

Octahedral tilt relaxation decoupled from lattice parameters in epitaxial perovskite oxide films

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Epitaxial strain in perovskite oxide thin films is conventionally understood through lattice parameter modulation, characterized by the c/a ratio of the pseudocubic cell. However, internal atomic arrangements such as octahedral tilting can relax independently, a phenomenon that has remained largely unexplored. Here, we demonstrate that electrochemical operation induces internal structural relaxation in epitaxial $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ films while in-plane lattice parameters remain pinned to the substrate. Synchrotron x-ray diffraction reveals that prolonged electrochemical treatment drives the octahedral tilt mode from the as-grown strained configuration toward the bulk structure without conventional lattice parameter changes. This relaxation is enabled by ionic oxygen migration during electrochemical reactions, which reduces energy barriers between structural configurations. Our findings reveal a relaxation pathway in epitaxial oxides that operates independently of conventional lattice parameter relaxation, and demonstrate the importance of monitoring internal atomic arrangements under operating conditions. This establishes electrochemically driven ionic migration as a versatile tool for controlling internal structure in epitaxial oxides, opening opportunities for designing strain-engineered functional materials.

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I. INTRODUCTION

Epitaxial perovskite oxide films provide a versatile platform to explore functionalities beyond those of bulk crystals via epitaxial strain [1–4]. Conventionally, epitaxial strain is understood in terms of lattice parameter modulation caused by lattice mismatch: the in-plane lattice parameters of the film are constrained by the substrate, while the out-of-plane parameter adjusts through Poisson's effect [5,6]. This framework, often described by the c/a ratio of the pseudocubic cell, has been widely used to tune magnetism [7,8], ferroelectricity [9,10], and transport properties [8,11].

Yet, lattice parameters alone cannot fully capture the structural complexity of transition metal oxides. Octahedral tilting and bond-length modulation critically influence electronic states and macroscopic functionality [12–15]. Despite their importance [16–24], direct x-ray structure analysis of

epitaxial films using a sufficient number of Bragg reflections remains limited [25]. The broader landscape of lattice relaxation in perovskites therefore remains incomplete.

Epitaxial films are inherently metastable, with their as-grown structure representing a kinetically trapped configuration [26]. Structural relaxation toward more stable states can occur when energy barriers are reduced. Within oxide thin films, such barrier reduction may be facilitated by ionic migration under electrochemical conditions, as seen in oxygen-vacancy diffusion and related processes [27–29]. Whether electrochemically driven ion migration can trigger internal structural rearrangement—specifically changes in octahedral tilting—while maintaining epitaxial coherence with unchanged lattice parameters remains an open question.

$\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ (LSCO) provides an ideal platform to investigate this question. LSCO is a prototypical perovskite exhibiting rich structural complexity, including multiple octahedral tilt modes [30,31], and has been extensively studied as both a correlated oxide [32–34] and an oxygen-evolution catalyst [31,35–43]. During electrochemical operation, lattice oxygen participates in the catalytic reaction [35,37], creating conditions for oxygen ion redistribution. LSCO thin films are also known to undergo sudden catalytic deactivation during prolonged operation [36], yet whether internal structural evolution contributes to this phenomenon has remained largely unexplored.

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Here we examine epitaxial LSCO thin films before and after extended electrochemical treatment. Our structure analysis reveals a previously unrecognized relaxation mechanism: the octahedral tilt mode evolves toward the bulk structure while in-plane lattice parameters remain pinned to the substrate. This finding demonstrates that ionic migration under electrochemical conditions can drive internal structural relaxation without conventional lattice parameter changes, establishing a pathway for strain accommodation in epitaxial oxides independent of conventional dislocation-mediated relaxation. This finding has broad implications: it demonstrates that electrochemical operation can be used to deliberately control internal structure in epitaxial films, providing a postgrowth tuning mechanism, which is inaccessible through conventional thermal or mechanical processes.

II. EXPERIMENTS

Forty-nanometer-thick epitaxial $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ (LSCO) films were grown on SrTiO_3 (STO) (001) substrates ($10 \times 10 \times 0.5$ mm) by the pulsed laser deposition (PLD) method. A Nd:YAG laser was used to ablate the LSCO target with a fluence of 1.3 J cm^{-2} and a repetition rate of 2 Hz. The growth temperature was 873 K under an O_2 pressure of 0.1 Pa. The film thickness was controlled by the deposition duration (approximately 40 minutes).

Electrochemical treatments were performed on a piece of the LSCO film. A beaker-type electrochemical cell (VB1500, EC FRONTIER, Japan) was used for this process. The working electrode was the LSCO/STO film mounted in a sealed sample holder (AE9-3, EC FRONTIER, Japan). A platinum wire and an Ag/AgCl electrode served as the counter and reference electrodes, respectively. The electrolyte was 0.1 mol/L KOH aqueous solution. All electrodes were connected to a potentiostat (Electrochemical Measurement System HZ-7000, HOKUTO DENKO, Japan), and the electrochemical measurements were conducted in the stand-alone mode. Open circuit potential (OCP) measurements, cyclic voltammetry (CV) measurements, and chronoamperometry (CA) measurements were performed sequentially on the sample. The potential scan rate for the CV measurements was set to 20 mV/s. The CA measurement was carried out at +0.7 V for 1 hour. This treated sample is referred to as P07-1h. An additional sample without electrochemical treatment was prepared as a control sample and referred to as the pristine (PR) sample.

The out-of-plane lattice parameters and epitaxial quality of the two films were characterized by x-ray diffraction (X'Pert MRD system with PIXcel3D two-dimensional detector, Malvern Panalytical, Netherlands). A Cu x-ray source was used, and all the measurements were performed in the air at room temperature.

Bragg reflection intensities over a wide reciprocal space range for structure analyses were measured using the x-ray oscillation photograph method at BL-8B of the Photon Factory, KEK, Japan. The energy of the incident x-ray was 16 keV. The sample surface was inclined at approximately 2° to the incident x-ray beam, and all measurements were performed in air at room temperature. A large two-dimensional pixel array detector (PILATUS3 S 1M, DECTRIS, Switzerland) was used. Images were collected at 0.1° intervals around the ω axis

over a total range exceeding 90° . The measurements covered up to $\sqrt{h^2 + k^2} = 4.7$ and $l = 2.5$ for PR and 2 for P07-1h, using pseudocubic indexing. In order to extract integrated intensity of the film Bragg reflections from the oscillation photographs, substrate Bragg reflections were masked. The photographs were then converted to reciprocal space volume maps. The intensities of reflections coming from $1 \times 1 \times 1$ unit cells were obtained by three-dimensional fitting, while those of other reflections were obtained by numerical integration.

