Structural Phase Transitions to 2D and 3D Oxygen Vacancy Patterns in a Perovskite Film Induced by Electrical and Mechanical Nanoprobing

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Oxygen vacancy migration and ordering in perovskite oxides enable manipulation of material properties through changes in the cation oxidation state and the crystal lattice. In thin-films, oxygen vacancies conventionally order into equally spaced planes. Here, it is shown that the planar 2D symmetry is broken if a mechanical nanoprobe restricts the chemical lattice expansion that the vacancies generate. Using in situ scanning transmission electron microscopy, a transition from a perovskite structure to a 3D vacancy-ordered phase in an epitaxial La$_{2/3}$Sr$_{1/3}$MnO$_{3-\delta}$ film during voltage pulsing under local mechanical strain is imaged. The never-before-seen ordering pattern consists of a complex network of distorted oxygen tetrahedra, pentahedra, and octahedra that, together, produce a corrugated atomic structure with lattice constants varying between 3.5 and 4.6 Å. The giant lattice distortions respond sensitively to strain variations, offering prospects for non-volatile nanoscale physical property control driven by voltage and gated by strain.

1. Introduction

Active tuning of the oxygen stoichiometry through the migration of oxygen vacancies can radically alter the electrical resistivity\cite{1-7} and optical transparency\cite{8} of perovskite oxides. Of particular technological interest are controlled property changes induced by small voltages, enabling low-power memory\cite{1,2}, neuromorphic computing\cite{12,13} and other switchable ionotronic devices.\cite{14} Electric-field-directed oxygen vacancy migration can result in filament formation,\cite{2,12} the modification of functional interfaces,\cite{15,16} or trigger structural transitions to oxygen-vacancy-ordered phases.\cite{7,13,17} In epitaxial ABO$_3$ perovskite films, oxygen vacancies, and elastic strain coupled to each other via the crystal lattice\cite{18} providing a complex yet versatile playground for material manipulation through adjustments of the B–O–B bond lengths and bond angles. The presence of oxygen vacancies in perovskite oxides results in a chemical expansion of the crystal lattice due to the missing oxygen ion and changes in the cation oxidation state.\cite{19,20} Conversely, elastic strain modifies the energetics of oxygen vacancy formation and migration,\cite{21,22} altering their concentration\cite{23,24} or the orientation or periodicity of planar ordering patterns.\cite{25-27} The strain state of perovskite films is varied commonly by epitaxial growth onto different single-crystal substrates.\cite{23-26} Here, the film/substrate lattice mismatch compresses or expands the film structure in the substrate plane, while the crystal structure can adapt freely to this deformation along the perpendicular direction. Alternatively, a piezo-controlled probe can locally compress the perovskite lattice along the out-of-plane axis. The strain gradient that mechanical probing produces has been shown to move oxygen vacancies\cite{28-30} or inhibit structural phase transitions.\cite{13}

Here, we report the formation of a new oxygen-vacancy ordered structure in an epitaxial La$_{2/3}$Sr$_{1/3}$MnO$_{3-\delta}$ (LSMO) film under concurrent voltage and straining actuation by a nanoprobe in an in situ scanning transmission electron microscopy (STEM) experiment. In the absence of local straining, voltage pulses applied between a conducting Nb-doped SrTiO$_3$ (STO) substrate and a metal nanoprobe on top of the LSMO film trigger phase transitions between a perovskite and brownmillerite (BM) structure. Performing the same experiment while forcing the probe into the LSMO films drastically changes the ordering of oxygen vacancies. Instead of the 2D BM pattern, we directly observe the emergence of a 3D oxygen-vacancy-ordered structure. The new crystal structure forms if the lattice degrees of freedom are constrained in all directions while voltage pulses drive oxygen vacancies into a ≈40-nm-wide strained region of the LSMO film. Density-functional theory (DFT) calculations confirm a crossover from 2D to 3D oxygen vacancy ordering under out-of-plane lattice compression.
2. Results and Discussion

We grew LSMO films with a thickness of 20 nm on conducting Nb-doped STO (001) substrates using pulsed laser deposition. A 2:1 ratio of La and Sr was chosen because the metallic character of this composition enables thermal activation of oxygen vacancy migration through Joule heating. STEM measurements were conducted on a JEOL 2200FS TEM system with double Cs correctors. The samples were prepared into cross-sectional wedges by mechanical polishing and Ar ion milling (see Experimental Section). The surface of the LSMO film was exposed for external contacting on one side of the specimen. In situ electrical and mechanical probing experiments were performed by mounting the specimen on a half TEM Cu grid in a double-tilting electrical probing holder (Figure S1, Supporting Information). During STEM measurements, a piezo-controlled Pt/Ir nanoprobe contacted the surface of the LSMO film (Figure 1a).

