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Ferroelectric domain structures in low-strain BaTiO₃

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Epitaxial strain in ferroelectric films offers the possibility to enhance the piezoelectric performance utilizing low crystal symmetries and high density of domain walls. Ferroelectric BaTiO₃ has been predicted to order in a variety of phases and domain configurations when grown under low strain on low mismatched substrates, but little experimental evidence of that region of the phase diagram exist. In this work, epitaxial BaTiO₃ thin films are grown on NdScO₃ substrates under ~0.1% strain. A monoclinic ca_1/ca_2 phase, with 90 ° periodic in-plane domain configuration and small additional out-of-plane component of polarization, has been stabilized at room temperature and investigated by Piezoelectric Force Microscopy and X-ray Diffraction. Above 50 °C this phase is transformed into an a/c phase with alternating

in-plane and out-of-plane polarizations and forming zigzag domain walls between up-polarized and down polarized superdomains. Both types of domain patterns are highly anisotropic giving rise to very long domain walls. Above 130 °C the paraelectric phase is observed. The occurrence of a phase transition close to room temperature, a low symmetry ca_1/ca_2 phase and the formation of periodic domains make of this material a promising candidate for high piezoelectric response.

1. Introduction

Interplay between strain and polarization in ferroelectric perovskite epitaxial films can result in new polar states ^[1,2] and new functionalities ^[3–8]. Strain relaxation by the formation of ferroelastic domains can allow further functionalization due to the presence of domain walls ^[9–12] and periodic nanoscale structures ^[1,13–17].

The high piezoelectricity found in $PbZr_{1-x}Ti_xO_3$ (PZT) and related $PbTiO_3$ solid solutions materials originates in the existence of a monoclinic crystal structure and the formation of nanodomains at the Morphotrophic Phase Boundary (MPB) ^[18–20]. Ferroelastic nanodomain structures and low-symmetry monoclinic phases help accommodating the large elastic forces that develop at the MPB, providing elastic matching at the internal interfaces and inducing large piezoelectricity. In addition, the formation of ferroelastic nanodomains in thin films gives rise to novel effects such as flexoelectric polarization rotation in a/c domains ^[1], enhanced piezoelectricity by the flexoelectric effect in PZT nanostructures ^[21] or monoclinic areas of largely enhanced piezoresponse close to domain walls ^[22]. Thus, using epitaxial strain to induce different combinations of nanodomains with well-defined orientations and periodicities (domain engineering) opens a route to improved piezoelectrics, especially beneficial for the design of lead-free materials ^[23,24].

In classical lead-free ferroelectric BaTiO₃ single crystals, ferroelastic and ferroelectric 90 ° domains and non-ferroelastic and ferroelectric 180 ° domains are observed at room temperature^[25–29], consistent with the tetragonal crystal structure of the bulk crystal. Predictions for epitaxially strained BaTiO₃ thin films have resulted in different crystal symmetries and, thus, different domain structures^[30–37]. Particularly interesting are the predictions for films under low-strain values: even under zero nominal strain, the structure is modified by the elastic constraints imposed by the substrate and the different thermal expansion of film and substrate. Experimental realization of these phases is now becoming possible thanks to using substrates of the Rare-Earth Scandate family^[38,39]. In particular, using a Landau-Ginsburg-Devonshire-type nonlinear phenomenological theory, Koukhar et al. reported the BaTiO₃ phase diagram shown in **Figure 1**^[30]. This and other related work^[32,40,41] have predicted a rich and flat energy landscape with large variety of single-, multi- and metastable domain phases. Next to these many phase transitions (around which the piezoelectric responses are expected to greatly increase), monoclinic aa*/ca* and ca₁/ca₂ phases, not present in single crystals, have been predicted for low-strain values. . In this paper we test those predictions experimentally. We have stabilized two different domain structures with long and well-ordered domains: a room temperature monoclinic ca₁/ca₂ phase and either an a/c or an aa*/ca* phase above 50 °C.

2. Results and discussion

2.1. BaTiO₃ growth on NdScO₃ substrate

In this work BaTiO₃ (001)_{pc} films have been grown on NdScO₃ (001)_{pc}/(110)_o substrates (where subscripts *pc* and *o* refer to the pseudocubic and orthorhombic unit cells respectively) as NdScO₃ is the only currently commercial available substrate which provides low strain: the NdScO₃ in-plane lattice parameters are 4.002 Å (100)_{pc}/(002)_o and 4.014 Å (010)_{pc}/(-110)_o^[38]

which produce nominal room temperature misfit strains ϵ_s of -0.1% compressive strain and +0.2% tensile strain, respectively, for BaTiO₃ [42]; the average mismatch strain is therefore only +0.05%, i.e. marginally tensile but very close to zero.

