Synthesis of metastable Ruddlesden-Popper titanates, $(A\mathrm{TiO}_3)_nA\mathrm{O}$, with $n \geq 20$ by molecular-beam epitaxy

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Abstract

We outline a method to synthesize $(A\mathrm{TiO}_3)_nA\mathrm{O}$ Ruddlesden-Popper phases with high-*n*, where the *A*-site is a mixture of barium and strontium, by molecular-beam epitaxy. The precision and consistency of the method described is demonstrated by the growth of an unprecedented $(\mathrm{SrTiO}_3)_{50}\mathrm{SrO}$ epitaxial film. We proceed to investigate barium incorporation into the Ruddlesden-Popper structure, which is limited to a few percent in bulk, and we find that the amount of barium that can be incorporated depends on both the substrate temperature and the strain state of the film. At the optimal growth temperature, we demonstrate that as much as 33% barium can homogeneously populate the *A*-site when films are grown on SrTiO_3 (001) substrates, whereas up to 60% barium in films grown on TbScO_3 (110) substrates, which we attribute to the difference in strain.

This detailed synthetic study of high *n*, metastable Ruddlesden-Popper phases is pertinent to a variety of fields from quantum materials to tunable dielectrics.

Introduction

Ever since the discovery of high transition temperature (high-T_c) superconductivity in doped La_2CuO_4,[1] Ruddlesden-Popper oxides with formula $(ABO_3)_nAO$ have been an important class of compounds for condensed matter physics. These perovskite-related phases demonstrate diverse properties including high T_c and unconventional superconductivity,[1–5] colossal magnetoresistance,[6] exotic Mott instability,[7] metamagnetism,[8,9] electronic nematicity,[10,11] and low-loss tunable dielectricity.[12,13] Interestingly, research disproportionately focuses on the $n = 1$ and $n = 2$ members of the Ruddlesden-Popper series with chemical formula $(ABO_3)_1AO$[1–4,6,7,11] and $(ABO_3)_2AO$.[6,8–10] Attention to these series members is, at least in part, due to the amplified difficulty of synthesizing Ruddlesden-Popper phases with increasing *n* (excluding the $n = \infty$ perovskite phase). This difficulty is particularly obtrusive to bulk synthesis methods for which $n = 3$ is the highest value of *n* that has been achieved in single-phase samples of $(SrTiO_3)_nSrO$,[14] $(SrRuO_3)_nSrO$,[15] $(CaTiO_3)_nCaO$,[16] and $(LaNiO_3)_nLaO$.[17] TEM images of attempts to make bulk $(SrTiO_3)_nSrO$ phases with $n > 3$ show disordered syntactic intergrowths where *n* ranges from 2 to 8[18] because these phases are nearly degenerate in energy.

The highest value of *n* achieved to date by bulk techniques of any Ruddlesden-Popper oxide is $n = 4$[19] and for any Ruddlesden-Popper of any kind is $n = 7$.[20] For the cuprate superconductors, which have structures closely related to Ruddlesden-Popper phases,[2] the highest n of nearly single-phase samples is for the $n = 6$ phase, $HgBa_2Ca_5Cu_6O_{14+\delta}$ (Hg-1256).[21]

Accessing Ruddlesden-Popper phases with intermediate n (i.e., $4 < n < \infty$ for nickelates, ruthenates, and titanates) in oxide systems or in other homologous series, is possible using thin-film methods that exploit kinetics. More specifically, the order in which precise doses of the species contained in each monolayer are supplied to the substrate can build up a targeted member of a homologous series. Nonetheless, synthesis demands precise calibration and the surface kinetics during film growth have proven counterintuitive, prompting detailed studies on Ruddlesden-Popper thin film synthesis.[22–31] Many of these studies have investigated strontium titanate Ruddlesden-Popper phases with formula $(SrTiO_3)_nSrO$ as a comparatively simple model system with no charged monolayers, no octahedral rotations, and no volatile species.[22,25–29] Nonetheless, synthetic discoveries are often transferrable across material systems. For instance, the first demonstration of the synthetically challenging superconducting $(NdNiO_3)_5NdO$ phase by MBE[5] was published only three years after the first report of superconductivity in doped $NdNiO_2$.[32] The rapid progress was, in part, facilitated by experience developed in the $(SrTiO_3)_nSrO$ system.[22,26,27] The discovery of surface rearrangement during growth of titanate Ruddlesden-Popper phases[26] was subsequently proven to apply to nickelate Ruddlesden-Popper phases as well.[27] Similarly, out-of-phase boundaries caused by atomic steps on the substrate surface were first noted in Sr_2RuO_4 films[23] due to the fragility of superconductivity in this phase. These out-of-phase boundaries are, however, observable and parasitic in many Ruddlesden-Popper thin films. Their attribution to step edges inspired minimization of this defect by implementation of creative buffer layers,[30] Ruddlesden-Popper substrates ($LaSrAlO_4$),[31] or perovskite substrates with very low miscut.[33] In summary, improved understanding of Ruddlesden-Popper synthesis and structural characterization is shared across the diverse fields for which these crystals are attractive.

In this Letter, we develop a methodology to dramatically increase the accuracy and consistency with which Ruddlesden-Popper titanate films can be grown by MBE. The precision of this methodology is used here to grow a $(SrTiO_3)_{50}SrO$ film with a 5× greater periodicity than has been reported using more conventional growth strategies.[34,35] The repeatability of this method is leveraged to study the growth window for high quality $(A\mathrm{TiO_3})_{20}A\mathrm{O}$ films on $SrTiO_3$ (001) substrates, where the *A*-site is partially occupied by barium. We find that the structure crystallizes homogeneously with as much as 33% barium on the *A*-site when grown at the appropriate temperature. Note that, in bulk, only a few percent barium can be dissolved into $(SrTiO_3)_nSrO$ before barium orthotitanate (Ba_2TiO_4) impurities with a completely different crystal structure are observed.[36] When grown too cold, the intended horizontal double-rocksalt $(A\mathrm{O})_2$ Ruddlesden-Popper faults struggle to crystallize leading to a film with mostly vertical $(A\mathrm{O})_2$ faults. When grown too hot, the barium does not incorporate homogenously; rather, it is partially expelled from the Ruddlesden-Popper faults leading to a sawtooth pattern in barium concentration along the growth direction. This tendency toward inhomogeneity is dramatically exacerbated by increasing compressive strain; as much as 60% barium can be incorporated homogeneously if grown on a lattice matched substrate.[29] Our incorporation of metastable $(A\mathrm{O})_2$ faults into the perovskite $(Ba,Sr)TiO_3$ system, which is well studied for its tunable dielectric properties,[37–39] may prove a rewarding modification. Ruddlesden-Popper titanates containing all or mostly strontium are the highest performing tunable dielectrics ever measured thanks to their extraordinarily low dielectric loss at 100 GHz,[12,13] and increasing the barium content of Ruddlesden-Popper films could enable more flexible engineering of tunability while maintaining the low dielectric loss of Ruddlesden-Popper phases. Beyond titanates, we hope that this study will increase the accessibility of other high n Ruddlesden-Popper phases and embolden researchers to consider alloying with metastable phases by employing lattice matched substrates.

Methods

All syntheses were performed in a Veeco Gen10 MBE system in a chamber background pressure of 5×10^{-7} Torr of (O_2 + ~10% O_3). The (001) $SrTiO_3$ substrates were terminated following the procedure developed by Koster *et al*.[40] The fluxes of strontium and barium were supplied via conventional effusion cells, and titanium was evaporated using a Ti-Ball.[41] X-ray diffraction (XRD) spectra were collected using a Panalytical Empyrean diffractometer using Cu-$K_{\alpha 1}$ radiation, and atomic force microscopy (AFM) was performed using an Asylum Cypher ES Environmental AFM.

Results and Discussion

Even using MBE to deliver precise monolayer doses of the constituent elements, the difficulty of synthesizing Ruddlesden-Popper films, with formula $(ABO_3)_nAO$, is amplified as n increases. In the $(SrTiO_3)_nSrO$ system, it is common practice to calibrate the fluxes of strontium and titanium by monitoring RHEED intensity oscillations during shuttering,[42,43] but the highest n ever reported using such techniques is 10, $(SrTiO_3)_{10}SrO$.[34,35] Unfortunately, we find that conventional calibration is insufficient for the consistent growth of high quality $n \geq 10$ films of $(SrTiO_3)_nSrO$. This makes studying metastable barium-containing Ruddlesden-Popper titanates with formula $(A\mathrm{TiO_3})_nA\mathrm{O}$ extremely challenging because it is impossible to know whether a failed growth arose from imprecise calibration or improper growth conditions. Therefore, we begin by developing a method to consistently synthesize $(\mathrm{SrTiO_3})_{20}\mathrm{SrO}$ before studying barium incorporation.

Our strategy for optimizing film stoichiometry relies on the $\sqrt{2} \times \sqrt{2}$ reconstruction that has been previously observed by reflection high-energy electron diffraction (RHEED) when $\mathrm{SrTiO_3}$ films—grown on $(001)_p$ perovskite substrates, where the subscript p indicates pseudocubic indices—are terminated with $\gtrsim$1.2 monolayers of SrO.[44,45] This reconstruction is identified by half-order streaks that appear along the $[110]_p$ azimuth as seen in Fig. 1(d).[44,45] The appearance of a structural distortion in thin SrO epitaxially grown on $\mathrm{SrTiO_3}$ is not surprising given that SrO is under 7.6% tensile strain when commensurately strained to $\mathrm{SrTiO_3}$. One possible structural explanation that is consistent with the observed $\sqrt{2} \times \sqrt{2}$ reconstruction is suggested in Fig. 1(a), where two adjacent SrO formula units form a small cluster with interionic distances more comparable to those in bulk SrO. In addition to reconstructions, other studies have observed various nonidealities when attempting to grow SrO epitaxially on $\mathrm{SrTiO_3}$ such as island growth after as few as 2 monolayers of SrO are deposited[46] and observation of (111)-oriented SrO films.[47] In the supplemental information, we characterize epitaxial SrO films that are a few monolayers thick grown on (001)-oriented $\mathrm{SrTiO_3}$ *in situ* by RHEED at growth temperature and *ex situ* (i.e., after air exposure) by atomic force microscopy (AFM) at room temperature. By AFM, we observe the onset of clear surface roughening after 3 monolayers of SrO are deposited, and we observe that the period of RHEED intensity oscillations during SrO deposition has a local minimum after 2 complete monolayers are deposited, inconsistent with what is expected (and observed)[48,49] for RHEED oscillations from the bulk rock salt structure of SrO.