We used high-angle annular dark-field (HAADF) contrast to image the cross-sectional specimen. The oxygen concentration of the different structural phases was analyzed by electron energy loss spectroscopy (EELS).

We first discuss the use of the piezo-controlled nanoprobe for mechanical straining. In the experiments, we distinguish between two strain states. The different states are set by monitoring the electrical current across the sample as the probe approaches. By immediately halting the approach when the current is stable, we only apply a small force to the LSMO film. In this low contact-force (LCF) state, the nanoprobe does not deform the LSMO lattice structure (Figure 1b,c). We establish a high contact-force (HCF) state by pressing the probe further into the sample. Once halted, the probe compresses the out-of-plane lattice constant of the LSMO film by up to $-3.2\%$ (Figure 1b,c). The strained area of the LSMO film is slightly wider than the probe/LSMO contact size. Moreover, the lattice compression is largest in the center of the nanoprobe and the middle of the LSMO film. Finite-element simulations in COMSOL Multiphysics software replicate the strain distribution in the LSMO film under HCF (Figure 1b,c). From these simulations, we estimate an applied force of $3.5\,\mu N$ and a pressure of $5\times10^9\,Pa$ (Section S1, Supporting Information). Compared to the HCF state, the applied force in the experiments under LCF is at least three orders of magnitude smaller.

![Figure 1](https://www.advancedsciencenews.com/s0037-6957(21)00109-x)
Using in situ STEM, we image the evolution of the LSMO film structure while applying voltage pulses to the Nb-doped STO substrate (the nanoprobe is grounded). The pulses have a triangular shape and a duration of 20 ms. Figure 1d–g summarizes results for the LCF state. Starting from the initial LSMO perovskite structure (Figure 1d), an oxygen-vacancy-ordered BM structure nucleates in the middle of LSMO film and laterally grows at positive voltage (Figure 1e,f). Reversal of the voltage polarity switches the film structure back to the perovskite phase (Figure 1g). The structural evolution depicted in Figure 1d–g replicates previously published data. Switching of the LSMO structure near the nanoprobe is explained by the generation and redistribution of positively charged oxygen vacancies through Joule heating and electric-field-directed vacancy migration. To clarify this, we briefly summarize the oxidation state of the sample during voltage cycling: At the start of the experiment, the perovskite La$_{2/3}$Sr$_{1/3}$MnO$_3$-δ film is approximately stoichiometric (δ = 0). Joule heating during the first voltage cycle raises the temperature of the sample, especially near the nanoprobe where the current density is largest. Electro-thermal simulations on our material system predict a temperature increase to about 700 K for voltage pulses that trigger the structural transitions. Because the sample is placed in the vacuum column of our STEM system, the Joule heating effect generates oxygen vacancies. In combination with electric-field-directed vacancy migration towards the nanoprobe during positive voltage pulsing (applied voltage on Nb-doped STO substrate with probe grounded), this triggers ordering into the BM structure when the oxygen vacancy concentration becomes critical (δ = 0.5). Subsequent cycling of the voltage polarity drives the vacancies away and back into the contact area of the LSMO film, inducing reversible transitions between the BM phase and the perovskite structure. Concurrently, Joule heating enhances the total number of vacancies during each cycle. At some point (typically after 3–5 full cycles), the number of vacancies becomes so large that it is no longer possible to reestablish the perovskite phase within the contact area of the LSMO film. Besides oxygen vacancy migration, the application of a voltage also moves holes in LSMO from one Mn cation to another. Cation vacancies that may also be present in the manganite film are unlikely to react to voltage pulses due to their low mobility at the temperatures reached in our experiments.