Structure analyses were performed by using Bayesian inference and the exchange Monte Carlo (MC) method, implemented in our modified version of CTR-structure [44,45]. The cost function $E(\Theta) = -\frac{1}{N} \ln P(\Theta | I_{\text{obs}})$, where $P(\Theta | I_{\text{obs}})$ denotes the conditional probability of structure parameters Θ under the condition of observed intensity I_{obs} and N denotes the number of data points, was monitored throughout the MC calculations. The structure Θ providing lowest E is the most probable structure [44,45]. The structure model of the $2 \times 2 \times 2$ LSCO unit cell was constructed based on the Glazer classification [46,47] of octahedral tilting.

X-ray absorption spectroscopy (XAS) measurements were performed at the BL07U and BL08U beamlines of Nano-Terasu, Japan. The spectra from O K edge (520–570 eV) and Co $L_{3,2}$ edge (770–810 eV) were acquired in partial fluorescence yield (PFY) mode by monitoring the O K_{α} and Co $L_{\alpha 2}$ emission lines using a silicon drift detector; The probing depth in the PFY mode is 50–100 nm, which exceeds the film thickness. Therefore, Co XAS provides the information of the entire film, and O XAS measures a noticeable amount of substrate as well as the entire film. All spectra were normalized by setting the pre-edge intensity to zero and the average postedge intensity to unity.

III. RESULTS AND ANALYSES

The working electrode current as a function of potential (i.e., CV) is presented in Fig. 1(a). The current density increased sharply around +0.6 V, indicating that the threshold potential for the oxygen evolution reaction (OER) of this film is approximately +0.6 V. Figure 1(b) shows the result of CA measurement at +0.7 V. The current density dropped rapidly to almost zero after about 700 s, indicating that the OER had stopped. This piece of sample was labeled as P07-1h. A similar current drop during OER has also been reported previously [36], demonstrating that this catalytic deactivation is intrinsic. The abrupt current drop indicates that the catalyst undergoes a substantial change during operation, although the origin of the deactivation cannot be identified from the electrochemical data alone [36]. To determine whether this deactivation is accompanied by structural changes, detailed x-ray diffraction measurements were performed on the two samples: pristine (PR) and P07-1h. The out-of-plane lattice parameters and epitaxial quality of the two films were characterized by x-ray diffraction. Peak profiles of the pseudocubic 002 Bragg reflections for the PR and P07-1h samples are shown in Fig. 2(a). Reciprocal space maps measured around the 103 peaks for both samples are shown in Fig. 2(b). The maps demonstrate that the in-plane lattice parameters are locked to that of the substrate (3.905 Å), regardless of

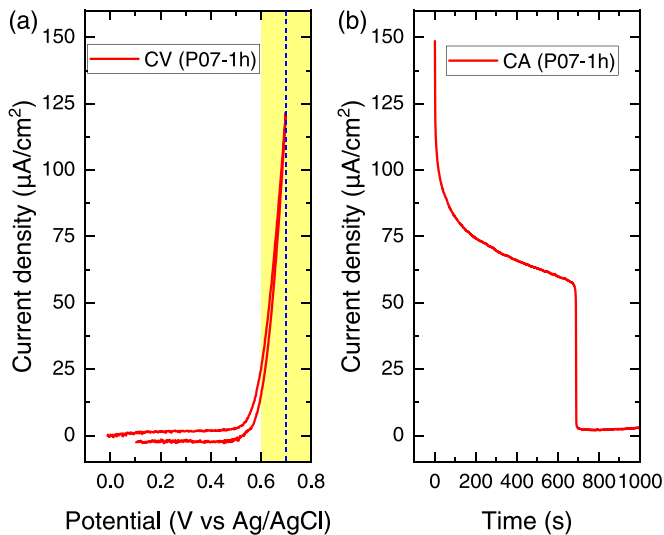


FIG. 1. (a) CV curve. The potential region where the OER occurs is highlighted. The blue dashed line indicates the potential (+0.7 V) used for the CA measurement. (b) CA curve. The current density dropped at approximately 700 s.

the electrochemical treatment. The out-of-plane pseudocubic lattice parameters (c_{pc}) for the PR and P07-1h samples are 3.80875(15) Å and 3.8437(2) Å, respectively. A lattice expansion of 0.9% was observed for P07-1h, strongly indicating that a structural change occurred in this film after the prolonged electrochemical treatment.

Since the lattice expansion in oxide films is often regarded as a signature of oxygen vacancy introduction [48,49], we performed x-ray absorption spectroscopy (XAS) measurements to examine the Co oxidation state, as shown in Fig. 2(c). The Co $L_{3,2}$ edge showed no significant evidence of enhanced oxygen vacancy concentration in the P07-1h sample. This indicated that the lattice expansion observed in P07-1h originated from a different mechanism rather than from increased oxygen deficiency. The only noticeable change in the XAS spectra was an increase in the signal around 529 eV, which corresponds to the t_{2g} unoccupied states; P07-1h exhibited a larger t_{2g} unoccupied state density than PR. The increase in signal around 529 eV was found only at the position where the electrochemical treatment was applied, showing the effects of the electrochemical operation on the electronic state (see the Supplemental Material [50] for details). Co L -edge XAS indicated that the oxidation state of Co was very close to 3+ with a slight trace of the 4+ component. The nominal valence of Co in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ is $3 + x - 2\delta$. Therefore, the upper limit of δ in this LSCO film is estimated to be $x/2 = 0.15$.

Wide-range reciprocal space maps at the $l = 1$ and $l = \frac{3}{2}$ planes for the PR and P07-1h samples are presented in Fig. 3. The diffraction patterns are plotted on a logarithmic scale for the $hk1$ planes and on a linear scale for the $hk\frac{3}{2}$ planes. Thermal diffuse scattering was observed around the strong substrate Bragg peaks in panels (a) and (d). In addition, diffuse streaks are clearly visible on the $hk\frac{3}{2}$ planes shown in panels (b) and (e), originating from the STO substrate [51]. Other than the diffuse scattering from the STO substrate, film Bragg reflections were observed in the vicinity of the substrate

Bragg reflections and at the positions characterized by the wave vector $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})_{pc}$. All these film Bragg reflections can be indexed by a $2 \times 2 \times 2$ unit cell. The reflection conditions for these two samples were identical: the even-even-even (reciprocal lattice points for the pseudocubic cell, eee) and odd-odd-odd $[(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})_{pc}$ positions, ooo] reflections exhibit finite intensities, except for the hhh reflections ($h = 2n + 1$). The observed diffraction condition indicated that the detailed structure taking into account the octahedral tilt was described by a $2 \times 2 \times 2$ unit cell without any cation displacement [16]. Based on this, we used Glazer notation [46,47] to represent the octahedral tilting modes. According to the reflection conditions, the tilt mode in Glazer notation is described by $a^-b^-c^-$, while they may exhibit higher symmetry. The octahedral tilt angles along the a , b , and c directions are denoted as φ_a , φ_b , and φ_c , respectively, as illustrated in Fig. 4(a).

