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Andrew D. Gamalski, Eric A. Stach, Yang Shao-Horn**

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Nanoscale structural oscillations in perovskite oxides induced by oxygen evolution

Binghong Han,¹ Kelsey A. Stoerzinger,¹ Vasiliki Tileli,³ Andrew D. Gamalski,⁴ Eric A. Stach,^{4} Yang Shao-Horn^{1,2*}*

¹Department of Materials Science and Engineering, ²Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, US.

³Institute of Materials, École Polytechnique Fédérale de Lausanne, Station 12, CH-1015 Lausanne, Switzerland.

⁴Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973-5000, US.

Corresponding Author

* Eric A. Stach: estach@bnl.gov, Telephone: (631) 344-2618

* Yang Shao-Horn: shaohorn@mit.edu, Telephone: (617) 253-2259

ABSTRACT

Understanding the interaction between water and oxides is critical for many technological applications, including energy storage, surface wetting/self-cleaning, photocatalysis and sensors. In this paper, we observed strong structural oscillations of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) in the presence of both H_2O vapor and electron irradiation using environmental transmission electron microscopy. These oscillations are related to the formation and collapse of gaseous bubbles. Electron energy loss spectroscopy provides direct evidence of O_2 formation in these bubbles due to the incorporation of H_2O into BSCF. $\text{SrCoO}_{3-\delta}$ was found to exhibit small oscillations, while none were observed for $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ and LaCoO_3 . The structural oscillations of BSCF can be attributed to the fact that its oxygen 2p-band center is close to the Fermi level, which leads to a low energy penalty for oxygen vacancy formation, high ion mobility, and high water uptake. This work provides surprising insights into the interaction between water and oxides under electron beam irradiation.

The interaction between water and oxides is important to control function in many technological applications, including water splitting^{1, 2, 3, 4, 5, 6, 7}, rechargeable metal-air batteries^{8, 9, 10, 11, 12}, surface wetting and self-cleaning^{13, 14, 15, 16}, photocatalysis^{15, 17, 18, 19, 20}, sensors¹⁵, and proton-conducting oxide membranes^{21, 22, 23, 24}. Recent studies have shown that decreasing coverage of hydroxyl groups on a perovskite oxide surface at the water/oxide interface not only reduces wetting and but also enhances oxygen reduction kinetics in a basic solution¹⁴. Moreover, oxygen vacancies ($V_O^{\bullet\bullet}$) in the perovskites are known to uptake water by $H_2O + V_O^{\bullet\bullet} + O_O^{\times} \rightarrow 2OH_O^{\bullet}$ ^{21, 22, 24} or $H_2O + 2h^{\bullet} + 2O_O^{\times} \rightarrow 2OH_O^{\bullet} + \frac{1}{2}O_2$ ²⁵ (here $O_O^{\times}$ and $OH_O^{\bullet}$ represent the oxygen atom and hydroxyl group in the lattice oxygen site, respectively). Notably, hydroxyl groups can be mobile within the structure, a process that is enabled by proton hopping among oxide ions, and which is widely known to occur in fuel cells^{21, 22, 24}, hydrogen pumps^{21, 22} and hydrogen sensors²². A previous density functional theory study has found a close relationship between oxygen vacancy formation and the bulk electronic structure of perovskites: the closer the O 2p-band center is to the Fermi level, the easier it is to create oxygen vacancies in the perovskite structure²⁶. Therefore, it is of scientific interest to examine the interaction of water with oxides that contain high concentrations of oxygen vacancies in the perovskite structure. One such material is $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF): it is of particular interest because it has a high water uptake²⁷, a high catalytic activity for the oxygen evolution reaction (OER) in basic solution^{3, 5, 11, 12}, fast oxygen surface exchange^{26, 28, 29}, fast transport kinetics at elevated temperatures³⁰, and a low energy penalty for oxygen vacancy formation²⁶.

