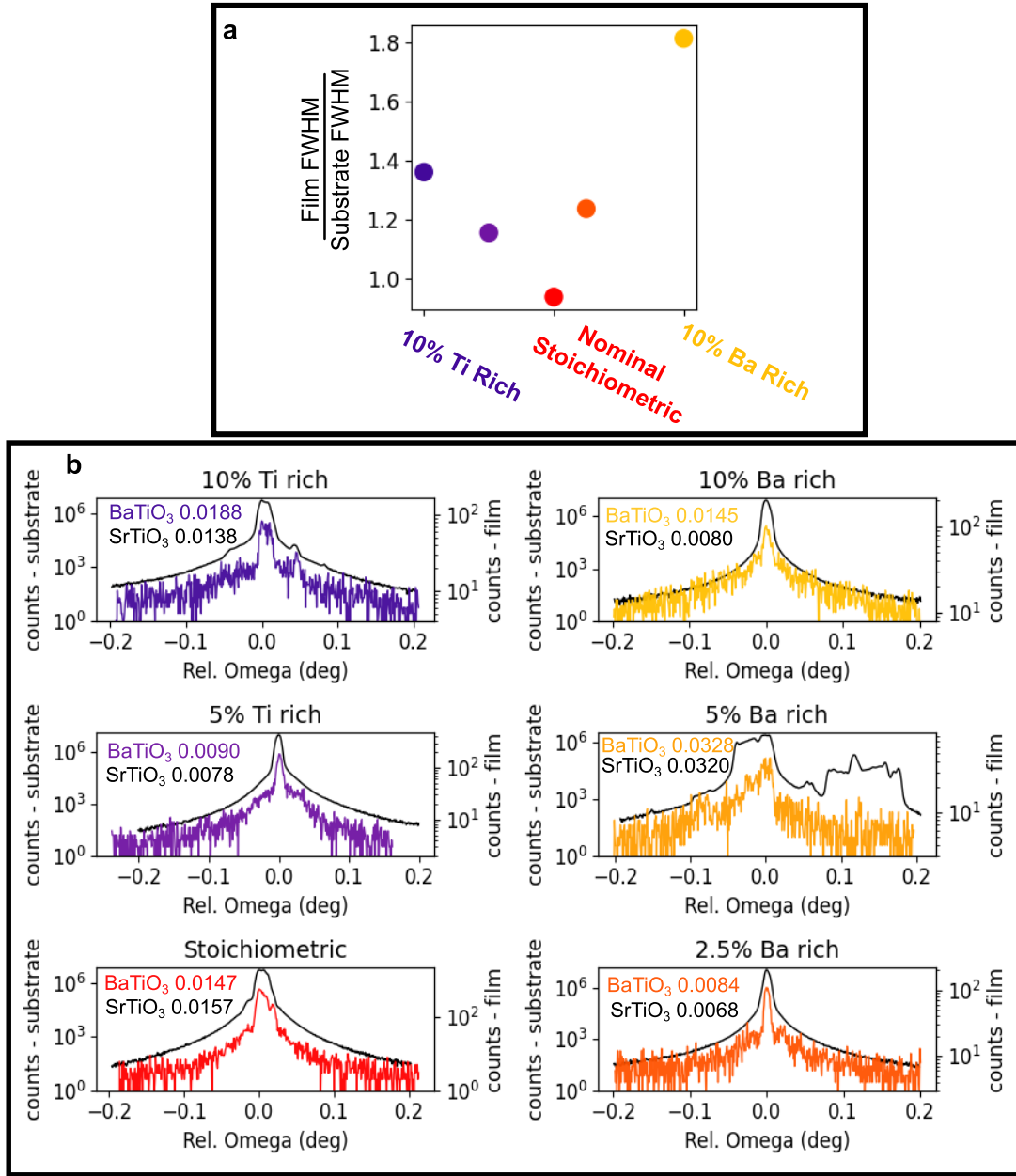


Figure S4. (a) Ratio of film full width half max (FWHM) to substrate FWHM for the 002 peak, which is a measure of the crystalline quality of the film. The stoichiometric film's FWHM is very similar to that of the substrates, while the barium-rich films FWHM increase more quickly than the titanium-rich films. (b) Rocking curves for each film (color) and substrate (black). FWHM for each film and substrate reported. Note that the 5% barium-rich sample had a very broad and irregular substrate rocking curve and so was excluded from summary panel (a).