Also critical to our development of a new calibration for $(SrTiO_3)_n SrO$ films, was the prior observation of layer rearrangement during growth.[26,27] It was noted that when growing $(SrTiO_3)_n SrO$ by MBE, if a TiO_2 monolayer is deposited atop two consecutive SrO monolayers, the TiO_2 will diffuse underneath; a horizontal $(AO)_2$ Ruddlesden-Popper fault only nucleates if TiO_2 is deposited atop an accumulation of three consecutive SrO monolayers on the surface of the growing film.[26,27] Inspired by these important observations, we develop a new procedure to improve the consistency with which $(SrTiO_3)_n SrO$ can be grown by MBE.

Our strategy starts by approximating the strontium and titanium fluxes—within a few percent of actual values—using the previously developed method of monitoring RHEED intensity oscillations during shuttering.[42] With a reasonable estimate of fluxes, we start a separate procedure for fine tuning the flux measurements. We first deposit approximately 2 SrO monolayers atop a TiO_2-terminated $SrTiO_3$ (001) substrate,[40] and then alternately deposit monolayers of TiO_2 and SrO until the calibration is complete—usually 40-60 cycles. Assuming the initial flux approximation is perfect, the surface composition would oscillate between termination with one monolayer of SrO at the end of the TiO_2 deposition step and termination with two monolayers of SrO at the end of the SrO deposition step. The TiO_2 layer diffuses beneath the SrO layer, as mentioned previously, meaning that a $(SrO)_2$ Ruddlesden-Popper fault would not crystallize using this procedure.[26,27] Because the surface is terminated with >1 monolayer of SrO for most of the recipe, the $\sqrt{2} \times \sqrt{2}$

reconstruction is observable for the majority of each cycle, absent only at the end of the TiO_2 deposition and the beginning of the SrO deposition. We demonstrate this point by monitoring the line profile of the RHEED pattern along the [110] azimuth—indicated by the red line in Fig. 1(c-d)—as this recipe is run. Plotting the line profile vs. time (Fig. 1(b)), we see that the half-order streaks are absent only at the end of the TiO_2 layer and the beginning of the SrO layer when the surface is terminated with approximately one monolayer of SrO. In addition, a video showing the appearance and disappearance of the reconstruction during this recipe is included in the supplemental information. This discussion is all assuming the fluxes are perfectly calculated, but this is not ordinarily the case.

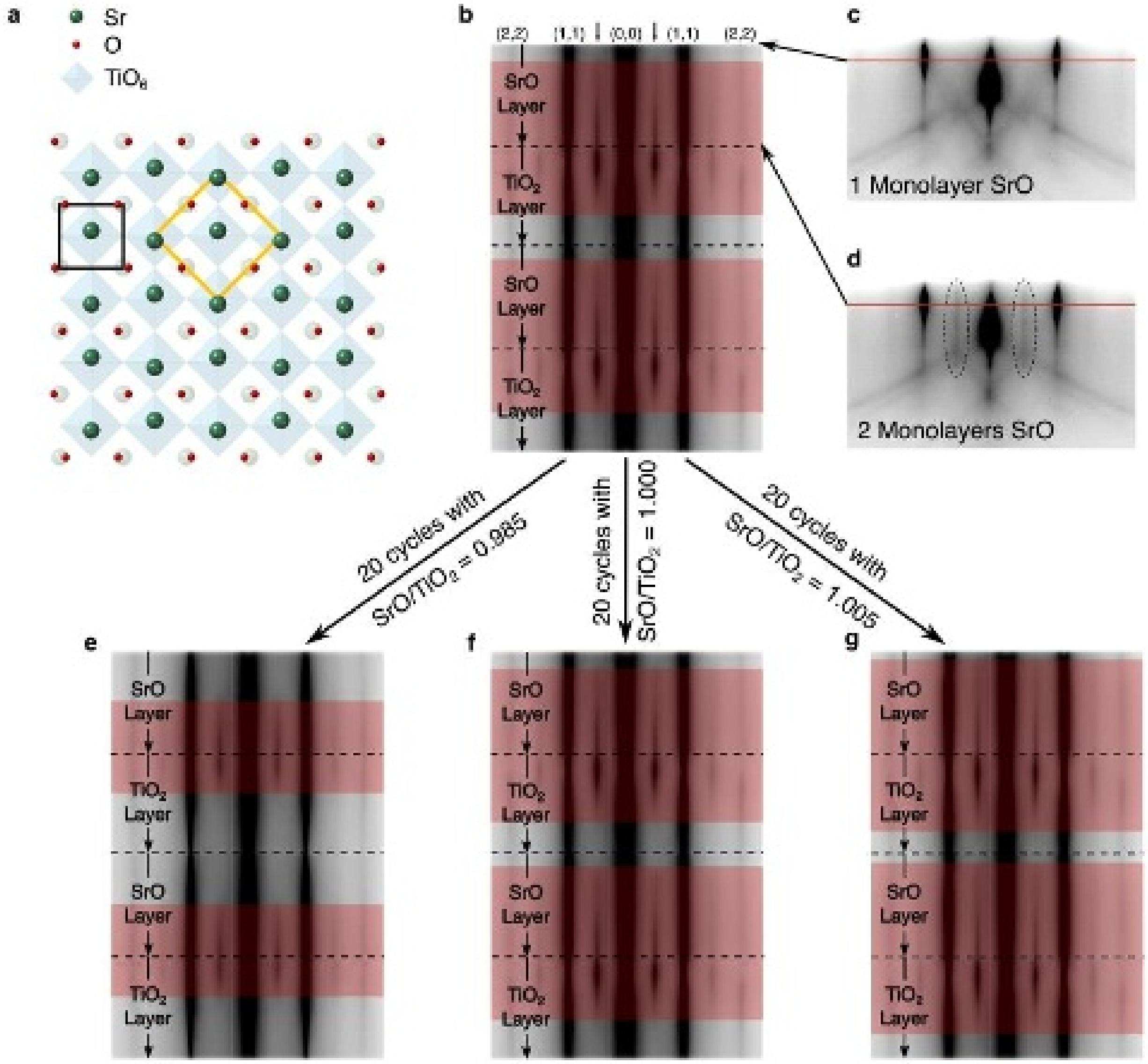

FIG. 1 (a) Proposed atomic arrangement for the $\sqrt{2}\times\sqrt{2}$ reconstruction observed when (001)-oriented, $SrTiO_3$ is terminated with 2 monolayers of SrO. The yellow square indicates the reconstructed surface cell, and the black square indicates the bulk unit cell. (b) Line profile of the RHEED image monitored over time during the shuttered deposition of approximate monolayer doses of SrO-TiO_2-SrO-TiO_2, where shuttering steps are separated by dashed lines. The portion of the scan highlighted in red (~75% of each cycle) indicates the presence of the $\sqrt{2}\times\sqrt{2}$ reconstruction. (c-d) Snapshots of the RHEED pattern along the [110] azimuth when the surface is terminated with (c) 1 monolayer and (d) 2 monolayers of SrO. The red lines indicate where the line profile was collected. (e-f) Line profile after alternating 20 consecutive ~1 monolayer doses of SrO and TiO_2 with different dose ratios. After 20 cycles with 1.5% excess TiO_2 per cycle (e), the

reconstruction is present for only ~45% of the cycle. After 20 equal doses of SrO and TiO_2 (f), the reconstruction remains present for ~75% of the cycle. After 20 cycles each with 0.5% excess SrO per cycle (e), the reconstruction is present for ~85% of the cycle.

Most likely, the SrO and TiO_2 doses are not perfectly matched, but observing the reconstruction during the calibration recipe enables quantitative determination and subsequent elimination of this nonstoichiometry. For example, if the dosage of TiO_2 is 1.5% greater than that of SrO, the $\sqrt{2} \times \sqrt{2}$ reconstruction (half-order streaks along the [110] azimuth in RHEED) will be visible for 1.5% less time each cycle. If during the first cycle the reconstruction is present for 75% of the cycle (Fig. 1(b)), then in the 20th cycle, the reconstruction will be present for only 45% of the cycle (Fig. 1(g)), an easily observable shift results from a relatively small flux mismatch. To resolve such a flux mismatch, we could increase the strontium shutter time by 1.5% or increase the temperature of the strontium source by 0.5 °C and continue observation (at our strontium source temperature of ~500 °C the flux change is approximately 3% per °C).[50] Figures 1(e) and 1(f) show similar line scan evolutions for different dosage ratios. For synthesizing $n = 20$ Ruddlesden-Popper phases, we aim to have the flux ratios optimized to better than 0.5% or equivalently, the Sr source within 0.2 °C of the perfect flux-matching temperature. This condition is confirmed by observing <10% change in the time the reconstruction is present over the course of 20 cycles. Note that the PID control of effusion cell temperatures used in this study results in temperature fluctuations of less than 0.1 °C, enabling the required precision to synthesize $n = 20$ Ruddlesden-Popper phases.

We find that this method of stoichiometry calibration enables more consistent synthesis of $n = 20$ Ruddlesden-Popper films compared to monitoring RHEED intensity oscillations during shuttered deposition alone [42] due to a number of advantages. For one, the old method is sensitive to the incident angle of the electron beam, which can easily lead to misinterpretation of the relative fluxes.[51] In addition, the updated method can be performed while rotating the substrate to ensure uniform coverage from each of the molecular beams, checking in on the [110] azimuth periodically to identify a mismatch in dosage. Most critically, this strategy gives insight into what is happening on the surface during growth of the Ruddlesden-Popper phases. This enables the grower to make adjustments that accommodate drifting fluxes or imperfect substrate termination in real time, rather than completely restarting. The advantage here is enormous when synthesizing $n = 20$ Ruddlesden-Popper phases for which a 1% drift in flux during the growth likely results in a failure to synthesize the target phase. An example of the drift correction protocol we employ is included in the supplemental information. Furthermore, precise termination of $SrTiO_3$ is more illusive than once believed.[52] This method is a sensitive probe of surface stoichiometry, and we find that as-prepared $SrTiO_3$ substrates are terminated with roughly 1.6 monolayers of TiO_2 rather than the commonly idealized model of single monolayer termination. One disadvantage of our method is that if the surface is ever terminated with >2 monolayers of SrO during stoichiometry calibration, $(SrO)_2$ Ruddlesden-Popper formation or excessive surface roughening[46] may occur, frustrating the calibration method. For this reason, we begin with a condition that we know is slightly TiO_2-rich (i.e., oscillating between termination with 0.9 monolayers of SrO and 1.9 monolayers of SrO during which the $\sqrt{2} \times \sqrt{2}$ reconstruction is present for 70% of the cycle) and slowly approach perfect stoichiometry. The method can also produce unclear results for slow growth rates (>30 s per monolayer) or very high substrate temperatures

(>850 °C), both of which we attribute to increased adatom diffusion length enabling excessive roughening of the SrO-rich surface—SrO grown epitaxially on $SrTiO_3$ has a tendency to roughen as discussed in the supplemental information and Ref[46].