Structure analyses were performed based on the Bragg intensities derived from the reciprocal space maps. The total numbers of eee and ooo reflections used in the MC analysis for the PR (P07-1h) sample were 20 and 58 (22 and 44). The number of eee reflections is limited due to overlap with intense substrate Bragg reflections. The structural parameters refined in this analysis were the scale factor, the octahedral tilt angles (φ_a , φ_b , and φ_c), and the isotropic atomic displacement parameters [$B_{iso}(A)$, $B_{iso}(B)$, and $B_{iso}(O)$]. The (001) surface of the STO substrate has fourfold rotational symmetry about the c axis and mirror symmetry with respect to the (100) and (110) planes. In contrast, the structure models of LSCO film under $a^-b^-c^-$ tilting mode do not necessarily possess these symmetries, which can result in possible twinning. The intensity distribution of the ooo reflections from the LSCO film was found to exhibit the same symmetry as the STO (001) surface. Therefore, a uniform twin ratio was assumed in the MC analyses.

The tilt angles φ_a , φ_b , and φ_c derived from the MC analysis are shown in Figs. 4(b) and 4(c), which display the probability density distributions for these parameters. The corresponding values for bulk $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($x = 0.3$) [52,53] are plotted as open symbols for comparison. The tilt angles (φ_a , φ_b , φ_c) for the PR and P07-1h samples were $[7.0(5)^\circ, 0.0(11)^\circ, 3.8(3)^\circ]$ and $[5.1(5)^\circ, 5.1(5)^\circ, 4.8(4)^\circ]$, respectively, indicating that their tilt modes were $a^-b^0c^-$ and $a^-a^-c^-$, respectively. Since x-ray diffraction is sensitive to the periodic structure, the observed tilt-mode transition reflects a change in the entire film rather than a surface-limited structural modification. The fitted isotropic atomic displacement parameters were $B_{iso}(A) = 3.4(4) \text{ Å}^2$, $B_{iso}(B) = 3.3(9) \text{ Å}^2$, and $B_{iso}(O) = 2.28(15) \text{ Å}^2$ for PR, and $B_{iso}(A) = 3.9(5) \text{ Å}^2$, $B_{iso}(B) = 3.3(9) \text{ Å}^2$, and $B_{iso}(O) = 2.4(3) \text{ Å}^2$ for P07-1h. These values are larger than those of bulk perovskites (for LaCoO_3 at 300 K, 0.28 Å², 0.29 Å², and 0.47 Å² for La, Co, and O, respectively [54]) by a factor of five to ten, but are comparable to the values reported for perovskite thin films or ultrathin films ($\sim 2 \text{ Å}^2$ [25,43]). The larger B_{iso} values for the cations compared with the oxygen site may result from the limited number of eee reflections used in the MC analysis. In particular, scattering from the B-site ions contributes only to the eee reflections, resulting in larger uncertainty in the B-site parameters.

MC analyses fixed at $a^-b^0c^-$ and $a^-a^-c^-$ modes were also performed to the datasets of the PR and P07-1h samples,

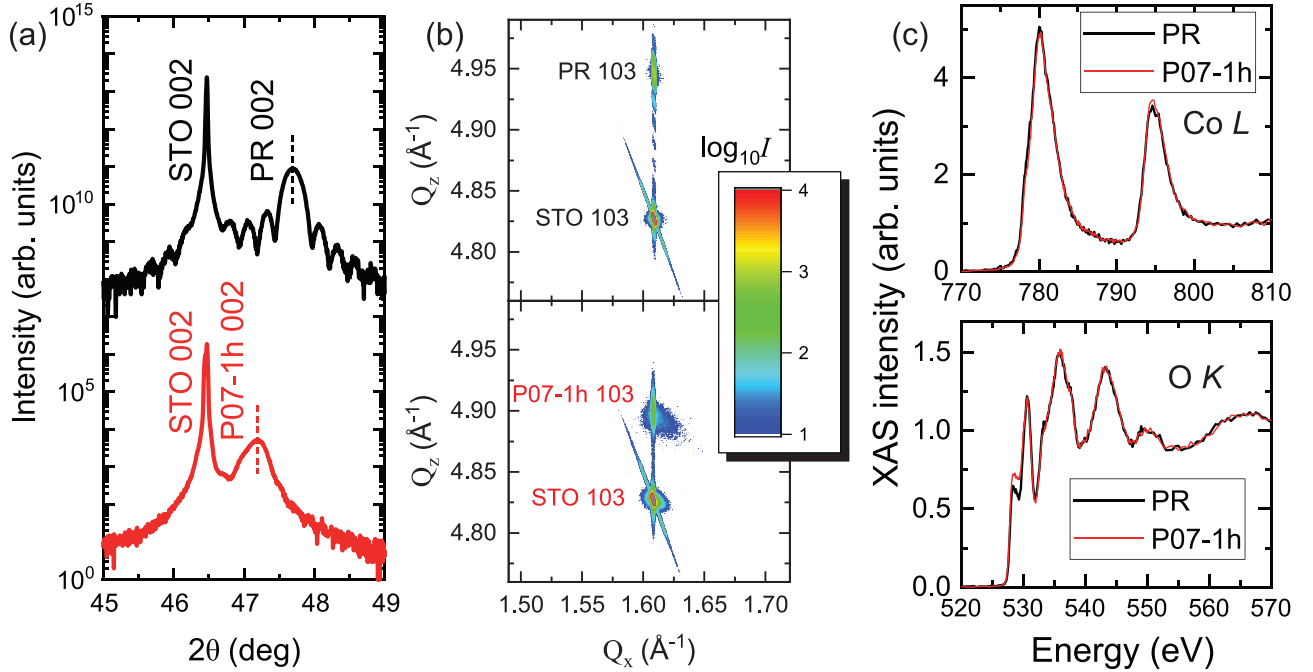


FIG. 2. (a) θ - 2θ profiles across pseudocubic 002 Bragg reflections for the (black) PR and (red) P07-1h samples. (b) Reciprocal space maps around STO 103 reflection. Both samples indicate that the films are fully strained to the substrate. (c) XAS spectra measured at (top) Co $L_{3,2}$ edge and (bottom) O K edge.