the titanium atom displacement next to this localized lattice constant measurement for a small region of each film. Here, we can see that in each film there are regions where the titanium atom is not displaced parallel to the c -axis of the unit cell as is required by the $P4mm$ space group.

S8. X-RAY ABSORPTION SPECTROSCOPY

We present X-ray absorption spectra from the Ti- $L_{2,3}$ edge and the O- K edge in Fig. S11 for 10% titanium-rich, 10 % barium-rich, and the stoichiometric BaTiO₃ films. Figure S11a shows the Ti- $L_{2,3}$ edge; a higher magnification presentation of the Ti- L_3 edge. All three spectra show the presence of 4 distinct peaks, consistent with the Ti⁴⁺ crystal

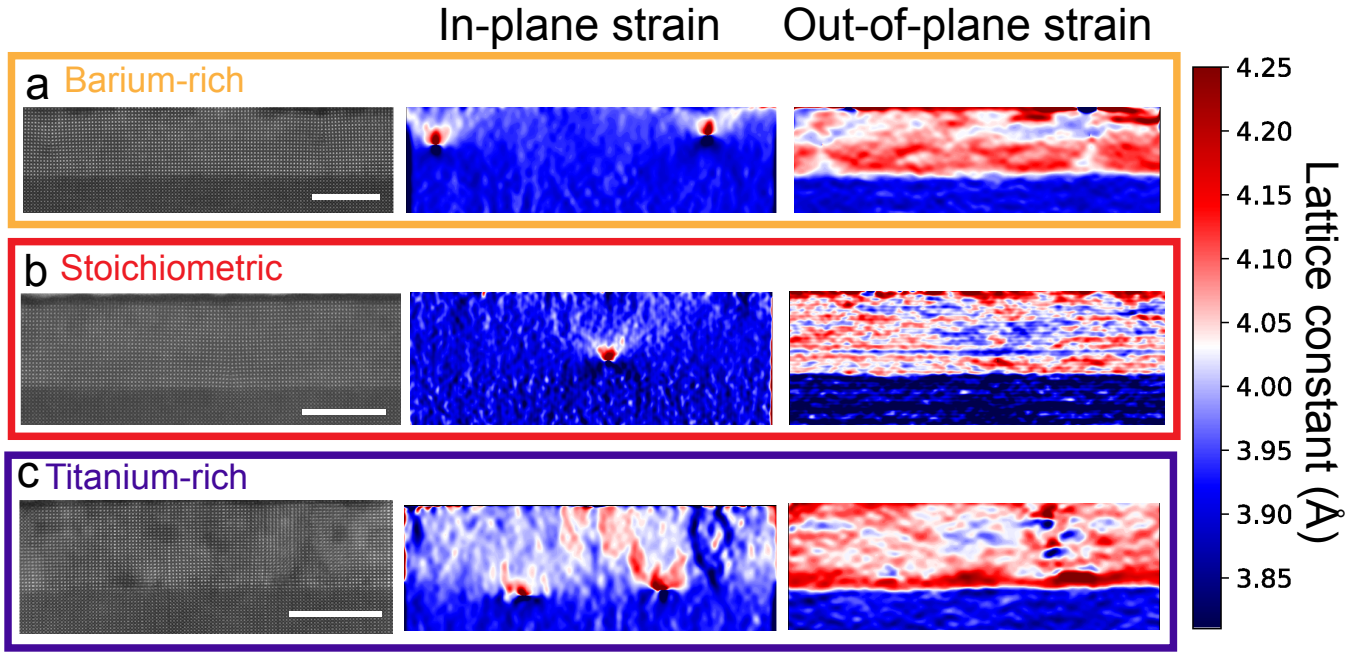


Figure S5. Strain maps generated from geometric phase analysis (GPA) of (a) the 10 % barium-rich film, (b) the stoichiometric film, and (c) the 10 % titanium-rich film. the high-angle annular dark field (HAADF) images used to generate these strain maps are shown on the left, out-of-plane strain is mapped in the center, and in-plane strain is on the right.