To investigate the interaction between water molecules and oxides, researchers have developed

several different *in situ* methods, including wetting angle measurements¹⁴, ambient pressure X-ray photoelectron spectroscopy (APXPS)^{31, 32, 33} and environmental transmission electron microscopy (ETEM)^{34, 35, 36}. APXPS measurements have established the reactivity of oxide surfaces with water, where the extent of reactivity can range from adsorption of less than a monolayer of hydroxyl groups to the formation of a metal hydroxide layer³³. However, the lateral spatial resolution of APXPS is on the order of tens of microns³², with the in plane probing depth on the order of a few nanometers for a lab-source apparatus. In contrast, ETEM allows atomic-scale observation of the interaction between gas/vapor and a solid, as well as the surface/subsurface layers of materials: this is because the information depth from high energy electrons far exceeds that of lower energy X-ray photoelectrons^{34, 35, 37, 38}. Previous ETEM studies have provided indirect evidence that electron irradiation can induce molecular oxygen evolution from $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ particles in the presence of H_2O , leading to the formation of SiO_2 on the particle surface in presence of SiH_4 ^{34, 35}. The observed SiO_2 may result from the oxidation reactions of SiH_4 with O_2 ^{34, 35} and/or H_2O ³⁹. However, there is no *direct* evidence of O_2 evolution triggered by electron irradiation. In addition to spatial information, electron microscopes allow spectroscopic information through electron energy loss spectroscopy (EELS). For example, a recent environmental scanning electron microscope (ESEM) study provided direct evidence of water trapping in the multilayer graphene oxide membrane, which was subsequently confirmed using EELS³⁸. Thus, ETEM is a powerful tool for studying the interaction between water vapor and oxides (especially those oxides prone to bulk uptake of water): it allows direct observation of structural changes with high-resolution real-space imaging and spectroscopic measurement of electronic changes with EELS in the same experiment, during reaction conditions.

In this study, we examine the interaction of H₂O with a select number of perovskite oxides using ETEM. Dramatic structural oscillations are observed, with the formation and collapse of gaseous bubbles inside BSCF particles, with the oscillation frequency increasing with greater electron dose rate and higher H₂O vapor pressure. In contrast, no structural oscillation is observed when BSCF is exposed to high vacuum (HV) or in presence of O₂ during electron beam (e-beam) irradiation. EELS data indicate that O₂ gas is generated during the structural oscillations in presence of water and e-beam irradiation, suggesting that the interaction of H₂O molecules with BSCF under e-beam irradiation leads to oxygen evolution. It is proposed that the oxygen evolution inside BSCF that occurs during the oscillations is a result of its high water uptake, facile oxygen vacancy formation and high oxygen ion mobility, all of which are related to the small energy difference between the O 2p-band center and the Fermi level in this material. On the other hand, SrCoO_{3-δ} (SCO) exhibits limited structural oscillations near the particle surface, while La_{0.5}Sr_{0.5}CoO_{3-δ} (LSC), LaCoO₃ (LCO) and LaMnO₃ (LMO) particles show no oscillation in presence of water vapor under e-beam irradiation: this is due to the larger energy difference between their O 2p-band centers and their Fermi levels. This work provides direct evidence for electron-beam induced oxygen evolution in perovskite oxides. It also shows that materials that have their O 2p-band center closer to the Fermi level and which have relatively low oxygen vacancy formation energy are able to promote oxygen evolution not only on their surface but also in their bulk, as well as being able to promote proton conduction in the oxide lattice.

Structure oscillations of BSCF in H₂O vapor under e-beam

BSCF was found to be stable in HV ($\approx 10^{-7}$ Torr) when imaged with 80 kV electrons (Supplementary Fig. S1a). Transmission electron diffraction patterns (TED) indicated a cubic structure consistent with the expected $\text{Pm}\bar{3}\text{m}$ space group, and consistent with previous studies⁴⁰ and powder X-ray diffraction (XRD) data (Supplementary Fig. S2). TED also indicated that the BSCF particles we studied are an aggregation of small crystallites, i.e. they are polycrystalline. Upon introduction of 30 mTorr of H_2O vapor at an electron dose rate of $1 \text{ e}/\text{\AA}^2\text{s}$, the surface of the BSCF particle immediately formed several dynamic, bubble-like hollow features along the edge of the particle (Fig. 1c). These bubble-like features were observed to oscillate continuously, with both inflation and deflation of the bubble size with time. A representative video of these structural oscillations is presented as Supplementary Movie 1. When the H_2O pressure was increased to 50 mTorr and the electron dose rate was increased to $10 \text{ e}/\text{\AA}^2\text{s}$, the frequency of the structural oscillations increased but the amplitude remained unchanged, as shown in Fig. 1d and Supplementary Movie 2. Here the change in the diameter of the largest bubble was measured over time to obtain the amplitude and frequency at both low and high H_2O vapor content and electron dose rate, and is presented in Fig. 1e and Fig. 1f. These structural oscillations continued without interruption for more than 10 minutes, and ceased immediately upon removal of H_2O from the microscope. In contrast, no structural oscillation was observed on BSCF in 80 mTorr of O_2 and at $500 \text{ e}/\text{\AA}^2\text{s}$ of electron dose rate (Supplementary Fig. 1b). This strongly suggests that the structural oscillation is closely related to the interaction between the oxide and water, rather than the high pressure of other gases in the ETEM chamber. Remarkably, our *in situ* TED showed that the core of the BSCF particles kept their original $\text{Pm}\bar{3}\text{m}$ crystalline structure during the oscillations, with the appearance and disappearance of diffraction reflections resulting from real