respectively. The resulting plots of the cost functions $E(\Theta) = -\frac{1}{N} \ln P(\Theta | I_{\text{obs}})$ are presented in Figs. 4(d) and 4(e). The inferred structural parameters show a clear preference for the $a^-b^0c^-$ distortion mode in the PR sample and the $a^-a^-c^-$ distortion mode in the P07-1h sample, with the difference exceeding the uncertainty associated with the analysis. Figures 4(f) and 4(g) demonstrate the observed intensity $I_{\text{obs}} + 10^2$ vs calculated intensity $I_{\text{calc}} + 10^2$ (10^2 was added to show forbidden reflections on the log-scale plot) based on the resulting structure model of the PR ($a^-b^0c^-$ mode) and P07-1h ($a^-a^-c^-$ mode) samples. The R values ($R = \frac{\sum |\sqrt{I_{\text{obs}}} - \sqrt{I_{\text{calc}}}|}{\sum \sqrt{I_{\text{obs}}}}$) of the PR and P07-1h samples are 0.108 and 0.129, respectively. These values are comparable to the previous report on the perovskite oxide thin film using isotropic atomic displacement parameters [55].

The structural parameters of the bulk [52,53], PR, and P07-1h samples are summarized in Table I. The film structures differ from that of the bulk by having in-plane Co-O bond lengths (d 's) approximately 2% longer. This elongation is caused by tensile strain from the substrate. The structural response to tensile strain observed here differs markedly from that reported for LaNiO_3 thin films [18,25]. In LaNiO_3 , tensile strain reduces φ_c and increases $\varphi_a = \varphi_b$ to accommodate the Ni-O bond length within the shortened c axis. In contrast, both PR and P07-1h exhibited large φ_c values despite the substantial tensile strain. This difference may originate from the flexibility of Co-O bond lengths, which arises from the high degree of freedom in the electronic states of Co.

IV. DISCUSSION

We first discuss the increase in the 529 eV feature observed in the O K -edge XAS spectra from the structural point of

view. The structural refinement revealed an expansion of the CoO_6 octahedra, corresponding to an increase in the average Co-O bond length. This structural change can be interpreted as an increase in the high-spin component of the Co ions. The high-spin component provides unoccupied t_{2g} states, which promote electron transfer from oxygen ligands to Co ions, thereby increasing the ligand-hole concentration [56]. The enhanced pre-edge intensity around 529 eV is consistent with this picture.

The most significant finding of this study is the unconventional nature of the observed relaxation. Conventional structural relaxation in epitaxial films typically manifests as changes in the in-plane lattice parameters from the substrate value toward the bulk value. In contrast, the relaxation observed here under electrochemical conditions involves no

TABLE I. Structural parameters of bulk $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($x = 0.3$) [52,53], PR, and P07-1h samples. Pseudocubic lattice constants (a_{pc} , b_{pc} , c_{pc}), Co-O-Co bond angles ($\theta_{a,b,c}$), and Co-O bond lengths ($d_{a,b,c}$) along the a , b , and c axes, and CoO_6 octahedral volumes are listed.

Structural parameters	bulk [52,53]	PR	P07-1h
a_{pc} ($\text{\AA}$)	3.83057	3.905	3.905
b_{pc} ($\text{\AA}$)	3.83057	3.905	3.905
c_{pc} ($\text{\AA}$)	3.83057	3.80875(15)	3.8437(2)
θ_a (deg)	166.6(3)	172.1(8)	166(2)
θ_b (deg)	166.6(3)	164.1(10)	166(2)
θ_c (deg)	166.6(3)	165.9(10)	165.2(13)
d_a ($\text{\AA}$)	1.928(1)	1.9572(9)	1.968(4)
d_b ($\text{\AA}$)	1.928(1)	1.972(2)	1.968(4)
d_c ($\text{\AA}$)	1.928(1)	1.919(2)	1.938(3)
CoO_6 volume ($\text{\AA}^3$)	9.5556(16)	9.87(2)	10.00(3)