field splitting[50]. While all spectra look similar, we note a small change in the Ti-L_3 edge shown in Fig. S11c. The peak at 453 eV slightly decreases for 10 % titanium-rich when compared to the stoichiometric spectrum. Furthermore, the 10 % barium-rich spectrum shows that both peaks increase in intensity showing two well distinct peaks at 452 eV and 453 eV. Previous work investigated the $\text{Ti-L}_{2,3}$ fine structure for a series of $\text{SrTiO}_{3-\delta}$ for $\delta = 0, 0.13$ and 0.25 . The sample with $\delta = 0.25$ ($\text{SrTiO}_{2.75}$) shows a loss of the distinct peak splitting, consistent with an onset of Ti^{3+} [50]. In contrast, our spectra are consistent with $\delta \leq 0.1$ for all samples with potentially a slightly higher Ti^{3+} concentration in the titanium-rich sample; we cannot determine the oxygen content more precisely from these measurements, particularly due to a potentially overlapping signal from the SrTiO_3 substrate.

There are additional variations observed in the O- K edge spectra shown in Fig. S11b,d. The spectral features and transitions in the 10 % titanium-rich, below 530 eV, closely resembles the stoichiometric film spectrum. This is especially true for the spectral features present below 530 eV. On the contrary, the 10% barium-rich film has distinct features such as the sudden peak increase at around 527 eV and peak broadening at around 536 eV. We note that the XAS measurements are performed in a grazing incident configuration, which makes them highly surface sensitive. Our XPS measurements, along with our TEM and AFM, show the presence of a distinct barium-rich surface phase, likely an amorphous BaO compound, in the barium-rich films. XAS measurements would be uniquely sensitive to this precipitate that lies on the surface of the film, rather than the remainder of the crystalline BaTiO_3 phase. Thus, we hesitate to draw conclusions about the composition of the interior BaTiO_3 layer of the barium-rich films from these measurements.

S9. LOW-ANGLE ANNULAR DARK FIELD IMAGING

To further explore the presence of oxygen vacancies in our films, we performed low-angle annular dark field (LAADF) STEM imaging of the 10% Ti-rich sample (Fig. S12). Previous work has demonstrated the use of this technique for identifying oxygen vacancies in SrTiO_3 , where the presence of oxygen vacancies enhances the image contrast due to electron beam dechanneling [39]. Both a HAADF-STEM and LAADF-STEM image were collected for the region imaged so as to directly compare the variations in contrast due to oxygen vacancies that become visible with LAADF-STEM imaging. The enhanced contrast in the low-angle annular dark field images is consistent with the presence of

