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Dynamics of Anisotropic Oxygen-Ion Migration in Strained Cobaltites

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determine the crucial role of the tolerance factor for OVC stability, and establish the strain-dependent phase diagram. Our work provides a practical guide for engineering OVC orientation that is applicable to ionic-oxide electronics.

KEYWORDS: oxygen vacancy channel, epitaxial strain, domain switching, oxygen-ion migration, in situ STEM

xygen-ion migration in transition metal oxides has attracted increasing interest in fundamental research and applications in solid oxide fuel cells, $^{1-3}$ fast catalytic reactions, 4 resistive switching memories, 5 electrochemical sensing,⁶ etc. Oxygen-ion migration in solids is ascribed to hopping toward lower energetic vacant oxygen sites. Ordering of the oxygen vacancy $(V_{\ddot{a}})$ emerges when their concentration reaches a fractional threshold in oxide parents,⁷ leads to the formation of the oxygen vacancy channel (OVC),⁸⁻¹¹ and stimulates various emergent quantum phenomena.¹²⁻¹⁸ More importantly, the creation or reorientation of the OVC introduces a topotactic phase transition such as the transformation from perovskite to brownmillerite (BM), resulting in a dramatic change in the physical and chemical properties including the metal-insulator transition, magnetic phase transition, and anisotropic ion conduction.^{11,19-24} The OVC usually serves as a fast channel for oxygen vacancy diffusion,^{17,18} playing the key role in regulating the migration pathway of oxygen ions and dominating the dynamic response to an external stimulus. Thus, a controllable orientation of the OVC is desirable for tailoring oxygen diffusion, as it is widely exploited in solid-state fuel cells, catalysts, and ion-batteries. A thoughtful understanding of the topochemical aspects of oxygen-ion migration will give us further insight into the

control parameters of oxygen-ion migration pathways and the utilization of the OVC in designing solid oxygen-ion conductors. $^{25-27}$

Strain engineering is a universal strategy to tune the atomic configuration of OVCs by directly altering the cation—oxygen bond length and oxygen vacancy formation energy (E_{Vo}). Moving an oxygen ion out of its equilibrium position along a specific migration pathway to the neighboring vacant lattice site is determined by the strain state of epitaxial thin films. It is reported that the orientation of OVCs in cobaltite,²⁸ chromate,²⁹ and ferrite³⁰ thin films can be readily controlled by strain. For instance, the periodicity and orientation of V_{o} layers are parallel (perpendicular) to the interface when the films are under compressive (tensile) strain.³¹ Recently, an unexpected zigzag-like V_{o} ordering in a compressively strained LaCoO_{2.5} film has been found, whereas the unique structure

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Figure 1. Direct observations of OVCs on strained LCO_xfilms. (a) Schematics of OVCs' evolution on the LaAlO₃ (LAO) and SrTiO₃ (STO) substrates. The LCO_x films will form alternated tetrahedra [CoO₄, yellow] and octahedra [CoO₆, blue] along the in-plane (out-of-plane) direction under tensile (compressive) strain. (b and c) HAADF images of LCO_{2.67} films on SrTiO₃ and LaAlO₃ substrates, respectively. 3*a*-LCO_{2.67} (3*c*-LCO_{2.67}) represents the domain orientation aligned in the out-of-plane (in-plane) direction.

cannot be formed through annealing a tensile-strained LaCoO₃(LCO₃) film.³² Previously, OVC formation under tensile strain has been studied by high-dose electron beam irradiation.^{33,34} The dynamic process in differently strained LaCoO_x (LCO_x) films toward further oxygen reduction to the metastable phases has not been visualized directly so far.

Here we report an *operando* transmission electron microscopy (TEM) investigation of dynamic structural evolution in LCO_x films during thermal annealing. We observe that the final stabilized LCO_{2.5} phases are distinct when the pristine LCO₃ films are under compressive and tensile strain states. The OVC evolutions of strained LCO_x films are recorded as a function of both annealing temperature and annealing time. By imaging the atomic-scale boundaries of OVC switching, this work provides direct evidence of the strain-mediated $V_{\ddot{o}}$ migration pathway from an octahedron. The associated lattice distortion and its strain dependency are quantified theoretically by mapping out the OVC phase diagram at the atomic scale.