BaTiO₃ films with thickness of 90 nm were grown on a NdScO₃ substrate (miscut angle 0.05-0.2 °), with a 6 nm thick, fully-strained, metallic SrRuO₃ bottom electrode, using Pulsed Laser Deposition (PLD). Atomic Force Microscopy (AFM) images of the substrate (and the electrode, not shown here) show flat terraces (see **Figure 2a**), while the surface of BaTiO₃ reveals an island growth-like structure (**Figures 2b-c**) with 4-5 clearly distinguishable unit cell steps. NdScO₃, SrRuO₃ and BaTiO₃ peaks are present in the θ -2 θ X-Ray Diffraction (XRD) scan around the (001)_{pc} Bragg peak [43-48] (**Figure 2d**) with superimposed finite size oscillations for the SrRuO₃ and BaTiO₃ films, indicating the high quality of the interfaces.

Figure 2e and **Figure 2f** show the off-specular BaTiO₃ (204)_{pc} and NdScO₃ (620)_o Bragg peaks of films grown with 0.20 mbar and 0.15 mbar oxygen pressure (P_{O2}) respectively. For P_{O2} = 0.20 mbar, the in-plane lattice parameters are equal for BaTiO₃ and NdScO₃, indicating full epitaxy. Instead, the films grown with P_{O2} = 0.15 mbar have additional peaks in the in-plane direction, caused by periodic domains. Indeed, changing P_{O2} during growth seems to affect the domain ordering: films grown at P_{O2} = 0.15 mbar films have ordered periodic domains with 100 nm periodicity, films grown at P_{O2} = 0.18 mbar show the same domain periodicity but with increased disorder and films grown at P_{O2} = 0.20 mbar films have disordered, non-periodic domains with sizes of about 500 nm. One way to explain these different results between these two kind is by considering that a higher concentration of oxygen vacancies (V_O) allows the lattice to better accommodate the strain by lowering the nucleation energy of domain walls, therefore promoting strain relaxation by an increasing amount of elastically favourable domains. Moreover, contrary to the usual situation where V_O increases the lattice parameters [49], it is found that increasing P_{O2} (or decreasing V_O) in the range from 0.15 to 0.20 mbar gives rise to an increase of the out-of-plane lattice parameter

from 4.015 to 4.022 ± 0.002 Å. An increase is also found when the domain pattern for a fixed V_O changes (by temperature) from a mostly in-plane ca_1/ca_2 to a more out-of-plane a/c domains. This increase of lattice parameter for lower V_O can be explained by considering an increase of out-of-plane domains when the film domain pattern gets more disordered.

2.2. Piezoelectric Force Microscopy domain configurations

Temperature-dependent Piezoelectric Force Microscopy (PFM) was used to characterize the domain states. Dual AC Resonance Tracking (DART) mode was used to separate the piezoresponse signal from the strong topological features from the island-like surface. 90° in-plane domains with walls along the $\langle 110 \rangle_{pc}$ axes are observed from lateral PFM images at room temperature, as seen in **Figure 3a-b**. These are consistent with both a periodic a_1/a_2 or ca_1/ca_2 domain structure (see **Figure S1** for more details) with a domain period of 100 nm and a strong preferential orientation for the walls to be parallel to one of the $\langle 110 \rangle_{pc}$ axes. The domains with the polarization along $\langle 010 \rangle_{pc}$ are about two times larger than the domains with polarization along $\langle 100 \rangle_{pc}$, caused by the larger substrate lattice parameter along the $[010]_{pc}$ direction.

At 50°C , a phase transition to an a/c phase takes place, as shown in **Figure 3c-d**. The transition is accompanied by a decrease of the domain periodicity to 70 nm. All the domain walls are then rotated by 45° and become parallel to only the $(010)_{pc}$ plane and not the $(100)_{pc}$ plane, because the significantly larger substrate in-plane lattice parameter towards $[010]_{pc}$ makes it favorable to have the long axis of the a-domains (the polarization axis) only along that direction. These domains are exceptionally long: domains of at least $10\ \mu\text{m}$ without disturbances (**Figure 3e**) are seen and seem to run across the full sample dimensions (5 mm). These domains are gathered in superdomains that differ from each other by a 180° rotation of the polarization (see **Figure S2** for more details). A zig-zag superdomain wall is formed in

Figure 3f-g, similar to those reported by Feigl et al. ^[50] in PZT films. The zigzag walls allow both in-plane and out-of-plane polarization in the a/c domains to change by a phase shift of the in-plane and out-of-plane components at both sides of the wall.