Figure 1h–k shows in situ STEM results for the same specimen in the HCF state. Again, a BM domain nucleates and grows at positive voltage (Figure 1i). However, before this phase expands over the entire film thickness, the oxygen vacancies reorder into a different pattern. The new oxygen-deficient structure fully occupies the strained area of the LSMO film in Figure 1j. Reversal of the voltage polarity directly switches the structure back to the initial perovskite phase without converting to the BM phase first. To compare the data for the two strain states better, we estimate the current density at the probe/LSMO contact (see values in Figure 1d–k and the Experimental Section). We find that similar current densities, that is, similar amounts of Joule heating, produce the BM structure under LCF and the new vacancy-ordered structure under HCF conditions. This information suggests that the oxygen vacancy content is approximately the same in both phases. EELS oxygen K-edge spectra recorded on the two structures confirm this observation (Section S2, Supporting Information).

Evolutions of the LSMO lattice constants during the structural transformations shed more light on the effect of strain. The BM phase forming under LCF consists of alternating octahedral MnO$_6$ and tetrahedral MnO$_4$ unit cells stacked along the out-of-plane c axis. Underbonding caused by oxygen deficiency in the tetrahedral layers enlarges the out-of-plane lattice constant (c$_0$), whereas the octahedral layers contract (c$_0$). The regular modulation of the BM crystal structure produces a characteristic bright/dark stripe contrast in the HAADF-STEM images. In our epitaxial LSMO films, the in-plane lattice constant of the BM phase matches that of the STO substrate (a = 3.905 Å). The average out-of-plane lattice constant (c = (c + c$_0$)/2) of the BM structure is measured as c = 4.19 Å (Figure 2a,b), which is substantially larger than the out-of-plane lattice constant of the initial perovskite phase (c = 3.87 Å). Thus, when oxygen vacancies are driven into the contact area of the LSMO film by positive voltage pulses and order into the BM structure, the crystal lattice expands by +8.3% along the c axis.

**Figure 2.** Lattice expansion during oxygen vacancy migration towards the LSMO contact area in experiments under LCF (a,b) and HCF (c,d). The lattice constants specify average values recorded along the indicated white lines. e,f) Evolution of the average out-of-plane and in-plane lattice constants underneath the nanoprobe (white lines in (b) and (d)) as a function of current density during voltage pulsing experiments.
Under HCF, the nanoprobe reduces the out-of-plane lattice constant of the initial perovskite structure to 3.75 Å. Now, the average out-of-plane lattice constant of the BM domain forming near the LSMO/STO interface is 3.91 Å (Figure 2c). This value is much smaller than the lattice constant of the BM structure in the LCF experiment (Figure 2a,b). The force applied by the nanoprobe thus hampers the out-of-plane lattice expansion needed for extending the BM phase across the full LSMO film thickness. Instead, the oxygen vacancies reorder into a different pattern upon further voltage pulsing. The average out-of-plane lattice constant of the new structure is 3.98 Å (Figure 2d). Concurrently, the average in-plane lattice constant of the LSMO film increases to 3.97 Å when the new structure forms. The lattice distortions vary a bit with location because of domain formation, which we discuss in more detail later. Outside the contact area of the LSMO film, a BM phase with reduced c parameter stabilizes in the HCF experiment (Figure 2d). At the marked location, the nanoprobe compresses the lattice of the initial perovskite structure by about −0.7%. This observation suggests that the BM phase is energetically more favorable than the new oxygen-vacancy-ordered structure for small perpendicular strain. Figure 2e,f depicts the evolutions of the in-plane and out-of-plane lattice constants as a function of current density. The transition from the LSMO perovskite structure to an oxygen-vacancy-ordered structure commences at 50 nA nm$^{-2}$ in both the LCF and HCF experiments. Whereas the out-of-plane lattice constant increases rapidly to the equilibrium BM value under LCF, compressive HCF strain hampers this lattice expansion. At about 70 nA nm$^{-2}$, the in-plane lattice constant enlarges under HCF, signifying reordering of oxygen vacancies into the new structure.