STRAIN DEPENDENCE OF OVCS' ORIENTATION IN ULTRATHIN COBALTITES

Previous theoretical and experimental work^{35–40} demonstrated that E_{Vo} in perovskite-type oxides depends on the strain and is highly anisotropic. Tensile strain dramatically reduces E_{Vo} , whereas compressive strain only changes E_{Vo} slightly. We choose LCO₃ as our protocol system due to the following two reasons. First of all, cobaltites have relatively low E_{Vo} (~1.5 eV)

and oxygen migration barrier ($\sim 0.8 \text{ eV}$), compared to other 3d transition metal oxides.⁴⁰ Second, earlier work shows that the stoichiometric LCO₃ epitaxial films exhibit an unconventional strain relaxation behavior, resulting in the stripe-like domain patterns due to the formation of OVCs.⁴¹⁻⁴⁴ The pseudocubic (*pc*) lattice constant of bulk LCO₃ is $a_{pc} = 3.81$ Å (Figure 1a). Single-crystalline SrTiO₃ (a = 3.905 Å) and LaAlO₃ ($a_{nc} = 3.79$ Å) substrates may introduce -0.5% (compressive) and +2.5%(tensile) strain to the as-grown LCO₃ films, respectively. Therefore, the LCO₃ thin film is expected to exhibit the unique structural evolution of the OVC under different strain states.⁴⁵ We choose LaAlO₃ as the capping layer on LCO₃ films because it has a lower oxygen migration barrier ($\sim 0.63 \text{ eV}$) and higher oxygen vacancy formation energy (4.2-6.5 eV) than those of cobaltites.⁴⁶⁻⁴⁸ Therefore, the oxygen could extract out of the films without deteriorating the crystal structure of the capping layer. X-ray diffraction and reflectivity measurements confirm the highly epitaxial, coherently grown, and smooth interface/ surface in the as-grown LaAlO₃/LCO₃ bilayers (Figure S1). The absence of periodic dark-strips in the pristine LCO₃ films of both strain states indicates that all LCO3 films are nearly stoichiometric (Figure S2). The oxygen had been gradually extracted from LCO₃ films by gradually increasing the temperature at the rate 5 °C/min in the ultrahigh-vacuum environment ($\sim 10^{-9}$ Torr) of STEM (Figures S3 and S4). Figure 1b and c shows the immediate high-angle annular darkfield (HAADF) STEM images of LCO_{2.67} phases under tensile and compressive strain states at an annealing temperature of T_a = 400 $^{\circ}$ C, respectively. As oxygen ion escaped out of the LCO₃



Figure 2. Structural evolution of OVCs in strained LCO_xultrathin films. Both specimens were *in situ* heated up from room temperature to the annealing temperature T_a . (a–d) HAADF images of a tensile-strained LCO_x film taken after annealing at $T_a = 450$ °C for 0, 2, 4, and 6 min waiting times. The 3*c*-LCO_{2.67} and 3*a*-LCO_{2.67} domains are marked in green and yellow, respectively. After 4 min, the LCO_x film transforms into the brownmillerite 2*c*-LCO_{2.5} partially and then changes into 2*c*-LCO_{2.5} (blue domains) entirely after 6 min. The white triangles indicate the positions of the edge dislocations. (e–h) HAADF images of a compressively strained LCO_x film taken consequently after annealing at $T_a = 500$ °C for 0, 2, 4, and 6 min waiting times. The 3*c*-LCO_{2.67} transforms into a new LCO_{2.5} (n-LCO_{2.5}) phase (purple domains). With increasing the annealing time, all n-LCO_{2.5} phases merge. The white scale bar is 5 nm. Yellow dashed lines indicate the interface positions.

films, the increased "dark-stripes" can be visualized in both samples. The LCO_{2.67} phases contain alternatively stacked one CoO₄ tetrahedral and two CoO₆ octahedral layers.⁴¹ Tensile strain would favor the creation of ordered $V_{\ddot{o}}$ in the films along the out-of-plane direction because the $V_{\ddot{o}}$ -related chemical expansion can reduce the lattice misfit strain.^{41–44} On the contrary, compressive strain leads to in-plane $V_{\ddot{o}}$ orderings, which are parallel to the interface due to the concomitant lattice elongation along the out-of-plane direction.