The minimum expected domain period of a/c phases can be calculated by considering the bulk c/a ratio and the substrate lattice parameter ^[15]. Following the calculations for this material combination, a 35 nm domain size for both a- and c-domains is obtained, corresponding exactly to the observed 70 nm total domain periodicity.

The resolution in these PFM images, however, is not enough to assign observed out-of-plane signal (not shown) in the apparent a_1/a_2 phase to real polarization (thus corresponding to the monoclinic ca_1/ca_2 phase) or crosstalk from in-plane polarization ^[29]; neither can observed additional in-plane polarization in the a/c phase be conclusively assigned to the monoclinic aa^*/ca^* phase or imperfect alignment of the sample. X-ray diffraction is used to conclude about the nature of the domain configurations.

2.3. X-ray Diffraction domain configurations

In-plane and out-of-plane XRD Reciprocal Space Maps (RSM) of the $(100)_{pc}$, $(110)_{pc}$ and $(001)_{pc}$ Bragg peaks in the room temperature phase, as shown in **Figure 4a-c**, display additional modulations in the diffuse scattering, corresponding to domain periodicity. It can be seen that the domains run along the $\langle 110 \rangle_{pc}$ direction with a real-space periodicity of 100 nm ^[51], fully consistent with the PFM data. Satellites around the different Bragg peaks do not present two-fold symmetry, as expected for a high preferential orientation of the domain walls, also observed in PFM. These in-plane XRD maps are similar to those observed for a_1/a_2 domain structures in $(\text{Pb,Sr})\text{TiO}_3$ ^[13]. However, additional intensity modulations (with the same 100 nm real-space in-plane periodicity) can also be seen around the out-of-plane $(001)_{pc}$ Bragg peak (see Figure 4c). Since XRD intensity scales as $|e^{i k_z z}|^2$, a modulation of the z-

component of the atomic displacements (and thus, out-of-plane polarization) is required. All the evidence combined seem to point to the predicted ca_1/ca_2 ^[30] phase, with a small out-of-plane polarization instability. One can notice that a projection of the domain periodicity (running along the $[110]_{pc}$ direction) onto other in-plane axes of the RSM gives a continuous apparent different domain period, calculated by *apparent domain size = domain period / cos(angle of rotation away from $[110]_{pc}$)*. So along the $\langle 100 \rangle_{pc}$ directions the apparent domain length is 140 nm and along the $[1-10]_{pc}$ direction (parallel to the walls) the domain length is infinite, leading to the disappearance of the domain peaks. The images can be found in **Figure S3**. Increasing the temperature to 80 °C, an a/c phase is observed. The XRD RSMs around the $(010)_{pc}$ and $(100)_{pc}$ Bragg peaks are given in **Figure 4d-e**. Intensity modulations are observed in the diffuse scattering in the $[010]_{pc}$ direction around the $(010)_{pc}$ Bragg peak with a real-space periodicity of 70 nm; while no periodic features are observed around the $(100)_{pc}$ Bragg peak. This is different than the observation of a/c domain structures in ultrathin $PbTiO_3$ grown on $DyScO_3$ ^[52], which produced periodic modulations in the $[100]_{pc}$ direction and domain peaks around the $(100)_{pc}$ Bragg peak. The difference in this work can be explained by the anisotropy of the walls in the present case (no domain wall along $(100)_{pc}$). XRD RSM around the $(001)_{pc}$ Bragg peak with a 70 nm real-space in-plane periodicity is given in **Figure 4f**. The intensity of these out-of-plane domain peaks is one order of magnitude higher than of the corresponding domain peaks for a ca_1/ca_2 phase, showing one order of magnitude higher out-of-plane polarization modulation in this a/c phase.

The theoretical phase diagram (see Figure 1) predicts a phase transition from the ca_1/ca_2 phase to the aa^*/ca^* phase, and a subsequent transition to the a/c phase for increasing temperature.

Using the current methods we are unable to distinguish the a/c from the aa^*/ca^* phase, so it is well possible that we are observing a monoclinic aa^*/ca^* phase instead of the a/c phase; there might be an additional phase transition between these last two phases.