space rotations of the crystalline lattice (Figs 1g and 1h, Supplementary Movie 3 and Supplementary Movie 4). More images and movies of the structural oscillations that occur in BSCF can be found in Supplementary Fig. S3 and Supplementary Movies 7-10.

We systematically investigated the effects of water pressure and electron dose rate on the frequency and amplitude of the oscillatory motion observed for BSCF. Fig. 2a shows the size evolution of the largest bubble in Particle B with increasing H₂O pressure from 0.4 mTorr (Supplementary Movie 7) to 11 mTorr (Supplementary Movie 8) subjected to a constant dose rate of 40 e/Å²s. As the pressure rose, the oscillation frequency increased from 0.29 to 1.25 Hz, while the maximum displacement dropped from 20.5 to 13.5 nm. Likewise, an increase in e-beam irradiation results in increased oscillation frequency and decreased oscillation amplitude, as shown in Fig. 2b. At a constant water pressure of 10 mTorr, increasing the electron dose rate from 20 e/Å²s (Particle C in Fig. 2b and Supplementary Movie 9) to 100 e/Å²s (Supplementary Movie 10), led to an increase in the oscillation frequency from 0.03 to 0.55 Hz, while the maximum displacement decreased from 14 to 8 nm.

The oscillation frequencies and amplitudes for the largest bubble in different particles (Particles A to D) over a range of electron dose rate and H₂O vapor conditions are shown in Figs 2c and 2d. We find that both H₂O vapor and e-beam irradiation is required to initiate the structural oscillations. Thresholds for the initiation of these structural oscillations were observed, minimizing H₂O pressure at high electron dose rate (e.g., Particle D, in 0.11 mTorr H₂O under 500 e/Å²s in Fig. 2c and Supplementary Movie 5) and limiting electron irradiation at high H₂O

pressure (e.g., Particle C in 10 mTorr H₂O under 20 e/Å²s in Fig. 2c and Supplementary Movie 6).

In addition, both higher electron dose and higher H₂O partial pressure increased the oscillation frequency, while only slightly decreasing the oscillation amplitude (Fig. 2c and 2d). The strong dependence on both H₂O pressure and electron dose rate indicates that these oscillations originate from a reaction that involves both electrons and H₂O, which appears to lead to the generation of a gas in the oxide. Such gas generation can cause the observed expansion/contraction of bubbles in the oxide lattice. The increased rate of gas generation may cause the hollow structure to grow and collapse more quickly, corresponding to the faster structural oscillations observed under high water pressure and electron dose rate conditions.

Immediately after water exposure and the observed structural oscillation, characterization of BSCF particles was performed in high vacuum. High-resolution TEM (HRTEM) images in Fig. 1b showed an amorphized layer (~2 nm) on the surface of Particle A, with the particle core retaining the original crystal structure. A similar amorphized layer was also observed in other particles (Supplementary Fig. S3d) after the structural oscillation. We speculate that the amorphous layer forms from the residue of the bubble structures that are created during the e-beam induced oscillation. We note that the core of the BSCF particles remained unchanged, which is consistent with the *in situ* TED observations.

EELS evidence of oxygen evolution from BSCF particles

EELS was collected from select BSCF areas before and during the introduction of H₂O vapor into the ETEM chamber. No appreciable change was observed in the characteristic peaks in the O

K-edge near-edge spectra of BSCF⁴¹ before and after exposure to H₂O vapor, indicating that the bulk of the BSCF particle is chemically stable during the process, which is consistent with the observations from the HRTEM images and TED patterns in Fig. 1. An increase in the molecular O₂ characteristic edge at ~531 eV was observed under 10 mTorr H₂O and 200 e/Å²s dose rate, which indicates that O₂ gas was generated⁴², as shown in Fig. 3a. In order to further confirm the presence of O₂ gas, we investigated the low-loss region from 12 to 40 eV (Fig. 3b). More noticeable O₂ low loss peaks were observed when compared to reference spectra from gaseous H₂O and O₂ in Fig. 3b and Supplementary Fig. S4; this is further strong evidence of the formation of O₂. The observation that the low loss peak of O₂ gas in Fig. 3b is much higher than the H K peak of H₂O and H₂ suggests that molecular O₂ is generated from BSCF; this cannot be attributed to background O-signal from H₂O.