Spontaneously, the ordered OVCs are formed within the tetrahedral CoO₄ layer in every one-third atomic plane,⁴⁹ producing the *dark-stripe* contrast in the HAADF images due to the increased La–La distance. Under tensile strain (on a SrTiO₃ substrate), $V_{\ddot{o}}$ sites prefer the ordered arrangement along the out-of-plane direction, resulting in vertical $V_{\ddot{o}}$ stripes mostly with 3*a* periodicity (denoted as 3*a*-LCO_{2.67} hereafter). In contrast, horizontal $V_{\ddot{o}}$ stripes with 3*c* periodicity (denoted as 3*c*-LCO_{2.67} hereafter) appeared in the films grown on the LaAlO₃ substrates, corresponding to the $V_{\ddot{o}}$ sites aligned in the in-plane CoO₄ layers.

EVOLUTION OF OVCS IN STRAINED LCO_X FILMS

The orientation of OVCs switches from the out-of-plane to the in-plane orientation when a small amount of oxygen vacancies was extracted under tensile strain at a slightly higher temperature of 450 °C. As shown in Figure 2a, the horizontal $V_{\ddot{o}}$ stripe domains (3*c*-LCO_{2.67}) first appear randomly in the 3*a*-LCO_{2.67} films and then propagate laterally. At increasing annealing time, the horizontal $V_{\ddot{o}}$ stripe domains emerge on the right side and then move toward the left region with vertical $V_{\ddot{o}}$ stripes within tens of seconds (the minimum imaging time frame in scanning mode). It is hampered by an edge dislocation labeled by a blue triangle (Figure 2b). After annealing at $T_a = 450$ °C around 2 min, the horizontal $V_{\ddot{o}}$

stripes cross the edge dislocation and overspread the whole film. After ~4 min of high-temperature annealing, the 3*c*-LCO_{2.67} film gradually transforms into the brownmillerite (BM) phase with 2*c* periodicity (denoted as 2*c*-LCO_{2.5}) and finally stabilizes at the 2*c*-LCO_{2.5} phase after a 6 min annealling time (Figure 2*c* and d). Please note that the OVCs' alignment switches when the 3*a*-LCO_{2.67} changes to 3*c*-LCO_{2.67} without changing the oxygen content. We could extract the moving speed of the domain boundary, which is ~15 nm/min. However, the domain boundaries change from vertical to horizontal alignment with further extracting oxygen to 2*c*-LCO_{2.5}.

The evolution behavior of OVCs in LCO_x films under compressive strain is dramatically different from that of a film under tensile strain. At $T_a = 500$ °C, we observe a new $V_{\ddot{o}}$ ordered phase with diagonal-aligned dark-stripes, which can be called n-LCO_{2.5} as reported in our recent work.³² The diagonal $V_{\ddot{o}}$ stripes first appear randomly in the 3*c*-LCO_{2.67} films as indicated by the inclined purple arrows in Figure 2e. At increasing annealing times, the n-LCO_{2.5} domains propagate laterally toward two sides in the moving speed of the domain wall of \sim 7 nm/min, accompanied by the disappearance of the horizontal $V_{\ddot{a}}$ stripes (Figure 2f and g). After around 6 min, the 3c-LCO_{2.67} completes the structural transformation to the *n*- $LCO_{2.5}$ phase in the entire film (Figure 2h). Both HAADF and annular bright field (ABF) images of n-LCO_{2.5} were recorded for identifying the atomic positions of each element (Figure \$5). From ABF images, we could visualize the tilt and distortion of CoO₅ square pyramids, which are dramatically distorted close to $V_{\ddot{a}}$ cites. The periodic OVCs along the diagonal direction were visualized directly, as indicated by the bright contrast in the ABF images. The dynamic process of dark-stripe formation and evolution under thermal annealing