For both structures, the periodic modulations of the diffuse scattering around the $(001)_{pc}$ Bragg peaks are detected at reciprocal lattice points coinciding with the a- and c-lattice parameters of bulk BaTiO₃. These bulk out-of-plane lattice parameters are conserved upon azimuthal rotation around $[001]_{pc}$, while the in-plane positions of the periodic modulations are changed, reflecting a change in periodicity. This observation suggests a lattice relaxation of the film from fully strained (at the Bragg peak) to fully relaxed a- and c-lattices. A strain gradient is thus most likely produced in both phases, inducing a flexoelectric polarization and thus an additional lowering of the symmetry, similar to what is observed in PbTiO₃ a/c domains ^[1].

2.3. Phase coexistence

If the material is cooled down fast enough, metastable a/c domains are observed to coexist within the ca_1/ca_2 phase at room temperature (**Figure S4**) for several days, giving evidence for the first order character of the a/c to ca_1/ca_2 phase transition. This observation stands in contrast to the theoretical prediction that ferroelectric transitions in mono-domain epitaxial BaTiO₃ should be second order due to clamping-induced renormalization of the quadratic coefficient of the polarization in the free energy ^[33], but it is fully consistent with the prediction for the ferroelectric-ferroelectric transition in polydomain films with a small amount of tensile strain ^[30]. Single crystal BaTiO₃ has similar remanence with monoclinic phase stability up to 100 K away from a thermotropic phase boundary ^[22,53].

2.4. Ferroelectric-to-paraelectric phase transition

The paraelectric transition temperature, the Curie temperature (T_C), of 130 °C is just slightly above the bulk value, confirming the low-strain state of the film as a high strain would

increase T_C further^[3]. Local piezoelectric loops can be obtained in the two ferroelectric states (ca_1/ca_2 and a/c phases) as shown in **Figure 5a**. Above T_C the piezoelectric loops disappear (**Figure 5b**), proving the ferroelectric origin of the piezoelectric loop and, simultaneously, the phase transition^[54]. Furthermore, the strained out-of-plane lattice parameter (in **Figure 5c**) decreases gradually near T_C (and at the 50 °C phase transition a small increase can be seen). Since the lattice parameter scales with P^2 (P is polarization)^[55], it represents a gradual decrease of the order parameter and thus a second order phase transition, representing a ferroelectric thin film under strain.

3. Conclusion

Two phase transitions have been stabilized in low-strain $BaTiO_3$ thin films on $NdScO_3$ substrates: the ca_1/ca_2 phase at room temperature changes into an a/c -like phase (a/c or aa^*/ca^* phase) above 50 °C, with the Curie temperature T_C of the paraelectric phase transition at 130 °C. The polarization freedom in this material is very large, as indicated by the monoclinic room temperature ca_1/ca_2 phase, the probable additional flexoelectric polarization induced by the nanodomains, the presence of metastable phases and phase coexistence and finally by the fact that there is a phase transition close to room temperature. So low-strain $BaTiO_3$ thin films show large potential for high piezoelectric responses. Additionally, contrary to most materials with such polarization freedom, $BaTiO_3$ on $NdScO_3$ exhibits well-ordered structures, especially the exceptionally ordered millimeter long a/c domains. This high order is critical in designing devices where ordered structures can have strong contributions and be exploited for tailoring physical properties.

4. Experimental Section

BaTiO₃ thin films have been deposited by Pulsed Laser Deposition, using a Lambda Physik COMPex Pro 205 KrF ($\lambda=248\text{nm}$) excimer ultraviolet laser and a Twente Solid State Technology reflection high-energy electron diffraction (RHEED) vacuum system. The target was a BaTiO₃ single crystal (MaTecK GmbH) and the deposition parameters were a background pressure of 10^{-7} mbar, a substrate temperature of 700-800 °C, a laser energy of 2 Jcm⁻², a spotsize of 2.6 mm², a target-substrate distance of 50 mm, a repetition rate of 5 Hz, cooling rate of 5 °C/min at 300 mbar P_{O2} after the growth and the growth P_{O2} was varied between 0.15 and 0.20 mbar. NdScO₃ substrates (CrysTec GmbH) were pre-treated to obtain single termination (adapted from Ref. [56]) for 4 hours at 900 °C in an oxygen flow and subsequently with 12 M NaOH and 1 M NaOH for several hours and a water/ethanol cleaning step.