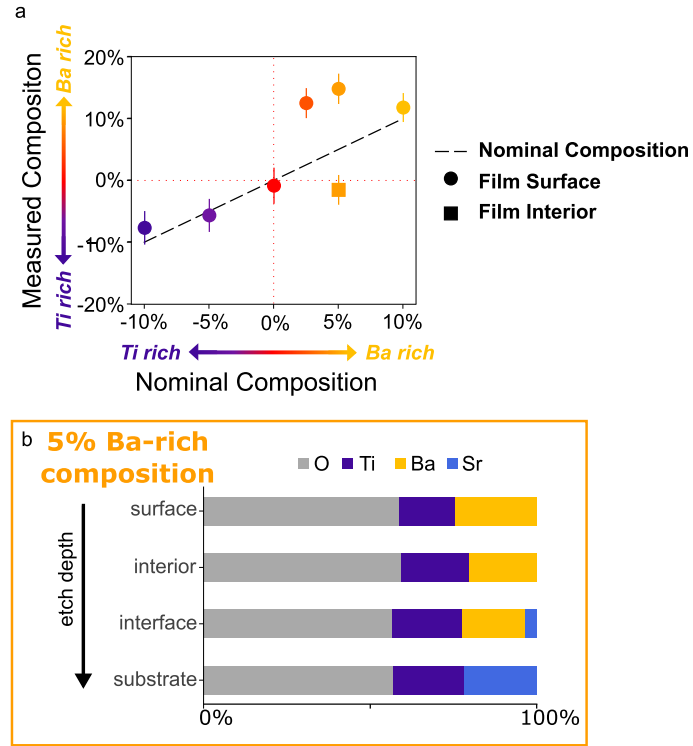


Figure S6. (a) XPS composition measurements of the surface of each film compared to the nominal composition. Film interior is shown for 5% barium-rich film. titanium-rich and stoichiometric films are in line with nominal composition. All barium-rich film surfaces are over 10% barium rich regardless of the nominal composition. Etching into the 5% barium-rich films demonstrates that the film interior is stoichiometric. (b) Depth profile of 5% barium-rich film. Surface is barium-rich compared to film interior. Measurements of the interface and substrate demonstrate complete etch of film during measurement.

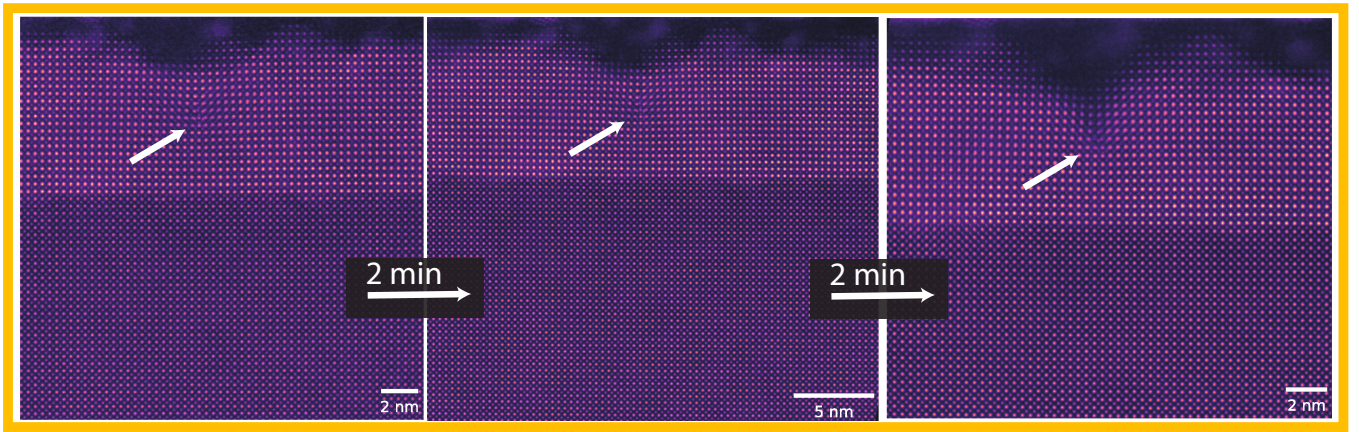


Figure S7. These three high-angle annular dark field (HAADF) scanning transmission electron microscope (STEM) images of the 10% barium-rich film highlight partial amorphization of the film observed during imaging. The white arrow highlights the same point defect, with each image taken two minutes apart. Over time, the film became amorphous along its surface and above the defect.

oxygen vacancies [39].