**Figure 3a** shows a high-resolution HAADF-STEM measurement of the new structural phase. In the image, the La/Sr atomic columns of the LSMO film appear bright. The corresponding Fast Fourier transform (FFT) pattern exhibits reflections at (±1/4,0,±1/4) (Figure 3b), indicating regular lattice modulations along the a and c axes on a length scale of four unit cells. The lattice-spacing maps of Figure 3c,d illustrate the symmetry of the crystal structure further. Variations of the in-plane lattice constant form a checkerboard-like pattern. At every fourth position, the in-plane lattice parameter increases radically to ≈4.6 Å (see line scan in Figure 3e). The locations that exhibit such a large lattice constant correspond to the vertically aligned elliptical voids in the HAADF-STEM image of Figure 3a. Minima in the in-plane lattice parameter (≈3.5 Å) are positioned between these voids. The out-of-plane lattice constant varies in a similar fashion (Figure 3d,f). Compared to the in-plane lattice-spacing map, the symmetry of the out-of-plane spacing pattern is rotated by 90°. Local lattice expansions along the c axis produce the horizontally aligned elliptical voids. The minimum and maximum out-of-plane lattice constants are also ≈3.5 Å and ≈4.6 Å. The crystal locations with the largest out-of-plane lattice constant coincide with those having the smallest in-plane lattice parameter and vice versa. To understand the atomic structure of the new oxygen-vacancy-ordered phase, it is instructive to label two distorted unit cells. Both cell types consist of La/Sr corner ions (marked by blue and green circles in Figure 3a) and a Mn center ion surrounded by oxygen. The tilting orientation of the two units with respect to the a and c axes interchange. In the new structure, stacking of these two building blocks in the vertical and horizontal directions produces a regular lattice corrugation with a period of four La/Sr ions and alternating enlargements of the in-plane and out-of-plane lattice constants.

We find that the new oxygen-vacancy-ordered phase varies across the LSMO film. The HAADF-STEM measurement in **Figure 4a** demonstrates this observation. The image, recorded in the film area marked by a dashed yellow box in Figure 1a, shows a gradual evolution of the crystal structure from the LSMO surface towards the center of the film. We distinguish three domains, marked as A, B, and C. In domain A, the distorted units labeled U1 and U2 tilt more with respect to the a
axis than the $c$ axis (left schematic in Figure 4a). This lattice distortion produces horizontally aligned elliptical voids, as illustrated in the top panels of Figure 4b. In domain C, the tilting angles of U1 and U2 with respect to the $a$ and $c$ axes are reversed (right schematic in Figure 4a). As a result, only vertically aligned voids form (Figure 4b, bottom panels). The apparent reversal of structural symmetry in domain A and domain C is illustrated further by the modulation of their in-plane and out-of-plane lattice constants (Figure S4, Supporting Information). In domain A, the $c$ parameter varies massively between $\approx 3.5$ Å and $\approx 4.9$ Å, while the modulation of the $a$ parameter is more modest ($\approx 3.6$ Å to $\approx 4.2$ Å). The lattice corrugations in the horizontal and vertical directions are opposite in domain C. The structure of domain B is comparable to the one discussed previously (Figure 3). Here, the units are distorted similarly with respect to both the $a$ and $c$ axes. Reversal of the tilting angles in subsequent units creates an alternating lattice expansion with horizontally and vertically aligned voids (Figure 4b, center panels). Figure 4c shows the evolution of the tilting angles along the white vertical arrow in Figure 4a. We also plot the out-of-plane lattice strain ($\varepsilon_{yy}$) as measured on the perovskite phase at the same location before the transition to the new oxygen-vacancy-ordered structure. As the compressive perpendicular strain increases from $\varepsilon_{yy} = -1.1\%$ at the LSMO surface to $\varepsilon_{yy} = -2.9\%$ in the center of the film, the tilting angles of the distorted unit cells with respect to the $a$ and $c$ axes diminish and increase, respectively. For small perpendicular compressive strain, the U1 and U2 units mainly tilt out of the film plane ($\pm 72^\circ$), while the epitaxial strain imposed by the substrate limits the tilting angles with respect to the $bc$ plane ($\pm 2.6^\circ$). Large $\varepsilon_{yy}$, in contrast, suppresses the tilts out of the $ab$ plane ($\pm 2.6^\circ$) and enforces larger distortions away from the $bc$ plane ($\pm 72^\circ$). The latter effect worsens the film-to-substrate lattice coherency. The measured correlations between the tilting angles and $\varepsilon_{yy}$ demonstrate how the competition between perpendicularly applied mechanical strain and in-plane epitaxial strain determines the distortion of the crystal lattice under vacancy-induced chemical expansion.