While the stoichiometry (or flux ratio) is precisely determined by this method, it remains to calibrate the absolute flux of the elements to enable a precise Ruddlesden-Popper film. The n values of the Ruddlesden-Popper phases adjacent to the $n = 20$ Ruddlesden-Popper (i.e., $n = 19$ and $n = 21$) differ by only 5%, meaning that if the stoichiometry is correct, but the absolute fluxes are 5% too high that an $n = 21$ film will be grown when attempting an $n = 20$ film. To precisely calibrate the absolute flux, we utilize an *ex situ* x-ray diffraction (XRD) approach developed previously to measure the periodicity of a Ruddlesden-Popper film so that the subsequent film can be quantitatively corrected.[29] Typically, we perform both the stoichiometry calibration and the periodicity calibration using a single calibration sample. We first calibrate stoichiometry by shuttering the growth of a perovskite with an SrO-rich surface as shown in Fig. 1(b), and adjusting source temperatures until the $\sqrt{2} \times \sqrt{2}$ reconstruction disappears when the TiO_2 layer is 80% complete for 20 consecutive cycles with the same programmed shutter time and source temperatures. Then on top of the perovskite, we deposit a 30-40 nm thick Ruddlesden-Popper film of the target series member,[22,26] measure the periodicity with XRD, and scale the TiO_2 and SrO shutter times in subsequent films using the deviation in periodicity from the ideal structure.[29] As reported previously, to intentionally crystallize $(SrO)_2$ faults in the Ruddlesden-Popper part of the film, we periodically deposit an additional SrO monolayer so that the surface is momentarily terminated with 3 monolayers of SrO.[26] As discussed in the supplemental information, we believe that the surface when terminated with 3 monolayers of SrO is substantially rougher than previously conceived, but nonetheless, we find that this procedure enables crystallization of the intended Ruddlesden-Popper phase.

The above procedure was developed at a substrate temperature of 750 °C measured by an optical pyrometer operating at a wavelength of 980 nm and a 5×10^{-7} Torr background pressure of about 10% ozone (and ~90% oxygen). Next, we go on to study the growth window for $(SrTiO_3)_{20}SrO$ films, performing a series of growths at different substrate temperatures while keeping the ozone pressure constant (Fig. 2). To reduce the probability of misinterpretation, we perform the growths in a random order on a single day and begin each growth with the stoichiometry calibration described previously to ensure that the source fluxes have not drifted between growths. For substrate temperatures lower than 740 °C, we see that the peaks anticipated in XRD are absent, but the film peak exhibits clear Laue oscillations. Above 860 °C, Ruddlesden-Popper peaks are visible in XRD, but Laue oscillations are absent. Using the previously established method for assessing the periodicity of Ruddlesden-Popper superlattices,[29] we find films grown at 875 °C, 825 °C, and 775 °C had periodicities (Λ) of 16.69 nm, 16.08 nm, and 16.21 nm, respectively, corresponding to correction factors ($c = \frac{\Lambda}{\Lambda_{Ideal}}$) of 1.038, 0.999, and 1.008. The highest quality $(SrTiO_3)_{20}SrO$ films were grown between 740 °C and 850 °C on (001)-oriented $SrTiO_3$ substrates.

To investigate the cause of failure outside this temperature window, we use a combination of *in situ* RHEED during growth and *ex situ* AFM after growth. Measuring AFM on samples grown at too high a temperature, we see large precipitates on the surface whereas for temperatures that are too low, we observe pits (Figs. 2(c)-2(f)).

Precipitates have previously been associated with SrO-rich $SrTiO_3$ surfaces, whereas pits have been observed for TiO_2-rich $SrTiO_3$ surfaces.[46,53] The observation of pits is initially surprising as all Ruddlesden-Popper compounds have excess SrO when compared to the perovskite $SrTiO_3$ phase.

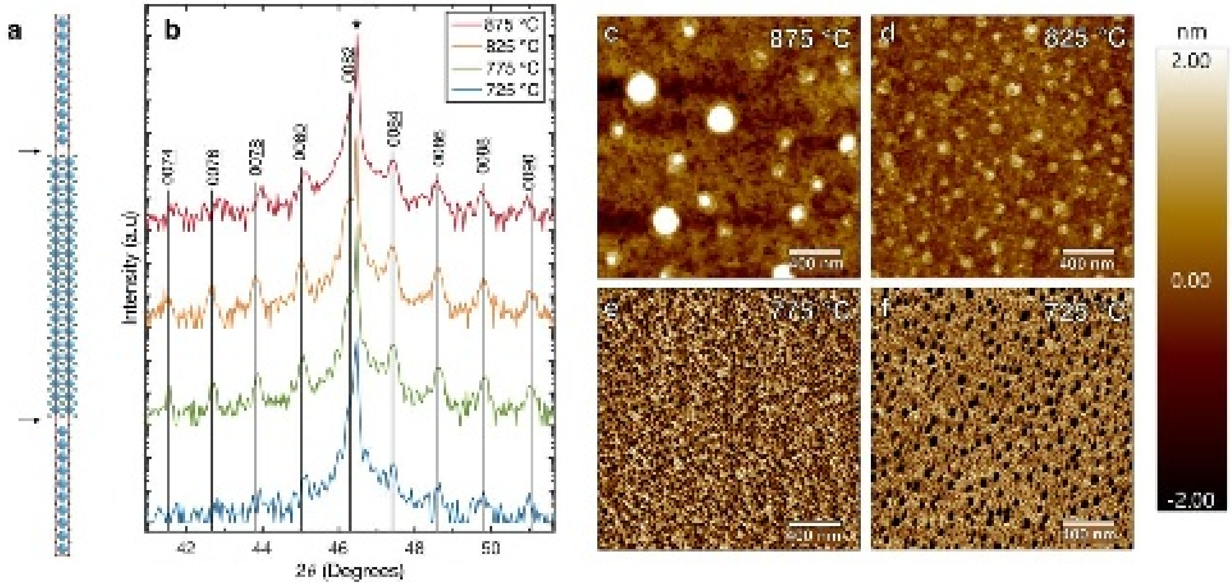

FIG. 2 (a) Unit cell of the $(SrTiO_3)_{20}SrO$ phase. Green spheres correspond to Sr atoms, TiO_6 octahedra are colored blue, and double SrO layers (which we refer to as $(SrO)_2$ faults) are indicated by arrows. (b) XRD θ-2θ scans of a series of $(SrTiO_3)_{20}SrO$ films attempted at various substrate temperatures. Vertical lines indicate the ideal peak positions. AFM images of the corresponding samples are shown in (c)-(f).

To get more insight, we monitor the $\sqrt{2}\times\sqrt{2}$ reconstruction during growth to understand how the surface stoichiometry evolves throughout the synthesis. Even for the best films, we always observe that after a $(SrO)_2$ Ruddlesden-Popper fault is crystallized (i.e., after momentarily terminating the surface with 3 monolayers of SrO), the reconstruction persists for the entirety of the next ~5 perovskite unit cells. This observation suggests that immediately after $(SrO)_2$ crystallization the surface has more SrO than the idealized growth in which a continuous $(SrO)_2$ fault is crystallized, and the surface stoichiometry again alternates between termination with 1 monolayer of SrO at the end of a TiO_2 deposition step and 2 monolayers of SrO at the end of a SrO deposition step. After ~5 perovskite unit cells the $\sqrt{2} \times \sqrt{2}$ reconstruction begins to disappear near the end of the TiO_2 dose, and subsequently, the reconstruction is observed less time each cycle, indicating that the SrO-excess on the surface is slowly diminished. We interpret this observation as evidence that the $(SrO)_2$ Ruddlesden-Popper fault that we intend to deposit is incomplete; it does not cover the full surface of the sample, leading to an initial excess of uncrystallized SrO adatoms on the surface. We attribute the incomplete crystallization of $(SrO)_2$ faults to roughness and stoichiometric inhomogeneity on the surface of the film. From comparing the AFM images in Fig. 3(c-f) to those of 3 monolayers of epitaxial SrO (Fig. S1(k)), it is clear that surface inhomogeneity is compounded during film growth. We interpret that the excess SrO required for crystallization fails to diffuse to precisely where it is needed to form a perfect $(SrO)_2$ fault.

Due to the topology of $(SrO)_2$ faults, either a vertical fault or a partial dislocation with an in-plane offset of $\frac{a}{2}[110]$ must form when the intended horizontal fault is incompletely crystallized. For $n > 3$ Ruddlesden-Popper thin films, vertical faults are consistently observed,[12,13,22,24–26,28,34,54,55] whereas the authors are not aware of any studies in which faults terminated with partial dislocations are reported. We conclude that vertical faults and the RHEED observation of excess SrO on the surface after attempted crystallization of a horizontal fault are both caused by the incomplete crystallization of the horizontal fault. To clarify, we interpret that the vertical fault is structurally mandated by the incomplete horizontal fault, not induced by excess SrO on the film surface. As film growth continues, the SrO excess on the surface is slowly depleted because it is crystallized into $(SrO)_2$ vertical faults, leading to reduced presence of the $\sqrt{2} \times \sqrt{2}$ reconstruction with each perovskite cycle.