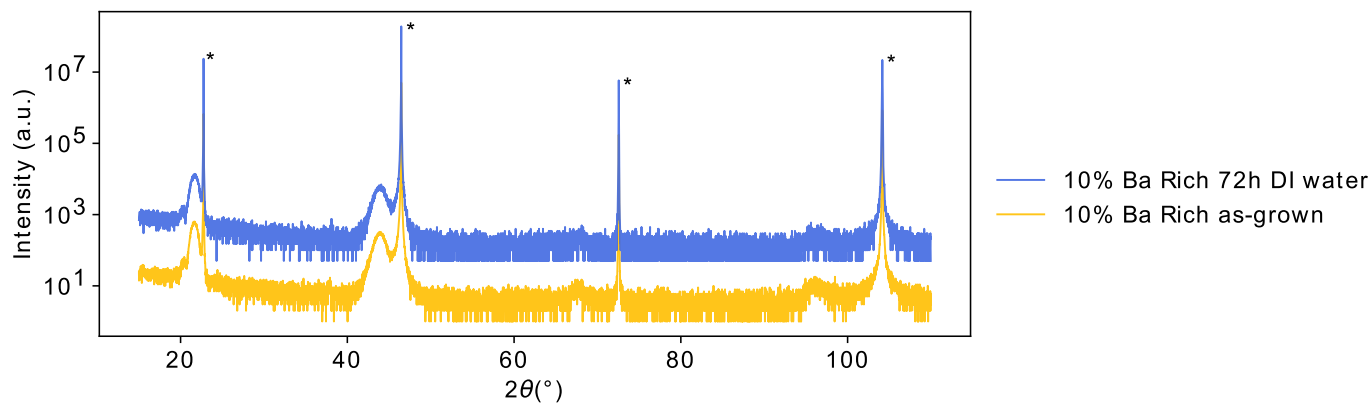


Figure S8. XRD pattern for the barium-rich film before (as-grown) and after 72 hour DI water treatment. Despite the dramatic change in the surface roughness, the X-ray diffraction pattern of the underlying film has not changed significantly.