In the in situ STEM experiments, the oxygen vacancies accumulate in the LSMO film underneath the nanoprobe during the application of positive voltage pulses. Under HCF, the vacancies first order in the BM phase before the new structure forms (Figure 1i,j). Because the oxygen-vacancy concentrations of both ordered structures are comparable (Section S2, Supporting Information), the transition from the BM phase to the new structure is driven mainly by vacancy reordering.

In Figure 5, we illustrate a possible vacancy migration process that could account for the structural transformation. Starting from the BM structure with alternating layers of MnO$_4$ tetrahedra and MnO$_6$ octahedra, the coordination of every fourth Mn ion inside the tetrahedral layers changes by local vacancy migration (the positions are marked by dark green shading in the top left panel of Figure 5a). During the reordering process, oxygen vacancies in the MnO planes at these locations transfer from the $ab$ plane to the $bc$ plane (see lower panels of Figure 5a). The proposed migration route breaks the corner-sharing tetrahedra-octahedra links along the [110] direction and the tetrahedra-octahedra links along the [01–1] direction of the BM structure. The resulting new structure is a complex network of distorted MnO$_4$ tetrahedra, MnO$_3$ pentahedra, and MnO$_6$ octahedra, as illustrated on the right side of Figure 5a. The periodicity of the new crystal lattice corresponds to four La/Sr ions along the $a$ and $c$ axes, and two lattice spacings along the $b$ axis. Consequential changes in the coordination of the Mn ions of the LSMO film are illustrated in Figure 5b. In this figure, the units U1 and U2 discussed previously are labeled also. The units with most oxygen vacancies, that is, the MnO$_4$ tetrahedra, produce a large local chemical expansion. Depending on whether the vacancies are located in the $ab$ plane (dark green) or $bc$ plane (light green) in these units, the missing oxygen ion and changes in the Mn
oxidation state enlarges the in-plane or out-of-plane lattice constant, respectively.

To verify the proposed structural model of the new oxygen-vacancy-ordered LSMO phase, we compare its stability to that of the BM structure using DFT calculations. The in-plane lattice constants of both structures are set to those of the STO substrate. The effect of mechanical straining in the perpendicular direction is evaluated by performing calculations with different out-of-plane lattice constants. The solid curves in Figure 5c depict the energy of the two structural phases for ferromagnetic ordering (slightly different values are calculated for A-type antiferromagnetic ordering, see Tables S1 and S2, Supporting Information). As expected, the BM structure is energetically more favorable for large out-of-plane lattice constants. Perpendicular compressive strain, however, quickly increases the BM energy as it restricts the chemical expansion that oxygen vacancies produce. Because the energy of the new structure increases less drastically with decreasing \( c \), the two solid curves in Figure 5c cross at an out-of-plane lattice constant of 3.80 Å. In our in situ nanoprobing STEM experiments under HCF conditions, the initial perovskite structure compresses to \( c = 3.75 \) Å (Figure 2e). The DFT calculations thus qualitatively support the reordering of oxygen vacancies from a 2D to a 3D pattern under large compressive perpendicular strain. In Figure 5c, we also show the calculated energy of the new structure for 1.5% larger in-plane lattice constants (corresponding to the STEM data in Figure 2f). In this case, the energy of the new structure is lowered further, making a transition from the BM structure under perpendicular compressive strain even more likely. In Figure 5d, we overlay a STEM image simulation of the proposed new structure based on DFT refinements onto an experimental measurement. The two images match well. Although the proposed model reproduces essential features of the new oxygen-vacancy-ordered structure, we point out that vacancy ordering in our experimental samples might deviate from the calculated structure because of differences in oxygen deficiency and cation disorder.