When the growth temperature is too low, the reconstruction dissipates quickly after the attempted deposition of a $(SrO)_2$ Ruddlesden-Popper fault; it is present for <50% of the 20th perovskite cycle. We interpret that, at this colder temperature, the extra SrO is primarily accommodated by vertical $(SrO)_2$ faults, that quickly consume the excess SrO on the surface as the film continues to grow, making the $\sqrt{2} \times \sqrt{2}$ reconstruction present for a progressively smaller fraction of each cycle. Because the excess SrO is slowly depleted with each perovskite cycle, high n films with many perovskite cycles between horizontal $(SrO)_2$ layers are less tolerant of vertical fault formation than low n films; while not systematically investigated, we believe that the lower limit in temperature increases with n (excluding $n = \infty$). Although the $(SrO)_2$ is not crystallized horizontally as intended when grown at a relatively low substrate temperature of 725 °C, the local lattice parameter and atomic scattering factor must remain relatively fixed throughout the thickness of film to explain the observation of Laue oscillations even though it is actually rougher by AFM than the film grown at 875 °C. Because the surface is SrO-deficient compared to the ideal case, when we attempt to terminate the film with TiO_2 at the end of the growth, we actually create a TiO_2-rich surface explaining the observation of pits in AFM at low growth temperatures.[53] Conversely, if the temperature is too hot, we see more dramatic surface roughening and eventually precipitation of SrO on the surface. We interpret that Laue oscillations in XRD are suppressed because there is an inhomogeneous distribution of

$(SrO)_2$ faults due to the persistence of these large islands throughout the growth—i.e., we anticipate that more $(SrO)_2$ crystallizes near these large islands than far away from them.

Our observation that rather high growth temperatures are required to synthesize highly ordered $(SrTiO_3)_nSrO$ thin films is consistent with previous reports.[22,25,28,56] We posit that the dynamic layer rearrangement required to crystallize the target phase[26,27] requires high temperatures to overcome the energy barrier of out-of-plane diffusion. Interestingly, one previous study reported that the most successful growth of $(SrTiO_3)_5SrO$ occurs at the relatively low temperature of 550 °C by PLD.[54] In their work, Iwazaki et al. suggest that lower substrate temperatures are necessary to avoid island growth of the SrO layer but comment that such low temperatures result in poor crystallinity. It is also possible that at 550 °C, no layer rearrangement occurs, enabling growth of low-crystallinity Ruddlesden-Popper films with the intuitive sequence of layers (i.e., with no layer rearrangement). Had this study investigated temperatures higher than 650 °C, it may have concluded that high-crystallinity Ruddlesden-Popper films could be synthesized at substrate temperatures sufficiently high to enable complete layer rearrangement.

At the optimal temperature of 810 °C, we showcase the strength of our methodology by synthesizing an $n = 50$, $(SrTiO_3)_{50}SrO$ film. The film is characterized in reciprocal space with XRD (Fig. 3(a)) and in real space with low-angle annular dark field scanning transmission electron microscopy (LAADF-STEM) (Fig. 3(b)). This feat surpasses the highest periodicity Ruddlesden-Popper ever reported with traditional flux calibration[34,35] by a factor of five; the previous report of an $n = 20$ film was accomplished with this new method.[29] While an $n = 20$ film can be accomplished with careful calibration, the margin for error when growing an $n = 50$ film is so small that adjustments—informed by using

RHEED to monitor the $\sqrt{2} \times \sqrt{2}$ reconstruction—were required during growth to maintain the optimal surface stoichiometry. It should be noted that such adjustments most likely resulted in a film with more excess SrO than the ideal structure to compensate for the SrO consumed by vertical faults, which we see are prevalent in Fig. 3(b). Nonetheless, we determine by analyzing the XRD spectrum that ordered horizontal faults were crystallized with an astounding periodicity of 39.19 nm, <1% from the optimum value of 39.55 nm (c = 0.991).[29]

We use LAADF-STEM (Fig. 3(b)) because it highlights faults even at low magnification, but interpreting this data is complicated because a STEM image is a projection of a lamella. Apparent T-junctions of $(SrO)_2$ faults, which would require a partial dislocation to form, arise when vertical $(SrO)_2$ faults do not extend through the entire thickness of the lamella. We analyze such a region more thoroughly using an atomically resolved high-angle annular dark field (HAADF)-STEM image (Fig. 3(c)). While the $(SrO)_2$ faults are harder to identify in HAADF-STEM, we see that Ti^{4+} ions (with less intensity and a smaller ionic radius) are offset horizontally by $\frac{a}{2}[110]$ in the upper left region compared to the lower region because they are separated by an $(SrO)_2$ antiphase boundary. We refer to these $(SrO)_2$ faults as antiphase boundaries because we are only considering the offset of perovskite unit cells parallel to the $(SrO)_2$ layers; perpendicular to the $(SrO)_2$ layers they are out-of-phase boundaries. This phase difference across the boundary is indicated by the overlayed perovskite unit cells—TiO_6 octahedra with the same phase as the upper left region are shaded orange and those with the same phase as the lower region are shaded blue. In the upper right region, there is no contrast between atomic columns because the orange and blue phases are superimposed in the projection due to an $(SrO)_2$ antiphase boundary perpendicular to the viewing direction partway through the lamella in this region of the scan. Figure 3(d) is a diagram of the atomic structure resulting in the HAADF-STEM image shown in Fig. 3(c), with the same color scheme for TiO_6 octahedra on opposite sides of the $(SrO)_2$ antiphase boundary.

As vertical faults do not extend through the entire lamella, accurately deducing their density from this data is nontrivial. The difference between the actual and apparent density of vertical faults depends on both the lamella's thickness, which is approximately 30 nm, and the typical distance that a (100)-oriented vertical fault extends before turning 90° into a (010)-oriented vertical fault. From Fig. 3(c), we can conclude from the prevalence of apparent T-junctions that the vertical faults change direction on a substantially shorter length scale than the lamella's thickness, meaning that the vertical fault density is less than we calculate from simply counting vertical lines in Fig. 3(b) (200 μm^{-1} or 1 fault per 5 nm). In the supplemental information, we work toward approximating the vertical fault density more accurately, ultimately concluding that the vertical fault density in this $n = 50$ film is roughly 90 μm^{-1}, exceeding the horizontal fault density (~51 μm^{-1}) by almost a factor of two.

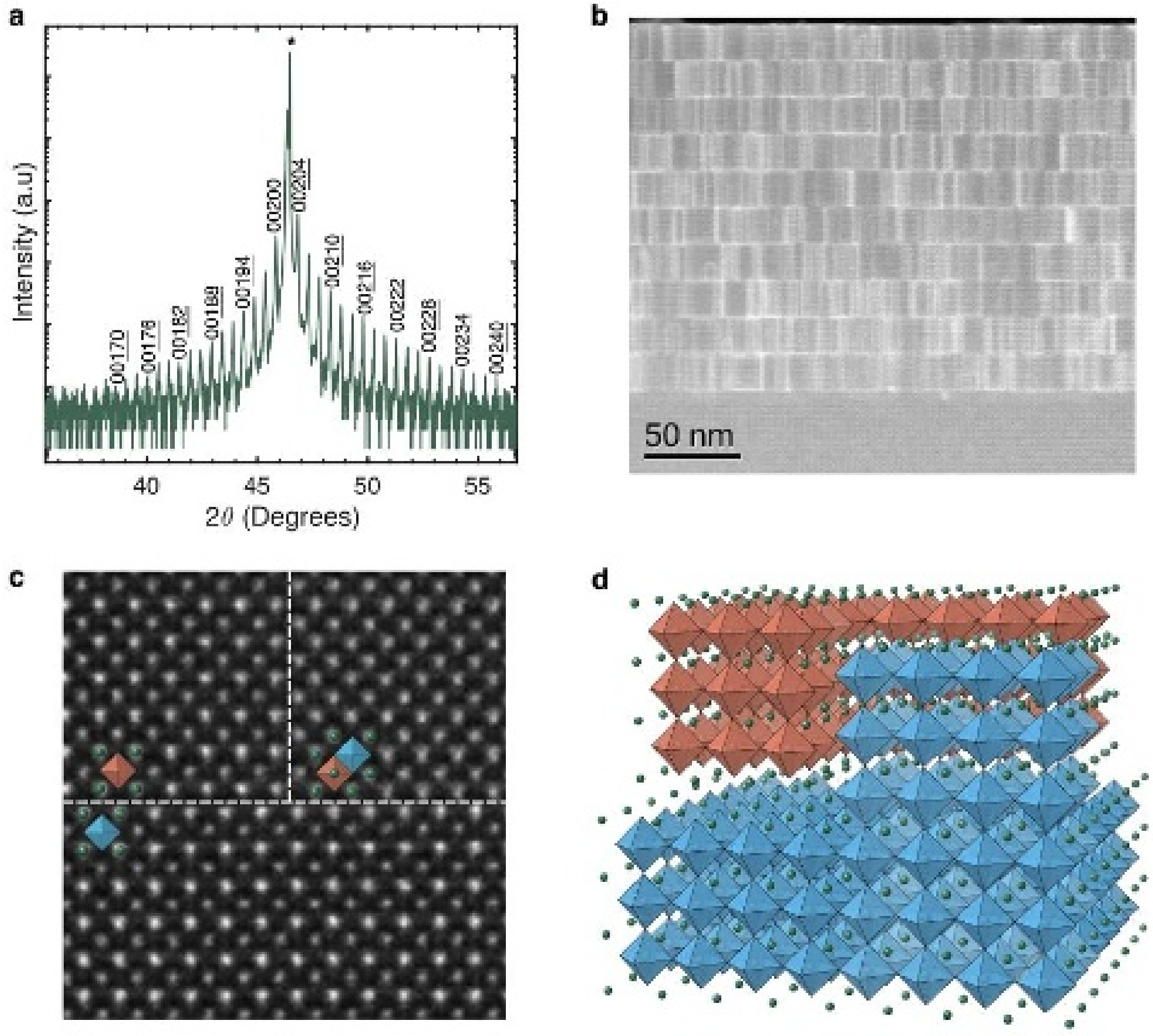

FIG. 3 (a) XRD θ-2θ scan of a 200 nm thick $(SrTiO_3)_{50}SrO$ film grown on $SrTiO_3$ (001). (b) LAADF-STEM image of the same film. (c) HAADF-STEM image and (d) atomic model of a region in which a vertical fault that does not extend through the entire lamella intersects a horizontal fault ($(SrO)_2$ faults are indicated by white dashed lines in (c)). TiO_6 octahedra on one side of the $(SrO)_2$ antiphase boundary are shaded blue, TiO_6 octahedra on the other side are shaded orange, and all strontium ions are symbolized by green spheres.