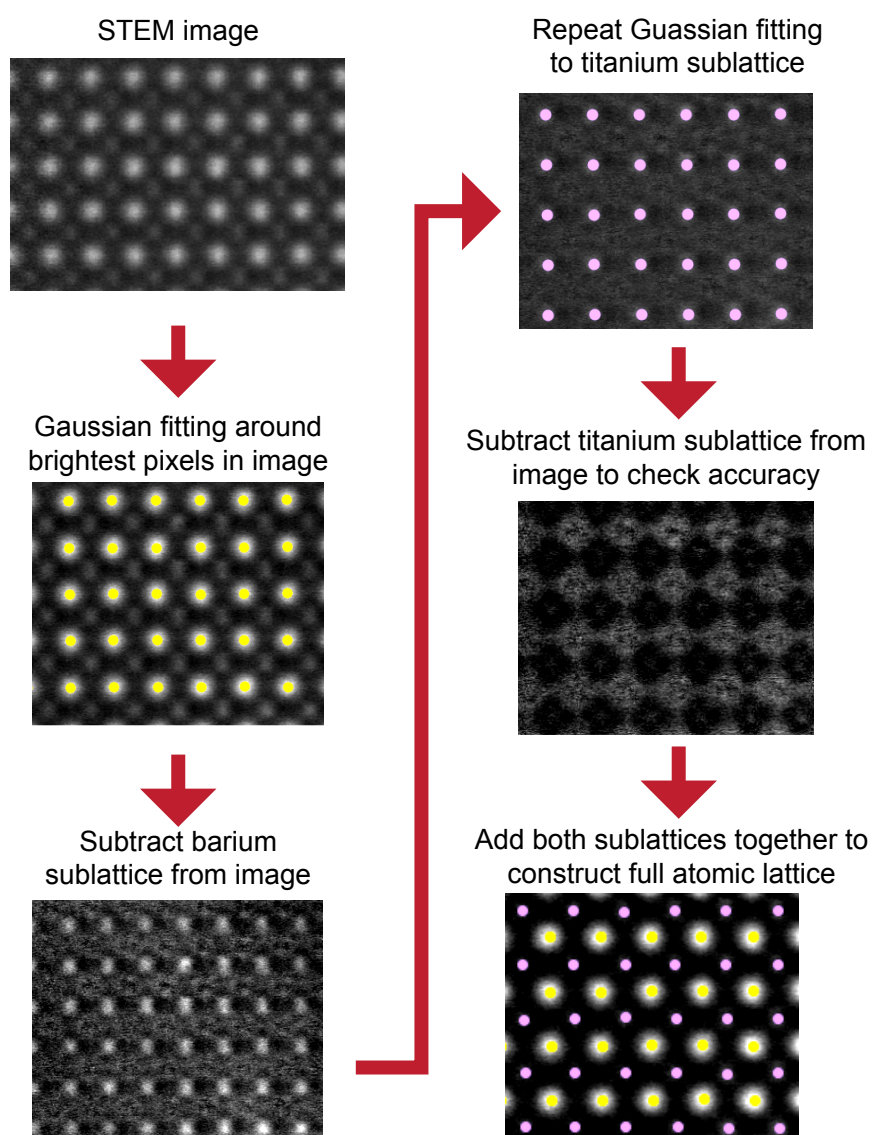


Figure S9. Schematic depiction of the Gaussian fitting method used to construct the atomic lattice.