The physical properties of \( \text{ABO}_3 \) perovskites alter drastically with the B–O–B bond lengths and bond angles through a changing degree of overlap between the \( d \) orbitals of the B-site cations and the \( p \) orbitals of the oxygen anions. Distortions and rotations of oxygen octahedra, often designed by heteroepitaxial growth,[37,38] have been shown to change the electronic structure, to produce electronic and magnetic anisotropies,[11,39–41] and to stabilize ferroelectricity.[42,43] In this work, we demonstrate how migration and reordering of oxygen vacancies during simultaneous voltage pulsing and local mechanical straining produces a complex pattern of distorted oxygen tetrahedra, pentahedra, and octahedra in an epitaxial LSMO film. The atomic structure of the new phase varies sensitively

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**Figure 5.** Structural model of the 3D oxygen-vacancy-ordered LSMO structure and DFT calculations. a) Comparison of the BM structure and the proposed structure of the new phase. The location of oxygen vacancies in the two structural phases are marked by squares in the lower panels. The panels depict planar views of the green and orange supercells defined in (a). Vacancies at the lower and upper edges of the supercells are shown as dashed squares. The BM structure transforms into the new structure through the migration of oxygen vacancies from the \( ab \) plane to the \( bc \) plane in the central unit of the two supercells. b) Coordination of Mn ions in the BM structure and the new LSMO structure. The number of oxygen ions per two unit cells along the \( b \) axes are indicated. The proposed new structure is a complex network of distorted MnO\(_4\) tetrahedra, MnO\(_5\) pentahedra, and MnO\(_6\) octahedra. The U1 and U2 units with octahedral coordination (see Figure 4) are marked also. c) Calculated energy of the BM structure and the new LSMO structure as a function of out-of-plane lattice constant. The in-plane lattice constants in the DFT calculations are fixed to those of the STO substrate (solid lines) or are assumed to be 1.5% larger than those of the STO substrate (dashed line). d) Simulated STEM image based on the proposed structural model (inside dashed box) overlaid onto an experimental STEM image.
with the imposed strain. As illustrated in Figure 4c, the tilting angles of the units with octahedrally coordinated Mn ions alter from ±2.6° to ±2.2° when the perpendicular lattice strain increases from −1.1% to −2.9%. The ensuing impact on the lattice constants of the new structure is gigantic, with $a = 3.5$ Å and $c = 4.6$ Å (horizontally aligned voids) transforming to $a = 4.6$ Å and $c = 3.5$ Å (vertically aligned voids) at the locations of distorted MnO$_4$ tetrahedra (see Figures 3 and 4). Lattice distortions of this magnitude do not occur in the perovskite and BM phases under perpendicular strain. Because of the strong interplay between the lattice, charge, spin, and orbital degrees of freedom in transition-metal perovskite oxides, oxygen vacancy ordering in 3D, as demonstrated here, will drastically alter the physical properties of ABO$_3$-type films.

To assess how oxygen vacancy ordering affects magnetism in LSMO, we performed more DFT calculations. We find that the alternate stacking of octahedral and tetrahedral layers in the BM phase produces A-type antiferromagnetism under compressive perpendicular strain (Table S2, Supporting Information). This result agrees with a previous report on LSMO/STO$^{[11]}$ which also revealed that spins in the octahedral and tetrahedral layers order parallel and antiparallel, respectively. The calculated distributions of Mn magnetic moments shown in Figure S6, Supporting Information, displaying distinctive peaks at 3.70 $\mu_B$ and 4.35 $\mu_B$, confirm the existence of two magnetic sub-lattices. For the 3D oxygen-vacancy-ordered LSMO phase, the energy difference between ferromagnetic ordering and A-type antiferromagnetic ordering is more subtle, with the ferromagnetic phase being more stable under compressive perpendicular strain (Table S2, Supporting Information). We calculate three or four distinctive Mn moments for the ferromagnetic structure (Figure S6, Supporting Information), in line with the larger variety in oxygen coordination (MnO$_4$ tetrahedra, MnO$_3$ pentahedra, and MnO$_6$ octahedra) and the broad distributions of the Mn—O bond lengths and the Mn—O—Mn bond angles (Figure S7, Supporting Information). Based on the DFT calculations, nanoprobing could thus induce a transition from A-type antiferromagnetism to ferromagnetism through the reordering of oxygen vacancies from a 2D BM structure to a 3D-ordered pattern.