Having developed a methodology to synthesize $(SrTiO_3)_{20}SrO$, we move on to the more general compound $(A\mathrm{TiO}_3)_{20}A\mathrm{O}$, where the *A*-site is occupied by a mixture of barium and strontium. We begin by studying the case of dilute barium concentrations grown commensurately on $SrTiO_3$ substrates, using essentially the same procedure employed for $(SrTiO_3)_{20}SrO$, with minor modifications. Firstly, in addition to the initial flux approximation previously performed by monitoring the RHEED intensity during shuttered deposition of $SrTiO_3$, we also approximate the barium flux by shuttering $BaTiO_3$ using the same methodology. Secondly, when depositing an AO layer in the flux fine-tuning step and in the Ruddlesden-Popper growth phase of the previous technique, we deposit a mixture of SrO and BaO in the appropriate ratios. For example, to grow $(A\mathrm{TiO}_3)_{20}A\mathrm{O}$ with $A = \mathrm{Ba}_{0.2}\mathrm{Sr}_{0.8}$, for each AO layer in the structure, we would instead sequentially deposit 0.4 monolayers of SrO followed by 0.2 monolayers of BaO followed by 0.4 monolayers of SrO, to achieve mixing of SrO and BaO in the targeted ratio. Finally, in the flux fine-tuning step, we adjust the barium and strontium dosages together—e.g., increase both the strontium and barium sources by ~1°C to resolve a 3% TiO_2-rich condition—to adjust the total A-site dosage while minimizing changes in the Sr/Ba ratio.

Testing A-site compositions with 15% and 33% barium, we see by XRD (Fig. 4) that while the minimum growth temperature to crystallize horizontal $(A\mathrm{O})_2$ Ruddlesden-Popper faults remains roughly constant (~730 °C), the maximum growth temperature for films with XRD spectra indicative of the highest structural order decreases with increasing barium content. As for pure $(SrTiO_3)_{20}SrO$, one component of structural disorder is the observation of randomly distributed vertical $(A\mathrm{O})_2$ Ruddlesden-Popper faults instead of ordered horizontal faults (Fig. 5(a) and 5(b)). We show by electron energy loss spectroscopy (EELS) that a different component of disorder comes from the inhomogeneous incorporation of barium on the A-sites in the $(A\mathrm{TiO}_3)_{20}A\mathrm{O}$ films (Fig.

5(c)).The effect of these two types of disorder on the XRD are different. Randomly distributed vertical $(AO)_2$ Ruddlesden-Popper faults do not diffract because they are not periodically ordered, meaning that no superlattice peaks are observed in such films, and the diffraction pattern resembles perovskite. For such films, i.e., those grown at substrate temperatures below 730 °C, we observe that Laue oscillations persist because the film has roughly the same out-of-plane lattice constant and local atomic scattering factor throughout its thickness. Inhomogeneous barium incorporation on the *A*-sites washes out the Laue oscillations because the local atomic scattering factor and local atomic spacing varies through the film's thickness, while the superlattice peaks remain present because the Ruddlesden-Popper faults are periodically ordered.

For $(A\mathrm{TiO}_3)_{20}A\mathrm{O}$ films with 15% Ba on the *A*-site, we begin to see barium inhomogeneity at 810 °C—based on the slightly misshapen $00\underline{82}$ peak and diminished Laue oscillations in the XRD θ-2θ scan—compared to 0% Ba films in which a well-ordered film was grown at 825 °C. Increasing the *A*-site occupancy to 33% Ba, we see clear loss of the Laue oscillations (due to barium inhomogeneity) at as low as 775 °C, and attempting 45% Ba we observe dramatic loss of the Laue oscillations at only 720 °C. Note that the superlattice peaks remain relatively sharp despite the loss of the Laue oscillations in these samples that are grown at higher than optimal substrate temperature. Interestingly, we find that XRD θ-2θ scans of samples with inaccurate periodicity are qualitatively similar to those with precise periodicity, provided that the *A*/Ti stoichiometry is accurate, and the substrate temperature is at least 740 °C. Even though the 15% barium $(A\mathrm{TiO}_3)_{20}A\mathrm{O}$ films grown at 810 °C, 775 °C, and 740 °C have errant periodicities (16.60 nm, 17.08 nm, and 16.96 nm with correction factors of 1.027, 1.057, and 1.049,

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respectively), the superlattice peaks are clear, and the Laue oscillations are strong when grown at appropriate temperatures. The 33% barium $(A\mathrm{TiO}_3)_{20}A\mathrm{O}$ films grown at 775 °C and 740 °C have periodicities of 16.82 nm and 16.24 nm corresponding to correction factors of 1.032 and 0.997, respectively, and the 45% barium $(A\mathrm{TiO}_3)_{20}A\mathrm{O}$ film grown at 740 °C has a periodicity of 17.12 nm corresponding to a correction factor of 1.043.

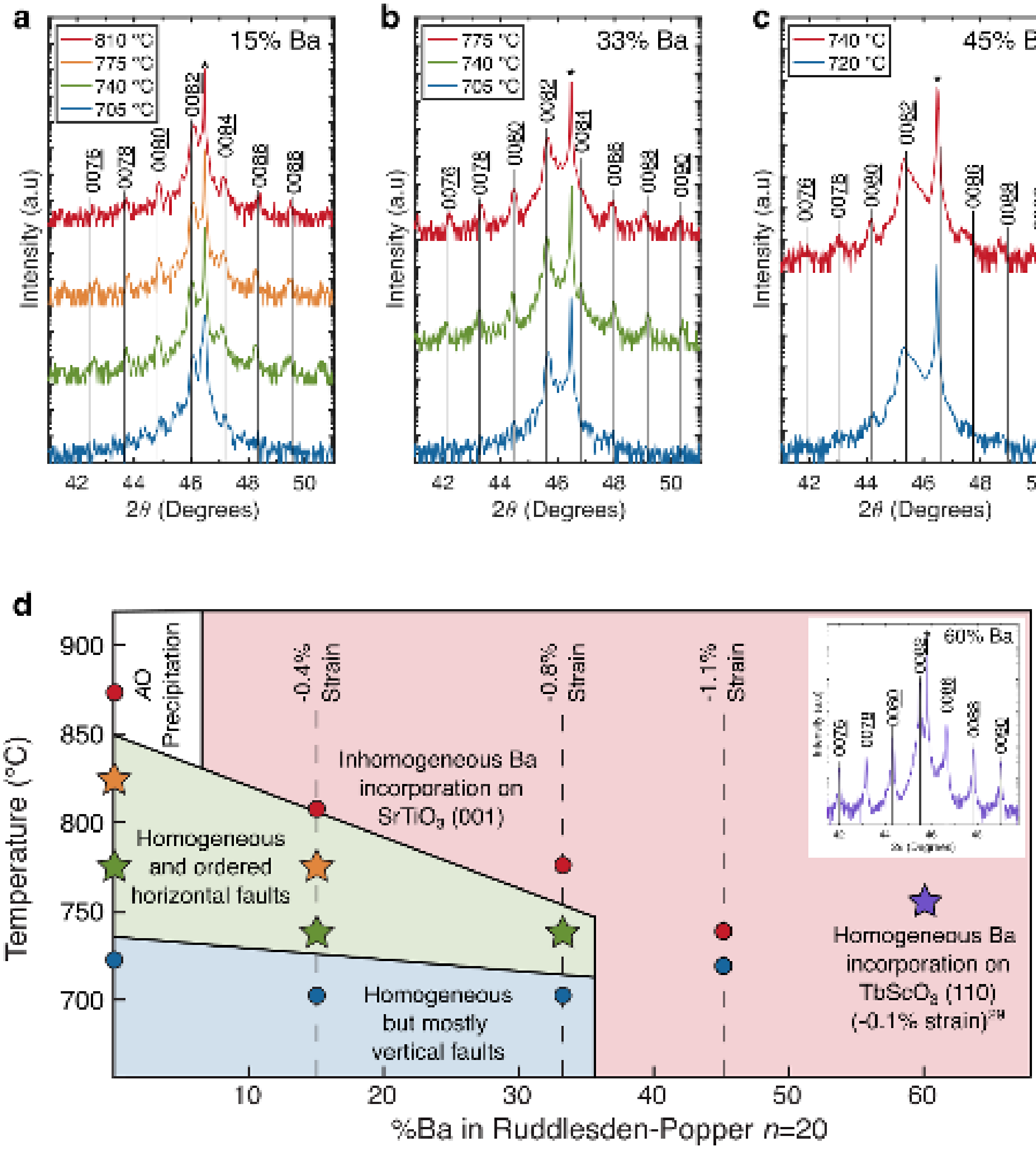

FIG. 4 (a-c) XRD θ-2θ scans for a series of $(A\mathrm{TiO_3})_{20}A\mathrm{O}$ films grown at different temperatures with barium concentrations of 15%, 33%, and 45%, respectively, on $SrTiO_3$ (001) substrates. (d) Diagram summarizing the optimal growth conditions for the growth of $(A\mathrm{TiO_3})_{20}A\mathrm{O}$ films on $SrTiO_3$ (001) substrates as a function of barium content and substrate temperature. The color of each data point corresponds to the color of the film's XRD spectrum in Fig. 2(b) and Fig. 4(a-c). Starred data points indicate conditions for which the highest quality films were synthesized, and the region shaded green indicates the "growth window" in which high quality films can be synthesized on $SrTiO_3$ (001) substrates. The purple star outside the growth window marks the growth conditions with which a high quality $(A\mathrm{TiO_3})_{20}A\mathrm{O}$ film was grown on a $TbScO_3$ (110) substrate from Ref. [29], and the inset shows the corresponding XRD θ-2θ scan of the previously reported film.

When discussing the $(SrTiO_3)_{20}SrO$ films, we argued that at lower temperatures, the $(SrO)_2$ Ruddlesden-Popper faults that formed were mostly vertical and that the inhomogeneity observed at growth temperatures above 850 °C was a result of the formation of large SrO islands. With the introduction of barium, we still observe mostly vertical faults at low temperatures (Fig. 5(a) and 5(b)), but interestingly, AFM indicates that films containing only 15% barium (Fig. 5(d) and 5(e)), are much smoother at all temperatures investigated than those containing 0% barium (Fig. 2(c)-2(f)). Therefore, we do not anticipate that the imperfection observed at high temperatures in barium-containing films has the same origin as that in pure $(SrTiO_3)_{20}SrO$. The stark difference in surface morphology for barium-containing films is possibly related to the reduced lattice mismatch of 5.7% for $Ba_{0.15}Sr_{0.85}O$ on (001)-oriented $SrTiO_3$. Notably, epitaxial BaO is known to grow smoothly on (001)-oriented $SrTiO_3$ with only -0.2% lattice mismatch.[57] Here, we analyze STEM and electron energy loss spectroscopy (EELS) of films outside the growth window to better understand their imperfections. Comparing LAADF-STEM of the 33% barium $(ATiO_3)_{20}AO$ films grown at substrate temperatures of 705 °C and 740 °C, we see in Fig. 5(a) that the sample that is grown at 705 °C has more vertical $(AO)_2$ faults. While the first horizontal $(AO)_2$ fault appears to crystallize nearly as well as the sample grown at 740 °C, the vertical faults that do form typically persist throughout the thickness of the film at 705 °C. In contrast, the film grown at 740 °C (Fig. 5(b)) has fewer vertical faults, and when they do form, they typically end—i.e., turn horizontally—with the subsequent $(AO)_2$ horizontal fault. Again, these vertical faults are always reported in $n > 3$ Ruddlesden-Popper films,[12,13,22,24–26,28,34,54,55] and their relative density compared to horizontal faults appears to increase with n.