Figure 3. Microscopic view and strain distribution of the domain boundaries in LCO_x ultrathin films. HAADF images of domain boundaries (a) between 3a-LCO_{2.67} and 3c-LCO_{2.67} in a tensile-strained film and (d) 3c-LCO_{2.67} and n-LCO_{2.57} in a compressive strained film. High-magnified HAADF images from red and blue squares are shown in (c) and (f), where the boundaries of OVC switching are indicated by red and blue, respectively. The in-plane and out-of-plane lattice strain mapping corresponding to (a) and (d) are shown in (b) and (e), respectively.

exhibits completely different pathways depending on epitaxial strain.

ATOMIC VIEW OF DOMAIN BOUNDARIES AND STRAIN DISTRIBUTIONS IN LCO_X FILMS

To reveal the atomic-resolved structural transition of OVCs, we compared the changes in the periodicity and orientation of $V_{\ddot{o}}$ stripes in the high-magnified HAADF images of LCO_x films grown on SrTiO₃ and LaAlO₃ substrates, shown in Figure 3a and d, respectively. Figure 3c shows the domain boundary between 3a-LCO_{2.67} and 3c-LCO_{2.67}. We find that the vertical $V_{\ddot{o}}$ stripes are not connected directly to the horizontal ones but

always blocked by an octahedral layer, marked in red shadow. The possible migration path of oxygen ions is illustrated in Figure S6. The oxygen ions will migrate from diagonal octahedron to the nearby tetrahedron, resulting in the rearrangement of dark stripes from vertically aligned to horizontally aligned. Meanwhile, the oxygen ions flow from an octahedron to a tetrahedron within the 3a-LCO_{2.67} domains in order to keep an octahedral layer at the domain boundary. Macroscopically, the 3c-LCO_{2.67} domains grow and 3a-LCO_{2.67} domains vanish. Finally, the dark stripes change their periodicity from 3c to 2c by increasing the numbers of $V_{\ddot{o}}$. Eventually, the 3c-LCO_{2.67} undergoes a topotactic structural transformation into BM-phase 2c-LCO_{2.5}. Strain evolution at



Figure 4. Strain-dependent oxygen migration and phase diagram of OVCs in cobaltites. (a) Oxygen vacancy formation energy $(E_{V\bar{o}})$ in LaCoO3 films mediated by substrate strain. (b) Migration barrier in the CoO₄ tetrahedra under tensile (upper panel) and compressive strain (lower panel). Oxygen-ion migration pathway for a LCO_x film under (c) tensile and (d) compressive strain. Red and purple spheres represent oxygen-ion and oxygen vacancies, respectively. (e) Phase diagram of OVCs. The oxygen content (x) is plotted as a function of misfit strain, which is caused by $V_{\bar{o}}$ -induced chemical expansion. Na and Nc are two intermediate states of LCO_x films during the phase transition under tensile and compressive strains, respectively. Note that the misfit strain and corresponding oxygen content are calculated directly from the STEM measurements.

the domain boundary between 3a-LCO_{2.67} and 3c-LCO_{2.67} was also quantitatively analyzed by La–La distance mapping (Figure 3b and Figure S7). An obvious strain distribution can be visualized by the color contrast of the lattice constants. A uniform contrast around the domain boundary suggests that the lattice mismatches have been well accommodated by horizontal stripes through the orientation switching of OVCs, indicating a smooth transition from the 3a-LCO_{2.67} to 3c-LCO_{2.67} domains.