At the same time, several characteristic edge signatures from carbonates (e.g. BaCO₃, SrCO₃) were found to increase under conditions where oscillations occurred in BSCF, including the O:2p-CO₃:2sp transition in the O K-edge⁴¹ (Fig. 3a) and the C:1s/π*-O:2p and C:1s/σ*-O:2p transition in the C K-edge⁴³ (Supplementary Fig. S5a). The formation of carbonates can be attributed to reactions between BSCF and the lacey carbon support of the TEM grid⁴⁴. It should be noted that structural oscillations were observed when BSCF particles were supported on a carbon-free SiN grid (Supplementary Fig. S5b and Supplementary Movie 16), suggesting the formation of carbonates is not the physical origin of the observed structural oscillations.

Mechanistic discussion of oxygen evolution from BSCF

Here we propose that the structural oscillation observed in BSCF in presence of H₂O vapor under e-beam irradiation is a result of oxygen generation upon water uptake within BSCF particles, as shown in Fig. 4a. This is supported by the following considerations. First, previous work has shown that BSCF particles have high oxygen nonstoichiometry in the perovskite structure and thus demonstrate significant H₂O uptake²⁷: $\text{H}_2\text{O} + \text{V}_\text{O}^{\bullet\bullet} + \text{O}_\text{O}^\times \rightarrow 2\text{OH}_\text{O}^\bullet$ ^{21, 22, 24} (Supplementary Fig. S6a) or $\text{H}_2\text{O} + 2\text{h}^\bullet + 2\text{O}_\text{O}^\times \rightarrow 2\text{OH}_\text{O}^\bullet + \frac{1}{2}\text{O}_2$ ²⁷. As H₂O reacts with BSCF to form hydroxyl ions (OH_O[•]) on the surface, hydroxyl ions can diffuse from the surface into the bulk lattice, which is facilitated by proton hopping from one O²⁻ ion site to the other²³. Second, high energy electrons at the BSCF particle surface can give rise to a positive electric potential due to the secondary electron emission effect, as suggested by a previous *in situ* ETEM study³⁵, which can be ~2 V vs. the standard hydrogen electrode (SHE) in the presence of an electron dose rate of 2000-11000 e/Å²s³⁵. This voltage is higher than the equilibrium potential for the oxidation of a hydroxyl group into molecular O₂ (E_{OH/O₂} is 0.82 V vs. SHE at pH 7). Therefore, the hydroxyl group on the lattice oxygen site will evolve molecular O₂ under the e-beam induced oxidative potential ($2\text{OH}_\text{O}^\bullet \rightarrow 2\text{V}_\text{O}^{\bullet\bullet} + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2e^-$, Supplementary Fig. S6b). This is because either the valence of transition metal ions is reduced or the electrons are removed from the oxide due to secondary electron emission under electron beam irradiation³⁵. If some H₂O gets into the lattice of BSCF, it may also be directly oxidized into O₂ by the e-beam induced holes ($\text{H}_2\text{O} + 2\text{h}^\bullet + 2\text{O}_\text{O}^\times \rightarrow 2\text{OH}_\text{O}^\bullet + \frac{1}{2}\text{O}_2$ ²⁷). The oxidative potential may also lead to the evolution of molecular O₂ from the perovskite lattice ($2\text{O}_\text{O}^\times \rightarrow 2\text{V}_\text{O}^{\bullet\bullet} + \text{O}_2 + 4e^-$) at low oxygen pressure⁴⁵. Any lattice oxygen vacancies generated during oxygen release from the BSCF lattice can be replenished as OH_O[•] through the capture of H₂O⁴⁶: this allows continuous O₂ generation within the lattice of BSCF. The

O₂ that is trapped and accumulating within the BSCF particles thus causes the formation and inflation of gas bubbles. When the bubbles grow to larger sizes and the thickness of their skin reduces below some critical thickness (of order 1 nm), the gas molecules inside will begin to leak away and start the deflation process. The oscillatory motion suggests that the stretched bubble surface can recover after shrinking, which may be due to the high mobility of oxygen ions in BSCF³⁰, which allows the O₂ to accumulate again to re-inflate the bubbles. Additional studies are required to investigate the gas leaking and surface recovery processes during the oscillation in further detail.