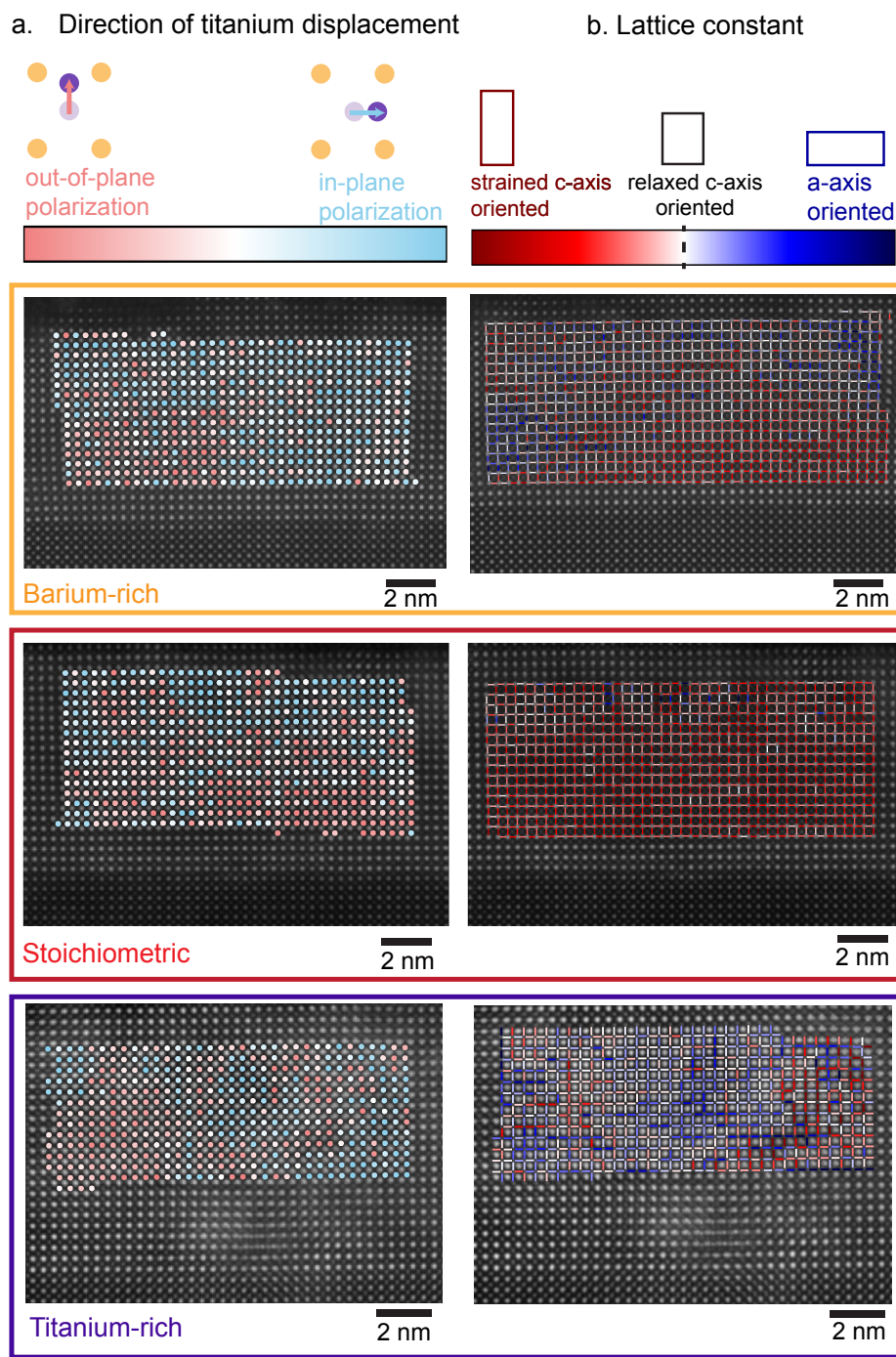


Figure S10. (a) Polar domain mapping of the barium-rich (top), stoichiometric (middle), and titanium-rich (bottom) films. A mix of in-plane and out of plane polarizations are seen in the stoichiometric, barium-rich, and titanium-rich films. (b) Mapping of the lattice spacing of the barium-rich (top), stoichiometric (middle), and titanium-rich (bottom) films. The lattice spacing is plotted as a percentage of the relaxed, c -axis out-of-plane, BaTiO_3 lattice constants, such that red corresponds to out-of-plane lattice spacing that is larger than the relaxed c -axis BaTiO_3 out-of-plane spacing, and blue corresponds to an out-of-plane spacing smaller than the relaxed c -axis value (i.e. a -axis oriented).