Figure 3f shows the high-magnified HAADF image around the domain boundary between 3c-LCO_{2.67} and n-LCO_{2.5}. The horizontal $V_{\ddot{o}}$ stripes with 2c and 3c periodicities coexist in $LCO_{2.67}$, indicating the oxygen content of LCO_x films derives from a stochiometric LCO_{2.67} and approaches toward LCO_{2.5}. The horizontal $V_{\ddot{o}}$ stripes in 3*c*-LCO_{2.67} with alternate [CoO₆] octahedron and [CoO₄] tetrahedron layers switch to the uniformed $[CoO_5]$ square pyramids in n-LCO_{2.5}. There is no blocking layer between the two distinct domains. The horizontal $V_{\ddot{o}}$ stripes are connected directly to the diagonal $V_{\ddot{o}}$ site of the n-LCO_{2.5} phase, indicating a comparable short oxygen-ion migration pathway. In this case, the oxygen ions migrate from the neighboring octahedron and tetrahedron vertically (Figure S8), resulting in the formation of pyramids. Different from the tensile-strained films, the n-LCO_{2.5} phase remains coherently strained by the LaAlO₃ substrate (Figure 3e and Figure S9). Although the in-plane and out-of-plane lattice constants change alternately along the diagonal direction within the n-LCO_{2.5} layer, the substrate's misfit strain can be perfectly transferred to the capping layers.

STRAIN-DEPENDENT OXYGEN MIGRATION AND PHASE DIAGRAM OF OVCS IN COBALTITES

To verify the influence of elastic strain on E_{Va} in the LaCoO₃ system, we performed first-principles calculations based on density function theory (Figure 4a and b). E_{Vo} reduces monotonously as the in-plane stain changes from the compressive to tensile strain state. Experimentally, we indeed observe a lower transition temperature of 3a-LCO_{2.67} than that of 3*c*-LCO_{2.67}. More importantly, the strain-dependent E_{Vo} determines the OVC orientation when the $V_{\ddot{a}}$ stripes form at the early stage. The phase transition from 3a-LCO_{2.67} to 3c-LCO_{2.67} undergoes a OVC switching by 90 deg. The oxygen ions rearrange within the films without changing the oxygen content. The strain-dependent OVC in 3a-LCO_{2.67} and 3c-LCO_{2.67} is reasonable in terms of minimization of the elastic energy at the interface between films and substrates. We believe that the oxygen extracts out of the strained LCO₃ films may have different migration pathways as the OVCs serve as oxygen-ion passes. To form 3a-LCO_{2.67}, the oxygen comes out of the capping layer directly in a short way and relatively short time, whereas the oxygen migrates a long way horizontally to the edges of films to get out of the films resulting in the 3c- $LCO_{2.67}$. This process takes a relatively long time. We believe that the anisotropic oxygen-ion migration under strain would exhibit the different ionic conducting speed and efficiency.

Next, we will discuss how the oxygen-ion migration proceeds in LCO_{2.67} during the orientation switching of the OVC. Two possible reaction processes at the atomic scale can be deduced based on the atomic structures of domain boundaries. When a 3a-LCO_{2.67} is tensile-strained, the O1 shared by the CoO₆ octahedron and CoO₄ tetrahedron preferentially moves to a vacant site Vo1 in the neighboring CoO₄ tetrahedron along the polyhedral edge with a migration barrier of ~0.95 eV, followed by multiple steps of ion migration along the O1-Vo1-Vo2 and O2-O1-Vo1 pathways. Finally, the oxygen ions migrate to a stable location and complete exchanges between the CoO₆ octahedron and CoO4 tetrahedron as indicated by the blue double arrows in Figure 4c. Consequently, the orientation switching of the OVC can be elucidated by cooperative multiple octahedra-tetrahedra exchanges. In comparison, when a compressive strain is applied to 3c-LCO₂₆₇, the migration barrier (\sim 1.03 eV) is slightly larger than the former case. This fact well-explains that a higher $V_{\tilde{o}}$ extraction temperature is needed for compressively strained LCO_x films. The final $V_{\ddot{o}}$ pattern in n-LCO_{2.5} films is in sharp contrast to that of BM-LCO_{2.5} on the SrTiO₃ substrate. Interestingly, the oxygen-ion migration can be interpreted in an easier way based on the uniform CoO₅ configuration, as shown in Figure 4d. The migration can be accompanied just by a successive O1-Vo1 and O2-O1 hopping, leading to a simultaneous transition from tetrahedron/octahedron into the CoO_5 square pyramids. The neighboring octahedron would transform into CoO₅ square pyramids by losing one O3 ion, as indicated by the green arrow. As a result, the OVC switches toward diagonal $V_{\ddot{a}}$ stripes can be elucidated by conserved octahedra-tetrahedra evolution and partial oxygen-ion loss.