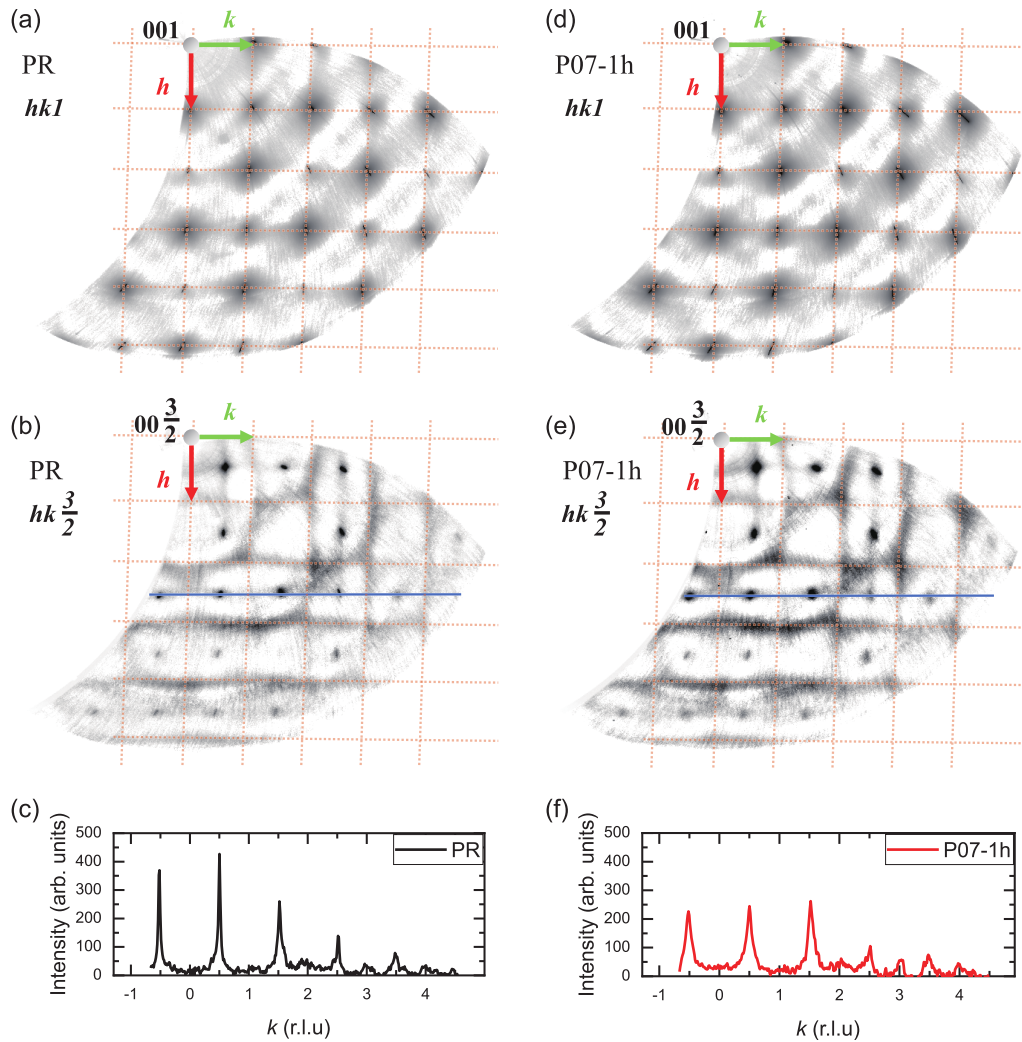


FIG. 3. The reciprocal space maps of the PR sample on the (a) $hk1$ and (b) $hk\frac{3}{2}$ planes, and (c) the line profile along the blue line in panel (b), $\frac{5}{2}k\frac{3}{2}$. Panels (d)–(f) show the corresponding data for P07-1h. Thin orange dashed grids in the reciprocal space maps indicate positions where either h or k is integer.

such lattice parameter changes but instead reflects rearrangements of the internal atomic structure. This demonstrates a fundamentally different relaxation pathway enabled by electrochemical driving forces.

We now discuss the mechanism underlying this distinct relaxation behavior. Epitaxial films are inherently metastable. During film growth, a kinetically stabilized structure forms at the interface. The octahedral tilt mode in the as-grown film represents a local minimum of the free energy, separated from other local minima and the global minimum by potential barriers, as illustrated in Fig. 4(h). Electrochemically induced relaxation occurs when these barriers are reduced. During the OER, oxygen ions in LSCO participate in the water-splitting reaction through a lattice oxygen mechanism [35,37]. This oxygen-ion migration, even without net oxygen loss, transiently modifies the local coordination environment and reduces the energy barriers separating different tilt configurations. The system can thus access alternative struc-

tural states while maintaining epitaxial coherence with the substrate.

This relaxation mechanism is likely not limited to LSCO but may be general to epitaxial perovskite oxides under electrochemical conditions. Moreover, the principle of electrochemically driven barrier reduction may extend beyond perovskites to other epitaxial oxide systems where ionic migration occurs under operating conditions. This suggests that internal structural relaxation could be a widespread but previously overlooked phenomenon in functional oxide thin films.

In oxide electronics, electron transfer integrals and exchange interactions depend sensitively on B-O-B bond angles and octahedral connectivity, influencing a wide range of functional properties. Even within a single material composition, different tilt modes imposed by substrates can lead to distinct electronic band structures and transport properties [18,57]. The electrochemically driven tilt-mode transition