3. Conclusion

In summary, we demonstrated transitions between a perovskite structure and ordered oxygen-deficient phases in an epitaxial LSMO film under concurrent voltage pulsing and mechanical nanoprobing. Using in situ STEM, we directly imaged the formation of a 3D oxygen vacancy pattern that would not form during epitaxial growth. The giant responsivity of this new structure to strain variations, the ability to switch the phase of epitaxial films by small voltage pulses, and the strong impact of vacancy ordering on magnetism open perspectives to a new class of ionotronic devices based on voltage control and mechanical gating. For applications, a closed system based on the redistribution of a fixed amount of vacancies would provide better endurance than the proof-of-principle experiments presented here. We anticipate other perovskite oxides that are prone to oxygen vacancy ordering, including SrFeO$_x$, SrCoO$_x$, and La$_{0.3}$Sr$_{0.7}$CoO$_y$, to show similar structural transitions under local mechanical straining.

4. Experimental Section

Thin-Film Growth: 20-nm-thick epitaxial LSMO films were grown onto conductive STO (001) substrates with 0.7 wt% Nb using pulsed laser deposition. To form a TiO$_2$-terminated surface, the substrates were etched in buffered hydrofluoric acid for 30 s and annealed in oxygen atmosphere at 950 °C for 1 h before loading them into the deposition system. The LSMO films were grown at 700 °C in an oxygen partial pressure of 0.5 mbar. The laser-pulse repetition rate and fluence were set to 4 Hz and 2.5 J/cm$^2$. After deposition, the samples were cooled down in 30 min in the same oxygen environment.

Fabrication of TEM Specimens: Cross-sectional specimens of the LSMO/STO samples were prepared for mounting onto a double-tilting HEI50 electrical probing holder from Nanofactory AB. As a first step in the fabrication process, we glued each side of the LSMO/STO sample to Si substrates to create a sandwich structure. Next, a narrow slice cut from the Si/sample/Si sandwich structure was thinned into a wedge shape using a MultiPrep polishing system (Allied High-Tech). The wedge with a cross-section of the LSMO film on its thin edge was mounted on a half TEM Cu grid using epoxy and polished to electron transparency by Ar ion milling in a Catan PIPS. Before mounting the Cu grid onto the electrical probing holder, we unglued the Si from the wedge using acetone. After Si removal, the piezo-controlled Pt/Ir probe could contact the LSMO film. We electrically connected the conducting STO substrate to the Cu grid by silver paste. The piezo-controlled Pt/Ir probe of the electrical probing holder was grounded and used as a local top contact (Figure 1a). From the ratio between the plasmon loss and zero loss peaks in EELS spectra, the thickness of the TEM specimen in the LSMO contact area was estimated as 30 nm.

In Situ STEM Measurements: The STEM images and EELS spectra were recorded using a double Cs-corrected JEOL 2200FS TEM. In the experiments, we used the Pt/Ir nanoprobe of the electrical probing holder to apply voltage pulses and local mechanical strain. Measurements under LCF were performed by monitoring the electrical current between the metal probe and the conducting STO substrate while piezo-electrically driving the probe towards the LSMO film. Once a stable current was obtained, we halted the approach. This initialization procedure resulted in a soft contact without any measurable deformation of the LSMO crystal structure. For experiments under HCF, we intentionally drove the Pt/Ir nanoprobe further into the LSMO film. When we halted the probe, the out-of-plane lattice of the perovskite LSMO film was compressed locally by up to −3.2% (Figure 1b,c). In situ STEM measurements were conducted by applying triangular voltage pulses with a duration of 20 ms to the STO substrate (Figure S1, Supporting Information). We swept the amplitude of the voltage pulses in 50 mV steps and recorded the electrical current during each pulse. STEM images with HAADF contrast were acquired immediately after each voltage pulse along the [010] zone axis. We note that establishing an HCF contact between the Pt/Ir probe and the LSMO film was not straightforward. The use of a strong force resulted in the nanoprobe sliding off the LSMO film at several instances. After such an event, we reconnected the probe using the same force. This process resulted in additional contamination between the nanoprobe and the LSMO film and, consequently, a larger contact resistance. From STEM images, we estimated the contact size to be approximately 30 and 50 nm along the edge of the TEM specimen in the LCF and HCF experiments, respectively. Together with a specimen thickness of 30 nm, we used these dimensions to estimate the maximum current density at the probe/LSMO contact during voltage pulsing (values given in Figure 1). Strain maps were extracted from high-resolution STEM images by geometric phase analysis using the FRWTools plugin.$^{[44,45]}$