Based on the distinct OVC states and the orientation switching behaviors observed in LCO_x films grown on SrTiO₃ and LaAlO₃ substates, we draw a phase diagram of the OVC in strained LCO_{3-x} films established as a function of misfit strain and oxygen content in Figure 4e. Epitaxial strain determines the initial orientation of the $V_{\ddot{\rho}}$ stripes, as evidenced by the vertical stripes on the tensile strain states and the horizontal stripes on the compressive strain states. When the LCO_x films are tensile-strained, the lattice structure first transits from LCO₃ into 3a-LCO_{2.67} and then further transforms into the 3c- $LCO_{2.67}$ state. Apparently, the OVC orientation concomitantly switches during the topotactic structural transition. The OVC orientation is maintained when the LCOx films transit into the 2c-LCO_{2.5}. We believe that the OVC orientation switching in the tensile-strained LCO_x films is attributed to the strain accommodation between the final state, i.e., 2c-LCO_{2.5}, and STO substrates., yielding to a +2.5% tensile strain. Of most interest, on the compressive strain regime, a new LCO_{2.5} phase emerged when a large number of oxygen ions is extracted from the 3c-LCO_{2.67} phase, forming a completely new V_ö ordering configuration.

The quantitative analysis on the V_{i} -induced chemical expansion is favorable for uncovering the mechanism of OVC orientation switching. At increasing the density of the V_{a} stripes, the large La–La distance d_{V_0} (4.39 ± 0.05 Å) in the $V_{\ddot{o}}$ ordered CoO₄ tetrahedral layers and the shortest one d_0 (3.66) \pm 0.05 Å) in the CoO₆ octahedral layers appear in 3*a*-LCO_{2.67} due to the lattice constant confinement from SrTiO₃ substrates. The highly compressively strained d_0 makes the structure of 3a-LCO_{2.67} unstable for accepting more $V_{\ddot{o}}$ and tends to switch toward the 3*c*-LCO_{2.67} with a relaxed d'_{O} (3.76 \pm 0.07 Å) and d'_{Vo} (4.33 \pm 0.05 Å) along the *c* axis. In 3*c*- $LCO_{2.67}$ on the LAO substrate case, the d_{V_0} (3.75 ± 0.10 Å) and d_0 (4.47 ± 0.12 Å) evolve to be 3.80 ± 0.11 Å and 4.57 ± 0.13 Å, respectively. We summarize the calculated atomic distances in Table S1. Finally, we define the d_{V_0}/d_0 ratio as the $V_{\ddot{o}}$ tolerance factor, which determines the OVC configuration in an epitaxial thin film. The $d_{Vo}/d_O \sim 1.2$ is obtained in 3a-LaCoO_{2.67} and 3c-LaCoO_{2.67} before the orientation switching of the OVC. We believe the calculation of this value will serve

as a criterion to evaluate the orientation stability of the OVC in oxygen-deficient perovskite oxide thin films with similar crystal structures.

In summary, we report strain-mediated distinct oxygen-ion migration pathways in ultrathin cobaltite thin films using in situ atomic-resolved STEM imaging. The evolution of OVCs is directly visualized as a function of annealing temperature and annealing time. We reveal the dynamic process of OVCs' propagation and orientation switching in LCO_x films under both tensile and compressive strain. Given a broad interest in oxygen-ion conductors, we construct a phase diagram of the OVC mediated by strain and oxygen content and provide OVC stability criteria with a conception of the tolerance factor. These findings suggest that the dedicated balance between chemical expansion and epitaxial strain dominates the formation and orientation of the OVC, providing a practical guide for engineering targeted OVC configurations in oxygendeficient functional oxide films. Given the abundance of perovskite oxides with ordered OVCs, our work offers an exciting opportunity to design predetermined OVCs, especially the vortex-like topological ionic conductive channels, which manifest themselves to engineer unique phases and functionalities in energy materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.1c04057.

Experimental methods and calculation details; macroscopic structural characterizations; STEM images recorded from room temperature to a stable temperature; strain distributions analyzed by GPA (PDF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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