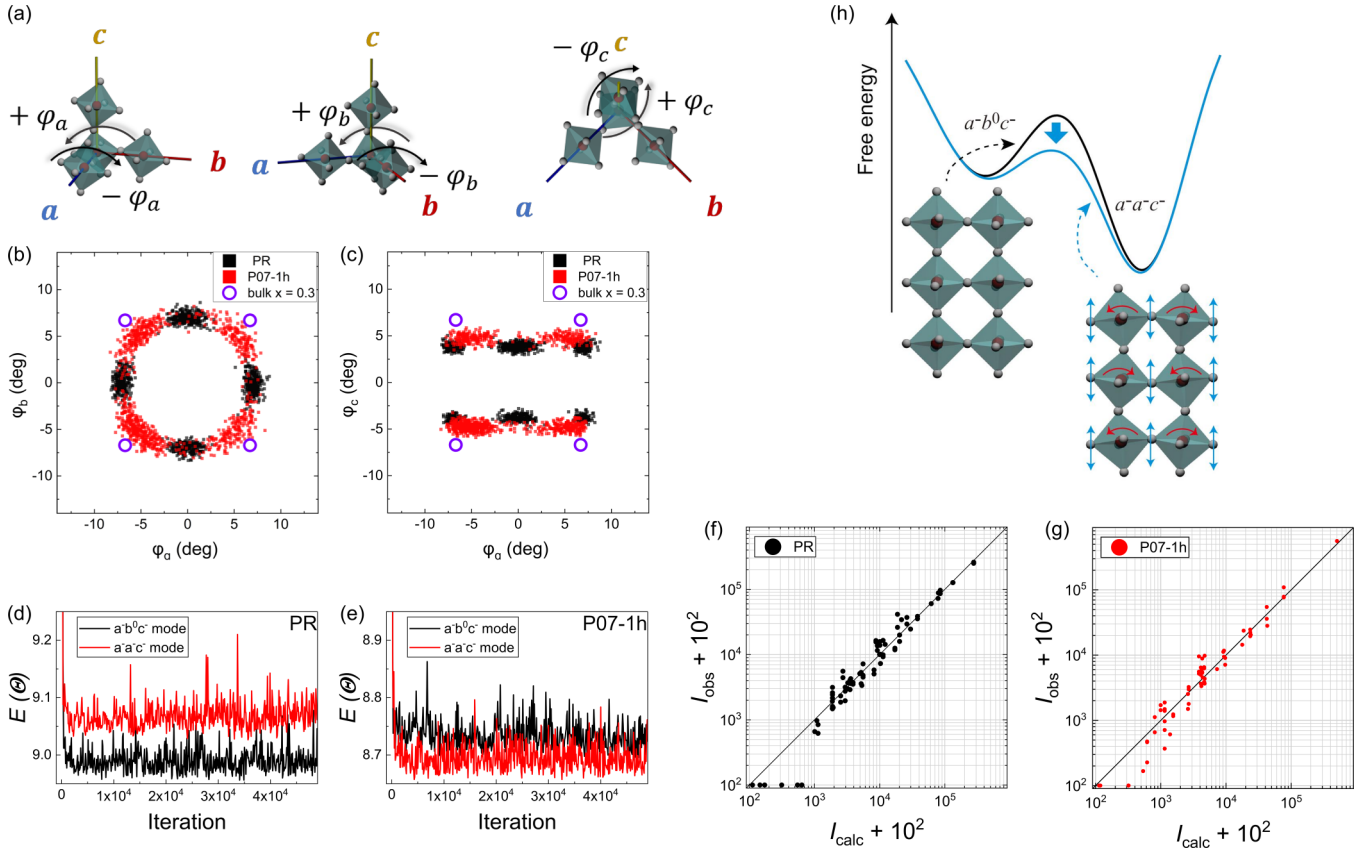


FIG. 4. (a) The schematics of the tilt angles ϕ_a , ϕ_b , and ϕ_c in the $a^-b^0c^-$ mode. (b), (c) Results of MC sampling probability distributions for the octahedral tilt angles ϕ_a vs ϕ_b , and ϕ_a vs ϕ_c , respectively. Those for bulk $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($x = 0.3$) [52,53] are also shown by open symbols for comparison. (d), (e) Cost functions generated during the MC sampling for PR and P07-1h samples using $a^-b^0c^-$ (black) and $a^-a^-c^-$ (red) modes, respectively. (f), (g) Observed intensity $I_{\text{obs}} + 10^2$ vs calculated intensity $I_{\text{calc}} + 10^2$ based on the resulting structure model of the PR ($a^-b^0c^-$ mode) and P07-1h ($a^-a^-c^-$ mode) samples, respectively. (h) Schematic of the free energy landscape. The structures of PR ($a^-b^0c^-$) and P07-1h ($a^-a^-c^-$) represent different local minima separated by a potential barrier. Electrochemically induced oxygen movement (cyan arrows) lowers this barrier, enabling tilt-mode transition between the two configurations.

demonstrated here introduces a route for postgrowth electronic structure tuning.

V. CONCLUSION

We have demonstrated a form of structural relaxation in epitaxial perovskite oxide thin films driven by electrochemical operation. Epitaxial $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ films grown on SrTiO_3 substrates exhibit a CoO_6 octahedral tilt mode distinct from that of bulk LSCO. After prolonged electrochemical treatment, the tilt mode and tilt angles converge to those of the bulk while the in-plane lattice parameters remain unchanged, establishing that electrochemical processes can induce internal structural relaxation without conventional lattice parameter relaxation.

The mechanism involves ionic oxygen migration during electrochemical reactions, which reduces energy barriers between structural configurations. This relaxation pathway represents a dimension of structural control in functional oxide thin films inaccessible through conventional thermal or strain-driven processes. This work establishes the importance of monitoring internal atomic arrangements, not just lattice parameters, when designing and operat-

ing functional thin films for energy conversion and other applications.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