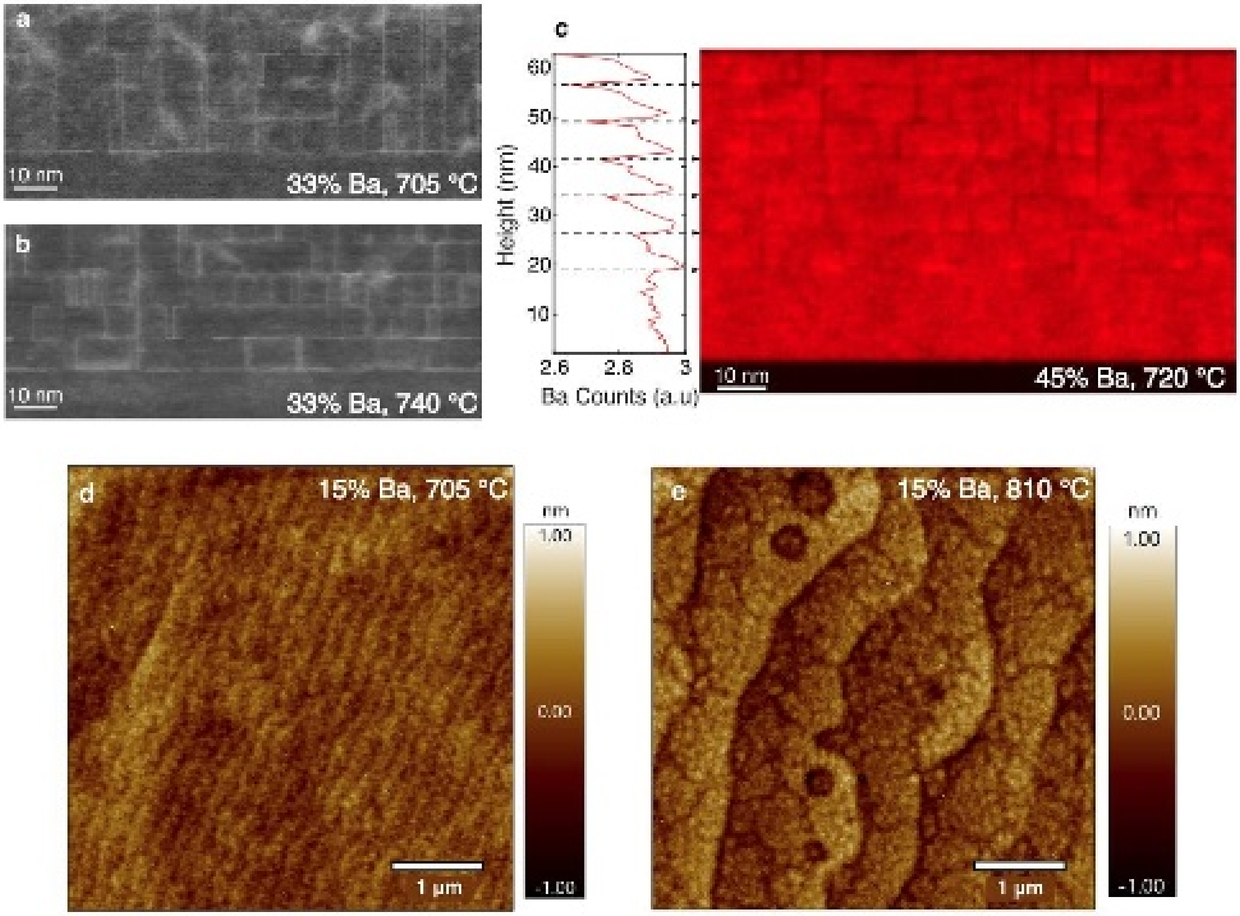

FIG. 5 LAADF-STEM images of the $(ATiO_3)_{20}AO$ films containing 33% barium grown on $SrTiO_3$ (001) at a substrate temperature of (a) 705 °C and (b) 740 °C. (c) EELS map of the $(ATiO_3)_{20}AO$ film containing 45%

barium grown on a $SrTiO_3$ (001) at a substrate temperature of 720 °C. (d-e) AFM images of $(ATiO_3)_{20}AO$ films containing 15% Ba grown at (d) 705 °C and (e) 810 °C on $SrTiO_3$ (001).

With the introduction of barium, we observe that the barium atoms are increasingly resistant to crystallizing into the $(AO)_2$ Ruddlesden-Popper fault as strain increases, particularly at higher substrate temperatures. This can be observed in XRD spectra by the loss of Laue oscillations as the growth temperature is increased, well before the loss of the superlattice peaks. As the barium incorporation becomes inhomogeneous, it first washes out the Laue oscillations and subsequently results in the appearance of asymmetric diffraction peaks. We investigate and confirm the microscopic origin of this effect with EELS, on the 45% Ba $(ATiO_3)_{20}AO$ sample grown at 720 °C because the inhomogeneity is clear by XRD, meaning the microstructural cause should be apparent with STEM-EELS. Integrating the barium intensity observed with EELS across the film and showing the profile along the growth direction (Fig. 5(c)), the inhomogeneous incorporation of barium into the structure is clear. The concentration of barium in the $(AO)_2$ layer is substantially less than the average barium content in the film, and the barium that is rejected from the $(AO)_2$ layer causes a spike in barium concentration immediately above the fault, which manifests as a sawtooth pattern of barium concentration. This inhomogeneity is at least partially caused by the increased strain in films with increasing barium content commensurately strained to $SrTiO_3$, as our previously reported $n = 20$, 60% Ba Ruddlesden-Popper film exhibits clear Laue oscillations when grown on $TbScO_3$ (110) under only -0.1% strain.[29] We speculate that the high strain state destabilizes the metastable phase, causing displacement of barium from the Ruddlesden-Popper fault, where its incorporation is thermodynamically unfavorable, into the perovskite matrix. This rearrangement is only observed when the temperature is sufficiently high that such rearrangement is kinetically enabled. Interestingly, we note that upward diffusion of barium, i.e., in the growth direction, in $((Ba,Sr)TiO_3)_nSrO$ has been observed previously in tensile strained films—see Fig. 2(d) of Ref. [[13]].

Conclusions

In this work, we outline a strategy to consistently synthesize Ruddlesden-Popper titanates with long *c*-axis periodicities (up to 39 nm) in the growth direction. The success of the strategy described is showcased by the demonstration of a $(SrTiO_3)_{50}SrO$ film. We go on to investigate the solubility of barium and find that the *A*-site can be occupied by at least 33% barium for epitaxial films grown on $SrTiO_3$ substrates at the appropriate substrate temperature. Attempts to grow Ruddlesden-Popper films at substrate temperatures below 730 °C result in incomplete crystallization of horizontal $(AO)_2$ faults, leading to films with primarily $(AO)_2$ vertical faults. Films grown at too high of a temperature can suffer from nucleation of *A*O precipitates on the surface or inhomogeneous incorporation of barium into the crystal structure. Due to the latter observation, the upper limit for substrate temperature falls with increasing barium content. From our previous demonstration of a $(ATiO_3)_{20}AO$ Ruddlesden-Popper with 60% barium homogeneously incorporated when grown on a $TbScO_3$ (110) substrate, it is clear that the upper limit of barium solubility when $(ATiO_3)_{20}AO$ films are grown on $SrTiO_3$ at 33% barium comes from strain; more than 33% barium can be homogenously incorporated by using substrates with a larger lattice parameter. We hope this detailed study will guide future syntheses of Ruddlesden-Popper phases that were previously thought inaccessible due to metastability or inadequate calibration techniques and enable their diverse physical properties to be established and exploited.

Supplementary Material

Supplementary material includes a document containing data and analysis of epitaxial SrO films that are 1-3 monolayers thick grown on $SrTiO_3$ (001), a procedure for correcting flux drift, and our method for approximation of the vertical fault density in the $(SrTiO_3)_{50}SrO$ film. In addition, a video showing the appearance and disappearance of ½-order streaks during deposition is included.

Acknowledgements

The synthesis science work at Cornell (M.B., J.S., and D.G.S.) was supported by the U.S. Department of Energy, Office of Basic Sciences, Division of Materials Sciences and Engineering, under Award No. DE-SC0002334. We also gratefully acknowledge support by Samsung Electronics Company. N. P. and D. A. T. acknowledge support by the National Science Foundation Grant DMR-2104918. Sample preparation was, in part, facilitated by the Cornell NanoScale Facility, a member of the National Nanotechnology Coordinated Infrastructure (NNCI), which is supported by the National Science Foundation (Grant No. NNCI-2025233). The authors thank Sean Christopher Palmer for his assistance with substrate preparation. Some images were generated using CrystalMaker: CrystalMaker Software Ltd. (www.crystalmaker.com).