Characterization was performed using AFM (Veeco Dimension V) and PFM in Dual AC Resonance Tracking (DART) mode (Asylum). X-ray diffraction measurements were done at both the PETRA III P08 beamline (DESY, Hamburg) operated at 9 keV ($\lambda = 1.37761 \text{ \AA}$) and a Panalytical X'Pert MRD Cradle (four axes) laboratory diffractometer, copper X-ray generator tube ($\lambda = 1.540598 \text{ \AA}$), both equipped with an Anton Paar heating stage.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 1. Pertsev phase diagram of misfit strain versus temperature for low-strain BaTiO₃. Thick lines represent first order and thin lines represent second order phase transitions. The predicted phases are the paraelectric phase ($P_x = P_y = P_z = 0$), c-phase ($P_x = P_y = 0, P_z \neq 0$), a/c-phase ($P_x \neq 0, P_y = P_z = 0$ and $P_x = P_y = 0, P_z \neq 0$), aa*/ca*-phase ($P_x \neq 0, P_y \neq 0, P_z = 0$ and $P_x = 0, P_y \neq 0, P_z \neq 0$), a₁/a₂-phase ($P_x \neq 0, P_y = P_z = 0$ and $P_x = P_z = 0, P_y \neq 0$) and ca₁/ca₂-phase ($P_x \neq 0, P_y = 0, P_z \neq 0$ and $P_x = 0, P_y \neq 0, P_z \neq 0$).^[30] Phase diagram adapted with permission from Ref.^[30] Copyright 2001, American Physical Society.

Figure 2. Epitaxial BaTiO₃ film. **a-b)** AFM images of respectively NdScO₃ substrate and BaTiO₃ film. Insets: the Reflective High-Energy Electron Diffraction (RHEED) images show respectively the flat orthorhombic surface structure of NdScO₃ and the island-growth mode of BaTiO₃. **c)** Cross-section (data as black line, sketch of unit-cell steps in green) of the BaTiO₃ islands displaying 4-5 unit cell steps, maintaining high quality epitaxy. **d)** $\theta/2\theta$ XRD scan (black circles) around (001) Bragg peak (film grown at $P_{O_2} = 0.15$ mbar). Fit of the data (blue line) with the fit parameters (c is the c -axis lattice parameter and t is the thickness of the film) [43–48]. **e-f)** Reciprocal Space Maps around $(204)_{pc}$ of both BaTiO₃ film and NdScO₃ substrate (corresponding to the $(602)_o$ Bragg reflection of the substrate), for films grown with P_{O_2} of 0.20 mbar and 0.15 mbar, respectively. Colors are in log scale. Close-up of the BaTiO₃ $(204)_{pc}$ peak showing no domains (**g**) or domains (**h**), corresponding to the red squares in (**e**) and (**f**) respectively.

Figure 3. **a)** Lateral amplitude PFM image at room temperature. **b)** Model for the ferroelectric polarization in the a_1/a_2 domains as a top view. **c)** Lateral amplitude PFM image at 70 °C. Inset: Fast Fourier Transform, the clear periodicity peaks correspond to the domain periodicity. **d)** 3D model for the ferroelectric polarization in these two sets of a/c domains forming superdomains. **e)** Topography and lateral amplitude PFM images at 70 °C (10 μm

image length), without disturbance of the nanodomain structures, except for the superdomains. **f)** Some superdomain boundaries produce zig-zag domains. **g)** Model of the polarization in the zig-zag domains.

Figure 4. RSM around (100) (a), (110) (b) and (001) (c) Bragg peaks at room temperature; RSM around (010) (d), (100) (e) and (001) (f) Bragg peaks at 80 °C. Colors are in log(10) scale.

Figure 5. PFM hysteresis loop of an effective piezoelectric constant $d_{33,e}$ and the corresponding phase at **a)** 70 °C (lower than T_C), and at **b)** 140 °C (higher than T_C). **c)** BaTiO₃ out-of-plane lattice parameter obtained from a θ - 2θ scan around (001) Bragg peak versus temperature.

BaTiO₃ thin films have been grown by Pulsed Laser Deposition on low-strain NdScO₃ substrates. A room-temperature monoclinic ca_1/ca_2 periodic domain configuration with in-plane and additional symmetry-lowering out-of-plane polarization is stabilized; while above 50 °C, an a/c domain configuration with very long domain walls is observed. This rich phase diagram with domains and lowered symmetry is promising for high piezoelectric response.