- [1] D. G. Schlom, L.-Q. Chen, X. Pan, A. Schmehl, and M. A. Zurbuchen, A thin film approach to engineering functionality into oxides, *J. Am. Ceram. Soc.* **91**, 2429 (2008).
- [2] J. M. Rondinelli, S. J. May, and J. W. Freeland, Control of octahedral connectivity in perovskite oxide heterostructures: An emerging route to multifunctional materials discovery, *MRS Bull.* **37**, 261 (2012).
- [3] J. M. Rondinelli and N. A. Spaldin, Structure and properties of functional oxide thin films: Insights from electronic-structure calculations, *Adv. Mater.* **23**, 3363 (2011).
- [4] R. Ramesh and N. A. Spaldin, Multiferroics: Progress and prospects in thin films, *Nat. Mater.* **6**, 21 (2007).
- [5] J. W. Matthews and A. E. Blakeslee, Defects in epitaxial multilayers: I. Misfit dislocations, *J. Cryst. Growth* **27**, 118 (1974).
- [6] A. Herklotz, D. Lee, E.-J. Guo, T. L. Meyer, J. R. Petrie, and H. N. Lee, Strain coupling of oxygen non-stoichiometry in perovskite thin films, *J. Phys.: Condens. Matter* **29**, 493001 (2017).
- [7] H. Yamada, Y. Ogawa, Y. Ishii, H. Sato, M. Kawasaki, H. Akoh, and Y. Tokura, Engineered interface of magnetic oxides, *Science* **305**, 646 (2004).
- [8] Y. Konishi, Z. Fang, M. Izumi, T. Manako, M. Kasai, H. Kuwahara, M. Kawasaki, K. Terakura, and Y. Tokura, Orbital-state-mediated phase-control of manganites, *J. Phys. Soc. Jpn.* **68**, 3790 (1999).
- [9] J. Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig, and R. Ramesh, Epitaxial BiFeO₃ multiferroic thin film heterostructures, *Science* **299**, 1719 (2003).
- [10] S. Li, Y. Wang, M. Yang, S. Xu, M. Liu, Q. Li, J. Miao, E.-J. Guo, K. Jin, L. Gu, Q. Zhang, J. Deng, X. Chen, and X. Xing, Ferroelectricity in low-permittivity SrZrO₃ epitaxial films, *Chem. Mater.* **35**, 2967 (2023).
- [11] Q. Gan, R. A. Rao, C. B. Eom, J. L. Garrett, and M. Lee, Direct measurement of strain effects on magnetic and electrical properties of epitaxial SrRuO₃ thin films, *Appl. Phys. Lett.* **72**, 978 (1998).
- [12] Z. Weng, L. Liu, Y. Hu, Y. Wei, P. Da, Z. Wu, Z. Mu, P. Xi, and C.-H. Yan, Significance of engineering the MnO₆ octahedral units to promote the oxygen reduction reaction of perovskite oxides, *Adv. Mater.* **36**, 2311102 (2024).
- [13] W. Li, B. Zhu, R. Zhu, Q. Wang, P. Lu, Y. Sun, C. Cafolla, Z. Qi, A. Chen, P. Gao, H. Wang, Q. He, K. H. L. Zhang, and J. L. MacManus-Driscoll, Atomic-scale control of electronic structure and ferromagnetic insulating state in perovskite oxide superlattices by long-range tuning of BO₆ octahedra, *Adv. Funct. Mater.* **30**, 2001984 (2020).
- [14] C. Ma, N. Lin, Z. Wang, S. Zhou, H. Yu, J. Lu, and H. Huang, Origin of spin-state crossover and electronic reconstruction at the surface of a LaCoO₃ nanoparticle, *Phys. Rev. B* **99**, 115401 (2019).
- [15] S. Li, J. Wang, Q. Zhang, M. A. Roldan, L. Shan, Q. Jin, S. Chen, Z. Wu, C. Wang, C. Ge, M. He, H. Guo, L. Gu, K.-J. Jin, and E.-J. Guo, Maximization of ferromagnetism in LaCoO₃ films by competing symmetry, *Phys. Rev. Mater.* **3**, 114409 (2019).
- [16] T. T. Fister, H. Zhou, Z. Luo, S. S. A. Seo, S. O. Hruszkewycz, D. L. Proffit, J. A. Eastman, P. H. Fuoss, P. M. Baldo, H. N. Lee, and D. D. Fong, Octahedral rotations in strained LaAlO₃/SrTiO₃ (001) heterostructures, *APL Mater.* **2**, 021102 (2014).
- [17] M. Brahlek, A. K. Choquette, C. R. Smith, R. Engel-Herbert, and S. J. May, Structural refinement of *Pbnm*-type perovskite films from analysis of half-order diffraction peaks, *J. Appl. Phys.* **121**, 045303 (2017).
- [18] S. J. May, J.-W. Kim, J. M. Rondinelli, E. Karapetrova, N. A. Spaldin, A. Bhattacharya, and P. J. Ryan, Quantifying octahedral rotations in strained perovskite oxide films, *Phys. Rev. B* **82**, 014110 (2010).
- [19] D. Kan, Y. Wakabayashi, H. Tajiri, and Y. Shimakawa, Interfacially engineered oxygen octahedral rotations and their impact on strain relief in coherently grown SrRuO₃ films, *Phys. Rev. B* **94**, 024112 (2016).
- [20] D. Kan, M. Anada, Y. Wakabayashi, H. Tajiri, and Y. Shimakawa, Oxygen octahedral distortions in compressively strained SrRuO₃ epitaxial thin films, *J. Appl. Phys.* **123**, 235303 (2018).
- [21] H. Meley, Karandeep, L. Oberson, J. de Bruijckere, D. T. L. Alexander, J.-M. Triscone, Ph. Ghosez, and S. Gariglio, Structural analysis of LaVO₃ thin films under epitaxial strain, *APL Mater.* **6**, 046102 (2018).
- [22] Y. Heo, D. Kan, M. Anada, Y. Wakabayashi, H. Tajiri, and Y. Shimakawa, Correlations between oxygen octahedral distortions and magnetic and transport properties in strained La_{0.5}Sr_{0.5}CoO₃ thin films, *Phys. Rev. B* **99**, 174420 (2019).
- [23] J. Fowlie, C. Lichtensteiger, M. Gibert, H. Meley, P. Willmott, and J.-M. Triscone, Thickness-dependent perovskite octahedral distortions at heterointerfaces, *Nano Lett.* **19**, 4188 (2019).
- [24] L. Qiao, J. H. Jang, D. J. Singh, Z. Gai, H. Xiao, A. Mehta, R. K. Vasudevan, A. Tselev, Z. Feng, H. Zhou, S. Li, W. Prellier, X. Zu, Z. Liu, A. Borisevich, A. P. Baddorf, and M. D. Biegalski, Dimensionality controlled octahedral symmetry-mismatch and functionalities in epitaxial LaCoO₃/SrTiO₃ heterostructures, *Nano Lett.* **15**, 4677 (2015).
- [25] F. Izumisawa, Y. Ishii, M. Kimura, T. Katase, T. Kamiya, J.-i. Yamaura, and Y. Wakabayashi, Symmetry change in LaNiO₃ films caused by epitaxial strain from LaAlO₃, SrTiO₃, and DyScO₃ pseudocubic (001) surfaces, *J. Appl. Phys.* **136**, 075303 (2024).
- [26] L. Yan, H. Niu, C. A. Bridges, P. A. Marshall, J. Hadermann, G. van Tendeloo, P. R. Chalker, and M. J. Rosseinsky, Unit-cell-level assembly of metastable transition-metal oxides by pulsed-laser deposition, *Angew. Chem. Int. Ed.* **46**, 4539 (2007).
- [27] X. Chen, J. Yu, and S. B. Adler, Thermal and chemical expansion of Sr-doped lanthanum cobalt oxide (La_{1-x}Sr_xCoO_{3-δ}), *Chem. Mater.* **17**, 4537 (2005).
- [28] H. Fujii, Y. Wakabayashi, and T. Doi, Early stages of iron anodic oxidation: Defective growth and density increase of oxide layer, *Phys. Rev. Mater.* **4**, 033401 (2020).
- [29] J. K. Wenderott, T. Billo, and D. D. Fong, Epitaxial oxide ionotronics: Interfaces and oxygen vacancies, *APL Mater.* **12**, 050901 (2024).
- [30] R. Caciuffo, D. Rinaldi, G. Barucca, J. Mira, J. Rivas, M. A. Señas-Rodríguez, P. G. Radaelli, D. Fiorani, and J. B. Goodenough, Structural details and magnetic order of La_{1-x}Sr_xCoO₃ ($x \leq 0.3$), *Phys. Rev. B* **59**, 1068 (1999).
- [31] X. Cheng, E. Fabbri, M. Nachtegaal, I. E. Castelli, M. El Kazzi, R. Haumont, N. Marzari, and T. J. Schmidt, Oxygen evolution reaction on La_{1-x}Sr_xCoO₃ perovskites: A combined