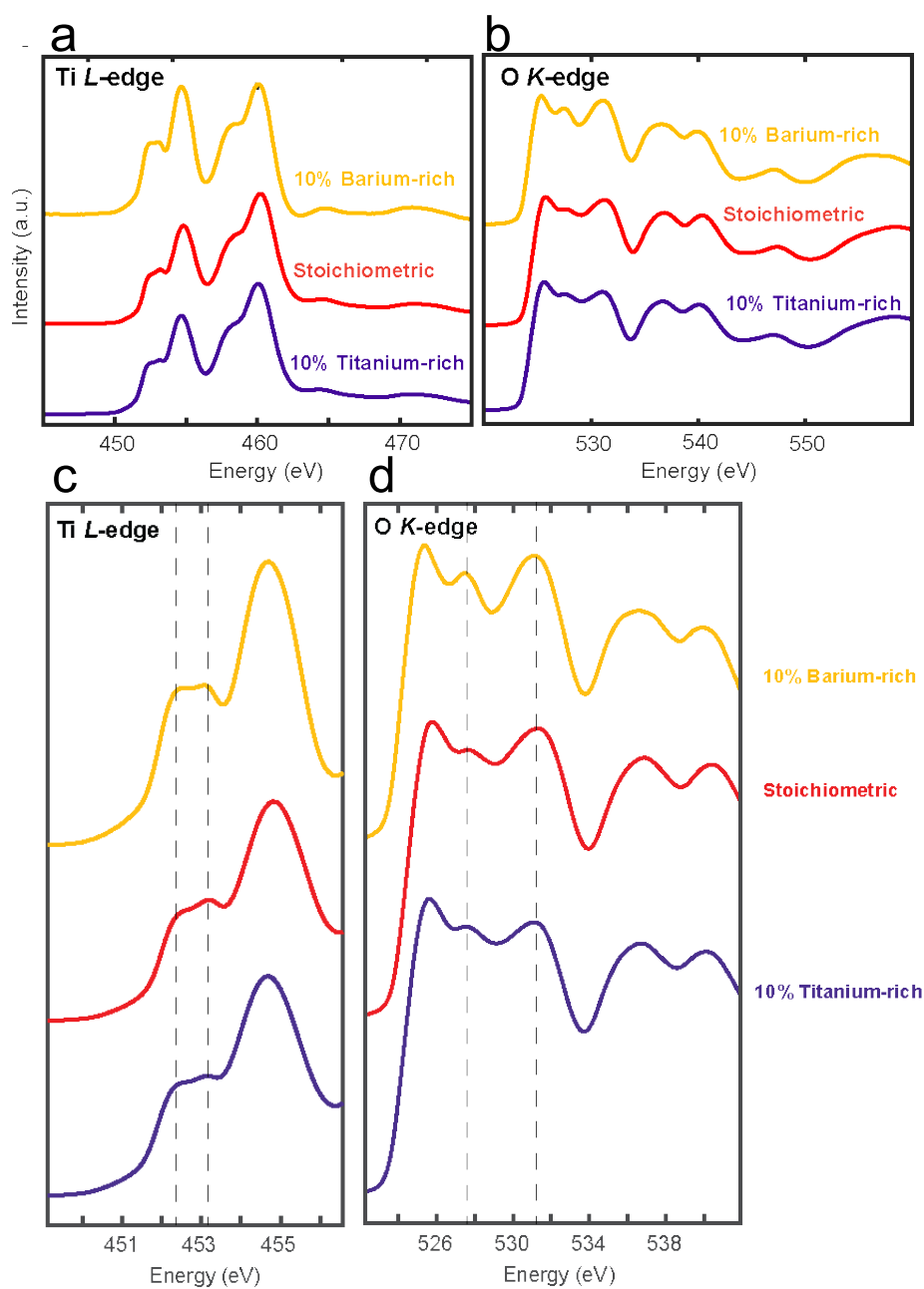
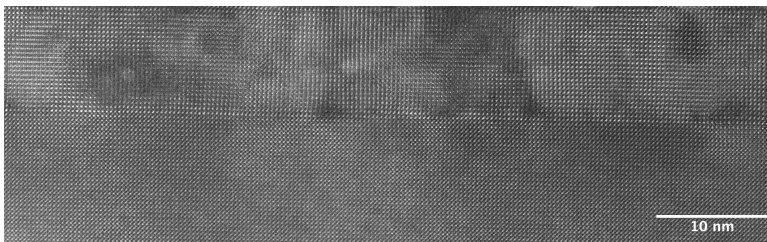


Figure S11. (a) XAS of 10% titanium-rich, 10% barium-rich, and stoichiometric BaTiO_3 films at the Ti-L edge. (b) XAS of the same films at the O-K edge. (c) Zoomed in XAS spectra for the Ti-L edge and (d) O-K edge.

a. HAADF of titanium rich film



b. LAADF of titanium rich film

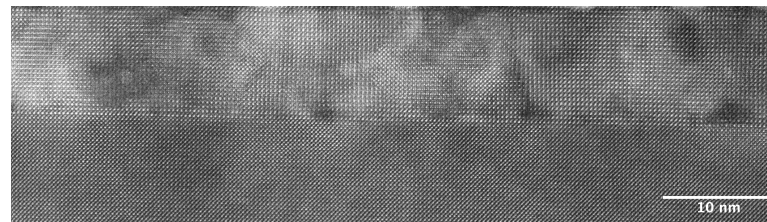


Figure S12. (a) High-angle (top) and (b) low-angle (bottom) annular dark field images of the 10% titanium-rich film. Enhanced contrast seen in the low-angle annular dark field image may be attributed to oxygen vacancies.