BaTiO₃

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Ferroelectric domain structures in low-strain BaTiO₃

Supporting Information

Ferroelectric domain structures in low-strain BaTiO₃

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Figure S1. Lateral amplitude and phase PFM images taken of a single area at room temperature. The polarization sensitivity for the lateral PFM image is indicated by the red arrow, vertical (a), horizontal (b) and diagonal (c). **d)** Model of the four types of superdomains found in these images, labelled A, B, C and D as in Figures a), b) and c). An example of how these domains can be reconstructed can be obtained by looking at superdomains A and B in (a) and (b). In (a), superdomain A has high phase for the $[0-10]_{pc}$ oriented polarization domains and intermediate phase for the $\langle 100 \rangle_{pc}$ oriented polarization domains. Then in superdomain B, the same intermediate phase can be found for the $\langle 100 \rangle_{pc}$ oriented polarization domains and high phase for the $[010]_{pc}$ oriented polarization domains. In (b), superdomain A has low ($[-100]_{pc}$ oriented polarization) and intermediate ($\langle 010 \rangle_{pc}$ oriented polarization) phases for its domains, and superdomains B has high ($[100]_{pc}$ oriented polarization) and intermediate ($\langle 010 \rangle_{pc}$ oriented polarization) phases for its domains. Similar arguments can be made for the other superdomains and the sample oriented at the $[110]_{pc}$ axis. **e)** Topography image of the area investigated by PFM. The superdomain walls are often correlated to topographic defects, suggesting that those defects are domain wall nucleation points.

Figure S2. PFM images taken at 70 °C. Vertical PFM image (a) and lateral PFM image with the polarization sensitivity along $[010]_{pc}$ (b) show domain contrast, while the lateral PFM image with polarization sensitivity along $[100]_{pc}$ (c) doesn't show any domain contrast. So these PFM results prove that the in-plane polarization of BaTiO_3 thin films is only along the $[010]_{pc}$ direction. Superdomains A (d) and B (e) are observed, where some of the superdomain walls (f) form zig-zag walls (g). The domain configuration can be found by considering the amplitudes of the piezoresponse. High piezoresponse (in-plane domains) of superdomain B crosses into intermediate piezoresponse (out-of-plane domains) of superdomain A; and intermediate piezoresponse (out-of-plane domains) of B crosses into low piezoresponse (in-plane domain rotated 180 °) of A. Similar observations can be made for the Vertical PFM image.

Figure S3. a) Measured (black squares) and calculated (red triangles) apparent domain size found from the intensity modulation in the diffuse scattering around the (001) Bragg peak, for

different azimuthal angles of rotation (ϕ) around the $[001]_{pc}$ axis. **b)** Model for the calculation of apparent domain size. Domains have periodicity along $[110]_{pc}$, and the in-plane axis measured by X-rays in the RSM around the $(001)_{pc}$ Bragg peak is determined by the angle ϕ . Then the apparent domain size is a function of the sine of that angle: apparent domain size = domain size / $\sin(\phi)$. In the figure it can be seen that the length that X-ray direction vector takes to cross one domain is equal to the apparent domain length observed in the RSM. The graph can be illustrated by RSMs: the in-plane spacing is maximum for a ϕ of -90° (**c**), corresponding to a minimum domain size; the domain peaks are absent for a ϕ of 0° (**d**), corresponding to infinite domain size; and the domain peaks are in between both situations for a ϕ of 135° (**e**).

Figure S4. XRD RSM around the $(010)_{pc}$ (**a**) and $(100)_{pc}$ (**b**) Bragg peaks at $T = 30^\circ\text{C}$ after fast cooldown. In both RSMs intensity modulation in the diffuse scattering along $[110]_{pc}$ can be observed, corresponding to the ca_1/ca_2 phase. On top of that, the $(010)_{pc}$ Bragg peak RSM gives intensity modulation along $[010]_{pc}$, while no such modulation is observed around the $(100)_{pc}$ Bragg peak, which is the signature of the a/c phase of these BaTiO_3 thin films. So it can be concluded that both phases coexist simultaneously in this fast cooled down film. (**c**) Amplitude out-of-plane PFM image of a small area showing indication of both ca_1/ca_2 and a/c phases. The observation of ca_1/ca_2 domains walls along $[110]$ in the out-of-plane mode could be either due to the real out-of-plane polarization or cross-talking with the in-plane components (as discussed previously). In addition, the domains with walls along the $[100]$ direction, consistent with those of the a/c domains observed at high temperature are weakly visible.