- experimental and theoretical study of their structural, electronic, and electrochemical properties, *Chem. Mater.* **27**, 7662 (2015).
- [32] P. M. Raccach and J. B. Goodenough, A localized-electron to collective-electron transition in the system (La, Sr)CoO₃, *J. Appl. Phys.* **39**, 1209 (1968).
- [33] M. Itoh, I. Natori, S. Kubota, and K. Motoya, Spin-glass behavior and magnetic phase diagram of La_{1-x}Sr_xCoO₃ (0 ≤ x ≤ 0.5) studied by magnetization measurements, *J. Phys. Soc. Jpn.* **63**, 1486 (1994).
- [34] K. Asai, O. Yokokura, N. Nishimori, H. Chou, J. M. Tranquada, G. Shirane, S. Higuchi, Y. Okajima, and K. Kohn, Neutron-scattering study of the spin-state transition and magnetic correlations in La_{1-x}Sr_xCoO₃ (x = 0 and 0.08), *Phys. Rev. B* **50**, 3025 (1994).
- [35] A. Grimaud, O. Diaz-Morales, B. Han, W. T. Hong, Y.-L. Lee, L. Giordano, K. A. Stoerzinger, M. T. M. Koper, and Y. Shao-Horn, Activating lattice oxygen redox reactions in metal oxides to catalyse oxygen evolution, *Nat. Chem.* **9**, 457 (2017).
- [36] M. L. Weber, G. Lole, A. Kormanyos, A. Schwiers, L. Heymann, F. D. Speck, T. Meyer, R. Dittmann, S. Cherevko, C. Jooss, C. Baeumer, and F. Gunkel, Atomistic insights into activation and degradation of La_{0.6}Sr_{0.4}CoO_{3-δ} electrocatalysts under oxygen evolution conditions, *J. Am. Chem. Soc.* **144**, 17966 (2022).
- [37] J. T. Mefford, X. Rong, A. M. Abakumov, W. G. Hardin, S. Dai, A. M. Kolpak, K. P. Johnston, and K. J. Stevenson, Water electrolysis on La_{1-x}Sr_xCoO_{3-δ} perovskite electrocatalysts, *Nat. Commun.* **7**, 11053 (2016).
- [38] X. Liu, L. Zhang, Y. Zheng, Z. Guo, Y. Zhu, H. Chen, F. Li, P. Liu, B. Yu, X. Wang, J. Liu, Y. Chen, and M. Liu, Uncovering the effect of lattice strain and oxygen deficiency on electrocatalytic activity of perovskite cobaltite thin films, *Adv. Sci.* **6**, 1801898 (2019).
- [39] C. Yang, C. Laberty-Robert, D. Batuk, G. Cibir, A. V. Chadwick, V. Pimenta, W. Yin, L. Zhang, J.-M. Tarascon, and A. Grimaud, Phosphate ion functionalization of perovskite surfaces for enhanced oxygen evolution reaction, *J. Phys. Chem. Lett.* **8**, 3466 (2017).
- [40] Y. Lu, A. Ma, Y. Yu, R. Tan, C. Liu, P. Zhang, D. Liu, and J. Gui, Engineering oxygen vacancies into LaCoO₃ perovskite for efficient electrocatalytic oxygen evolution, *ACS Sustain. Chem. Eng.* **7**, 2906 (2019).
- [41] Y. Matsumoto, H. Manabe, and E. Sato, Oxygen evolution on La_{1-x}Sr_xCoO₃ electrodes in alkaline solutions, *J. Electrochem. Soc.* **127**, 811 (1980).
- [42] Z. Shen, M. Qu, J. Shi, F. E. Oropeza, V. A. de la Peña O'Shea, G. Gorni, C. M. Tian, J. P. Hofmann, J. Cheng, J. Li, and K. H. L. Zhang, Correlating the electronic structure of perovskite La_{1-x}Sr_xCoO₃ with activity for the oxygen evolution reaction: The critical role of Co 3d hole state, *J. Energy Chem.* **65**, 637 (2022).
- [43] A. Fujisawa, X. Xu, Y. Ishii, H. Shimotani, Y. Inoue, Y. Miyahara, K. Miyazaki, and Y. Wakabayashi, Surface structure modulation of La_{0.6}Sr_{0.4}CoO₃ films on SrTiO₃ (001) substrate under electrochemical conditions, *ACS Appl. Mater. Interfaces* **17**, 57603 (2025).
- [44] M. Anada, Y. Nakanishi-Ohno, M. Okada, T. Kimura, and Y. Wakabayashi, Bayesian inference of metal oxide ultrathin film structure based on crystal truncation rod measurements, *J. Appl. Crystallogr.* **50**, 1611 (2017).
- [45] K. Nagai, M. Anada, Y. Nakanishi-Ohno, M. Okada, and Y. Wakabayashi, Robust surface structure analysis with reliable uncertainty estimation using the exchange Monte Carlo method, *J. Appl. Crystallogr.* **53**, 387 (2020).
- [46] A. M. Glazer, The classification of tilted octahedra in perovskites, *Acta Crystallogr. Sect. B* **28**, 3384 (1972).
- [47] A. M. Glazer, Simple ways of determining perovskite structures, *Acta Crystallogr. A* **31**, 756 (1975).
- [48] J. Walter, G. Yu, B. Yu, A. Grutter, B. Kirby, J. Borchers, Z. Zhang, H. Zhou, T. Birol, M. Greven, and C. Leighton, Ion-gel-gating-induced oxygen vacancy formation in epitaxial La_{0.5}Sr_{0.5}CoO_{3-δ} films from *in operando* x-ray and neutron scattering, *Phys. Rev. Mater.* **1**, 071403 (2017).
- [49] S. Zhang and G. Galli, Understanding the metal-to-insulator transition in La_{1-x}Sr_xCoO_{3-δ} and its applications for neuromorphic computing, *npj Comput. Mater.* **6**, 170 (2020).
- [50] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/72nx-sczv> for the results of the position dependent XAS measurements.
- [51] M. Kopecký, J. Fábry, and J. Kub, X-ray diffuse scattering in SrTiO₃ and model of atomic displacements, *J. Appl. Crystallogr.* **45**, 393 (2012).
- [52] A. Mineshige, M. Inaba, T. Yao, Z. Ogumi, K. Kikuchi, and M. Kawase, Crystal structure and metal-insulator transition of La_{1-x}Sr_xCoO₃, *J. Solid State Chem.* **121**, 423 (1996).
- [53] A. Mineshige, M. Kobune, S. Fujii, Z. Ogumi, M. Inaba, T. Yao, and K. Kikuchi, Metal-insulator transition and crystal structure of La_{1-x}Sr_xCoO₃ as functions of Sr-content, temperature, and oxygen partial pressure, *J. Solid State Chem.* **142**, 374 (1999).
- [54] P. Radaelli and S.-W. Cheong, Structural phenomena associated with the spin-state transition in LaCoO₃, *Phys. Rev. B* **66**, 094408 (2002).
- [55] T. Deguchi, T. Hara, Y. Ishii, H.-B. Li, A. N. Hattori, H. Tanaka, H. Sagayama, and Y. Wakabayashi, Long-period ordering induced by hydrogen doping in NdNiO₃ films on SrTiO₃ (001) substrates, *Phys. Rev. B* **113**, 174113 (2026).
- [56] M. Abbate, F. M. F. de Groot, J. C. Fuggle, A. Fujimori, O. Strebel, F. Lopez, M. Domke, G. Kaindl, G. A. Sawatzky, M. Takano, Y. Takeda, H. Eisaki, and S. Uchida, Controlled-valence properties of La_{1-x}Sr_xFeO₃ and La_{1-x}Sr_xMnO₃ studied by soft-x-ray absorption spectroscopy, *Phys. Rev. B* **46**, 4511 (1992).
- [57] M. C. Weber, M. Guennou, N. Dix, D. Pesquera, F. Sánchez, G. Herranz, J. Fontcuberta, L. López-Conesa, S. Estradé, F. Peiró, J. Iñiguez, and J. Kreisel, Multiple strain-induced phase transitions in LaNiO₃ thin films, *Phys. Rev. B* **94**, 014118 (2016).