Data Availability

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

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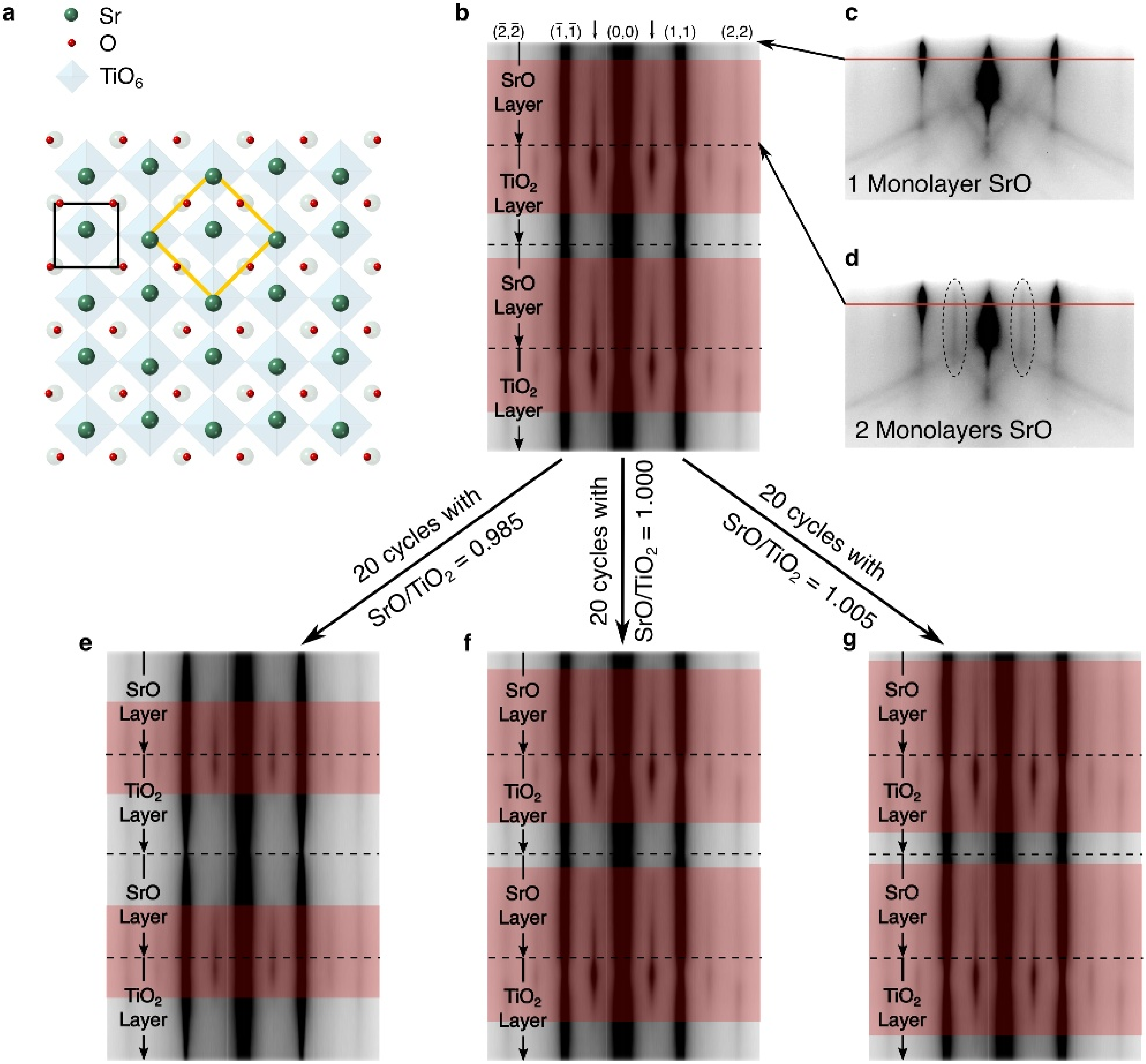
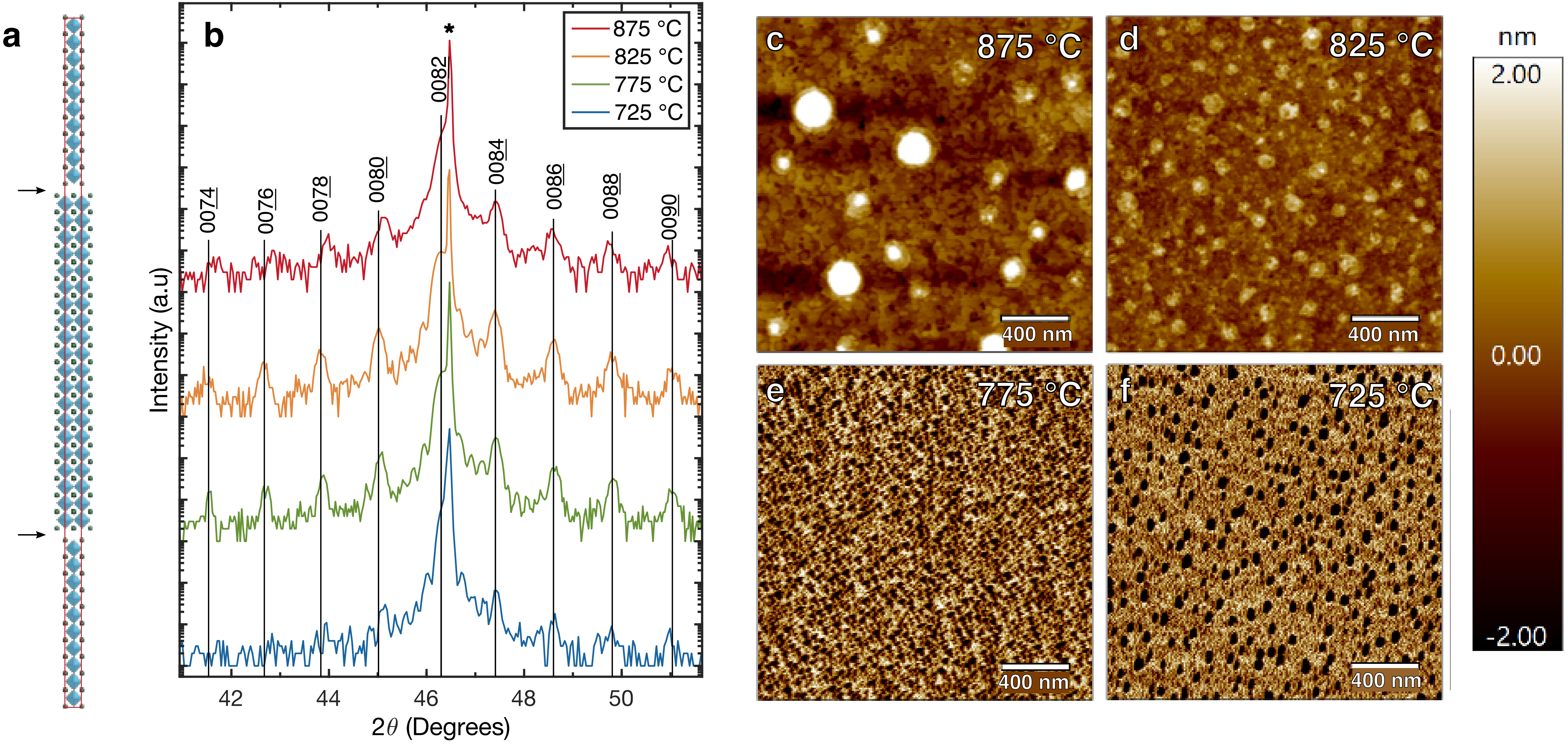
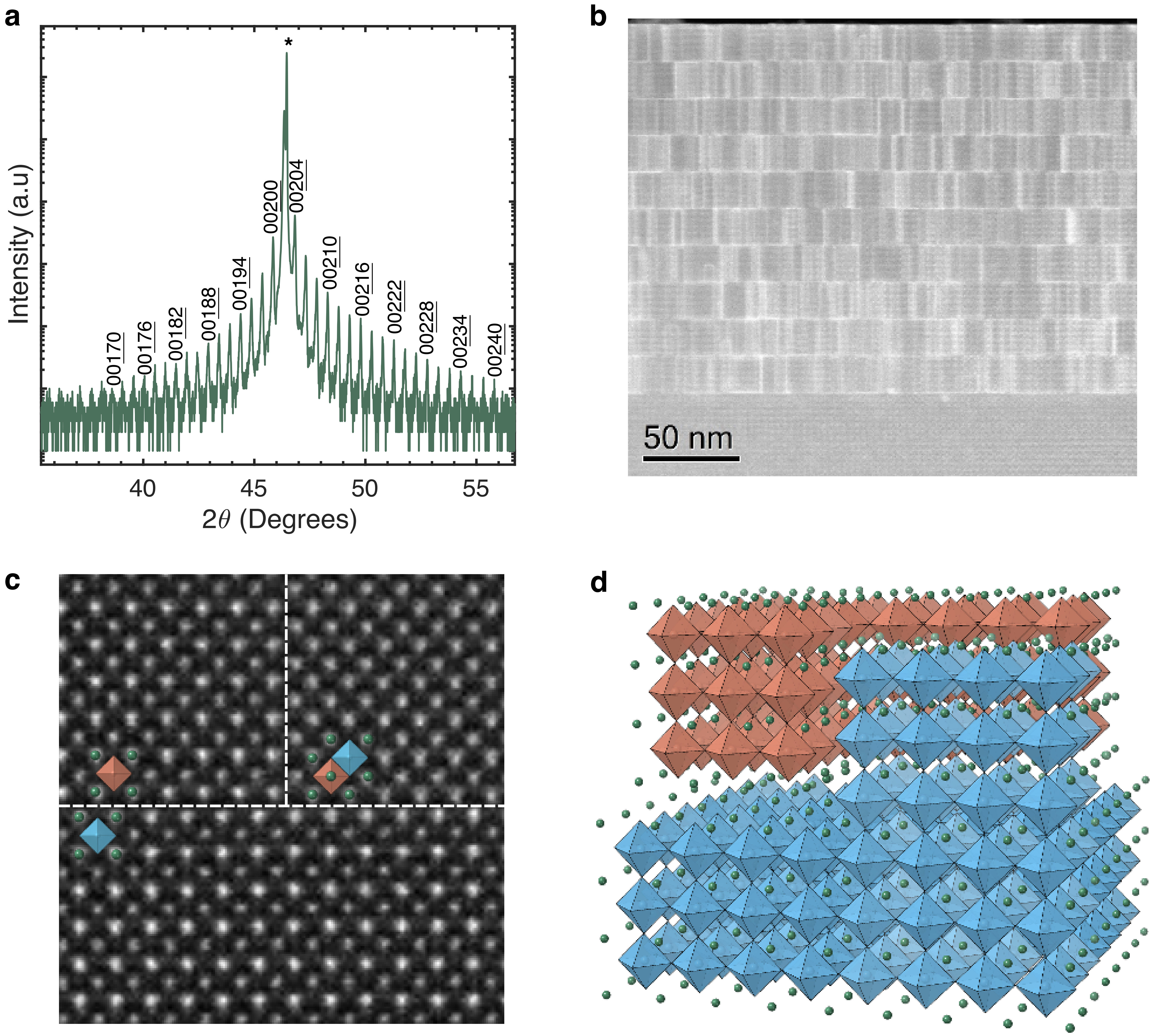
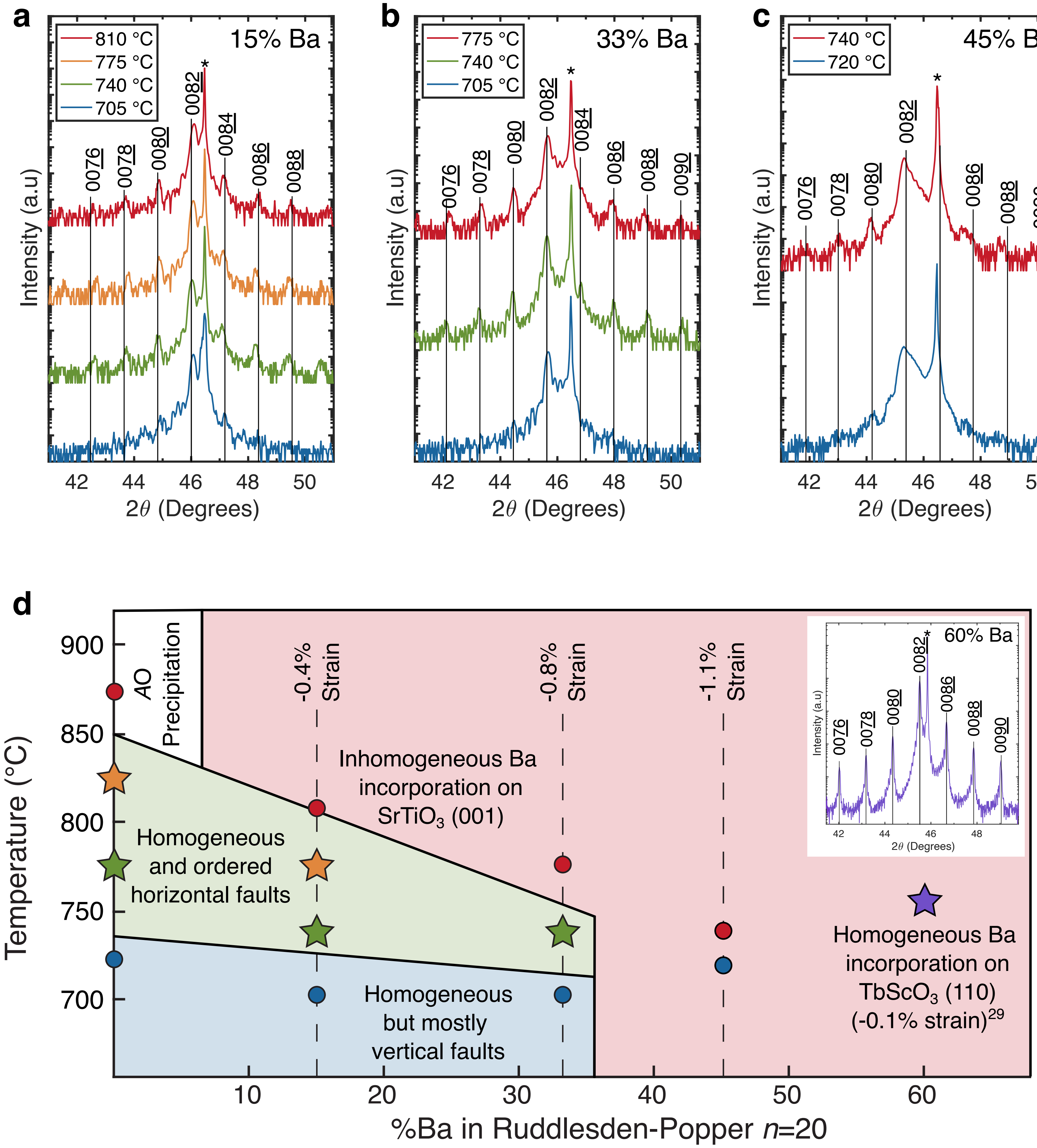
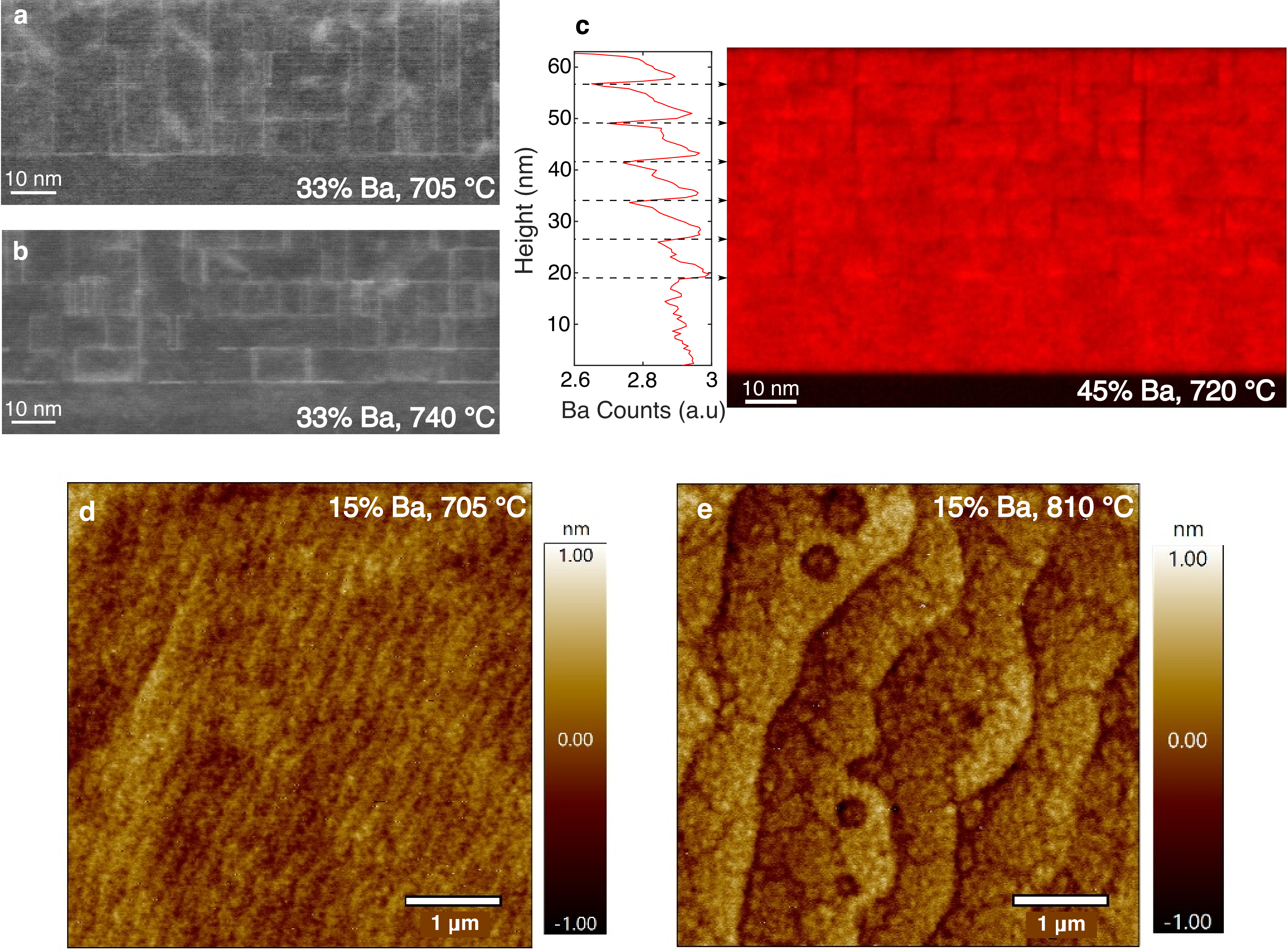