We used Matlab software and a script for 2D Gaussian fits to extract lattice spacing maps. EELS spectra were recorded on the different structural phases at zero bias voltage. The spatial resolution of these measurements was about 0.25 nm. For the analysis of EELS core-loss
peaks, background subtraction was performed using a power-law fit. We calculated the Mn $L_2/L_3$ intensity ratios of the different LSMO phases using a double arctan-function continuum model.\cite{46} The area under the $L_2$ and $L_3$ white lines was integrated over a 5 ± 0.5 eV energy window centered at the maximum of the peaks. We estimated the experimental errors in the calculated $L_2/L_3$ intensity ratios from the energy window range. HAADF-STEM image simulations of the proposed oxygen-vacancy-ordered structure were performed using multislice calculations in xHREM software. In the simulations, the aperture radius was 24 mrad, the third and fifth order Cs values were 0.005 and 0 mm, respectively, and the inner and outer angles of dark field were 70 and 370 mrad.

**DFT Calculations:** All density-functional theory calculations were carried out within the projector-augmented wave framework as implemented in the VASP software package.\cite{47,48} We used the recommended PAW setups with semi core states in valence (La, Sr $\text{sv}$, Ti $\text{sv}$, Mn $\text{pv}$, O). As a result, the plane-wave cutoff required to obtain good convergence of the total energy was fairly high (680 eV). For the exchange-correlation functional, we used PBEsol\cite{49} with a Hubbard $U$-correction of 3 eV applied to Mn $d$ orbitals.\cite{50} This methodology gave good lattice constants for STO and SrMnO$_3$ (SMO), as shown in Table S1, Supporting Information. The magnetic moment of SMO also compares well with experiments. Based on these findings, we decided to use the same parameters for LSMO.

While in situ STEM experiments were performed on LSMO films with 33% Sr, we utilized a Sr concentration of 25% in the DFT calculations for computational convenience. LSMO with this composition retains ferromagnetic ordering.\cite{51} To model stoichiometric La$_{0.75}$Sr$_{0.25}$MnO$_3$, we adopted a V$_2$O$_2$2 STO unit cell, that is, with two lattice vectors along the $<110>$ directions. The unit cell contained four A atoms, out of which three were set to La and one to Sr. The adopted k-point mesh was 4 $\times$ 4 $\times$ 6 for STO and 9 $\times$ 9 $\times$ 9 for LSMO. The BM phase was constructed along the $<110>$ directions from STO, as a 2 $\times$ 2 $\times$ 4 supercell. The lattice vectors were [220], [−110], and [−110−110]. The volume of the BM supercell was 16 times larger than that of the STO primitive cell and it contained four Sr atoms. The rows of oxygen vacancies were oriented along the second lattice vector, that is, along the [−110] direction. The used k-point mesh was 4 $\times$ 8 $\times$ 3. The calculated $a$ and $c$ lattice constants of the BM structure are larger than the STO values, whereas $b$ is smaller (Table S1, Supporting Information). We constructed the new structure from the BM structure by rotating the tetrahedra manually in a 4 $\times$ 4 $\times$ 4 supercell. The atomic structures of the three phases are shown in Figure S5, Supporting Information. The plotted energy values in Figure S5c correspond to the ferromagnetic phase. Table S2, Supporting Information, compares energy values of ferromagnetic and A-type antiferromagnetic phases of the BM and new structure with the in-plane lattice constants corresponding to those of the STO substrate. Energy values for the new structure with 1.5% larger in-plane lattice constants are summarized in Table S3, Supporting Information. Distributions of Mn magnetic moments, Mn–O bond lengths, and Mn–O–Mn bond angles in the BM structure and the 3D oxygen-vacancy-ordered structure are depicted in Figures S6 and S7, Supporting Information.

**Data Availability Statement**

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

**Keywords**

electric-field control of magnetism, mechanical nanoprobing, oxygen vacancy ordering, perovskite oxide, structural phase transition, transmission electron microscopy

Received: October 8, 2020
Revised: January 12, 2021
Published online: February 16, 2021

**Supporting Information**

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

**Acknowledgements**

This work was supported by the Academy of Finland (Grant Nos. 293929, 304291, 319218, 311058, and 316857). In situ STEM analysis was conducted at the Aalto University OtaNano-Nanomicroscopy Center (Aalto-NMC).

**Conflict of Interest**

The authors declare no conflict of interest.

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