a
Sr
O
TiO_6
b
$(\bar{2},\bar{2})$
$(\bar{1},\bar{1})$
(0,0)
(1,1)
(2,2)
SrO Layer
TiO_2 Layer
SrO Layer
TiO_2 Layer
c
1 Monolayer SrO
d
2 Monolayers SrO
20 cycles with $SrO/TiO_2 = 0.985$
20 cycles with $SrO/TiO_2 = 1.000$
20 cycles with $SrO/TiO_2 = 1.005$
e
f
g
SrO Layer
TiO_2 Layer
SrO Layer
TiO_2 Layer


a
b
875 °C
825 °C
775 °C
725 °C
*
0074
0076
0078
0080
0082
0084
0086
0088
0090
Intensity (a.u)
42
44
46
48
50
2θ (Degrees)
c
875 °C
400 nm
d
825 °C
400 nm
e
775 °C
400 nm
f
725 °C
400 nm
nm
2.00
0.00
-2.00


a
Intensity (a.u)
2θ (Degrees)
40
45
50
55
*
00170
00176
00182
00188
00194
00200
00204
00210
00216
00222
00228
00234
00240
b
50 nm
c
d


a
810 °C
775 °C
740 °C
705 °C
15% Ba
*
0076
0078
0080
0082
0084
0086
0088
Intensity (a.u)
42
44
46
48
50
2θ (Degrees)
b
775 °C
740 °C
705 °C
33% Ba
*
0076
0078
0080
0082
0084
0086
0088
0090
Intensity (a.u)
42
44
46
48
50
2θ (Degrees)
c
740 °C
720 °C
45% Ba
*
0076
0078
0080
0082
0086
0088
0090
Intensity (a.u)
42
44
46
48
50
2θ (Degrees)
d
900
850
800
750
700
Temperature (°C)
AO Precipitation
-0.4% Strain
-0.8% Strain
-1.1% Strain
Inhomogeneous Ba incorporation on SrTiO$_3$ (001)
Homogeneous and ordered horizontal faults
Homogeneous but mostly vertical faults
60% Ba
*
0076
0078
0080
0082
0086
0088
0090
Intensity (a.u)
42
44
46
48
2θ (Degrees)
Homogeneous Ba incorporation on TbScO$_3$ (110) (-0.1% strain)[29]
10
20
30
40
50
60
%Ba in Ruddlesden-Popper *n*=20


a
10 nm
33% Ba, 705 °C
b
10 nm
33% Ba, 740 °C
c
60
50
40
30
20
10
Height (nm)
2.6
2.8
3
Ba Counts (a.u)
10 nm
45% Ba, 720 °C
d
15% Ba, 705 °C
1 µm
nm
1.00
0.00
-1.00
e
15% Ba, 810 °C
1 µm
nm
1.00
0.00
-1.00