The above oscillation process can be described using a simple model, with the following first-order approximations. First, the oxygen gas in the bubbles can be treated as an ideal gas. Second, oxygen evolution and oxygen release are the rate-determining steps that control the bubble inflation and deflation, respectively. Third, the rates of oxygen evolution and release can be treated as constants. With these approximations, we find that $\Delta(d^2) \propto \Delta(t)$, where d is the bubble size and t is the time (a detailed derivation can be found in the Supplementary Information). This relationship can be tested by plotting the square of bubble size (d^2) against time using the data in Fig. 1e, as shown in Fig. 4b. The good agreement between the measured bubble size evolution and the modeling results implies that the proposed mechanism explains the observations well. The oscillation described in this model involves several dynamic steps (inflation of the bubble, leaking of oxygen through the surface skin, deflation of the bubble, and surface recovery). Thus the frequency and amplitude of the oscillations are not only determined by the water pressure and e-beam irradiation conditions, but are also influenced by the morphology, size and arrangement of

the small crystallites in BSCF particles, which can contribute to the different frequency and amplitude observed among different particles under similar conditions (Fig. 2). In addition, a different history of exposure to the electron beam dose and / or water pressure levels can also be responsible for the observed variability. Our model predicts that in the presence of a high water content and high e-beam dose rate, the water supply and splitting rates will be accelerated, which can lead to an accelerated gas formation rate during the bubble inflation process. The faster growth of bubbles may lead to a faster buildup of surface stress and cause the bubble to leak earlier. The above predictions are consistent with our experimental observation that the oscillation frequency increased and the amplitude slightly decreased when the samples were subjected to higher water pressure and higher electron dose rates.

Structure oscillations of SCO, LSC and LCO in H₂O vapor under e-beam irradiation

We also examined perovskite oxides with higher oxygen vacancy formation energies (E_{vac}) and/or reduced oxygen mobility in a similar manner. BSCF is known to have its O 2p-band center very close to the Fermi level²⁶ and a very low E_{vac} ²⁶, which facilitates the redox of its lattice oxygen and leads to high surface oxygen exchange kinetics³⁰ and oxygen ion mobility^{26, 30}. In comparison, brownmillerite SCO has larger energy gap between the O 2p-band center and the Fermi level^{26, 47}, higher E_{vac} ²⁶ and lower mobility of oxygen ions⁴⁸ (see Fig. 5). As a result, the lattice oscillations we observed in SCO were confined to very thin surface layers of ~1 nm, even under a harsh H₂O and e-beam irradiation condition (in 30 mTorr H₂O under 1250 e/Å²s, see Fig. 5). For LSC and LCO, which have the O 2p-band center farther away from the Fermi level and much higher E_{vac} , no structural oscillations were observed in >10 mTorr H₂O and under >100 e/Å²s dose rate (Fig. 5).

The absence of structural oscillations in these oxides can be attributed to the fact that the O 2p-band centers are far from the Fermi level, which correlates to an increased energy penalty for oxygen vacancy formation and reduces oxygen ion mobility. Therefore, it is difficult for these oxides to uptake H₂O to form OH₂[•], and the transport of oxygen or hydroxyl ions is sluggish, confining oxygen evolution to the surface of the oxides, with an inactive lattice. Moreover, by changing the transition metal ions from Co to Mn, the O 2p-band center further moves away from the Fermi level²⁶, therefore the structural oscillations were also absent for LMO (Supplementary Fig. S7) and Pr_{1-x}Ca_xMnO₃ (previously reported and studied on the same instrument in 112 mTorr H₂O under 5000 e/Å²s³⁵). The above observations provided direct evidence that tuning the O 2p-band center closer to the Fermi level and reducing the energy penalty for oxygen vacancy formation can facilitate water uptake and ion transport in oxides, which can activate the oxygen evolution not only on the surface but also inside the oxides when subjected to e-beam irradiation. These observations not only provide deeper insight into the activity and stability of highly active perovskite OER catalysts, but also open new possibilities in the design and development of many new materials. The work described herein presents the first direct evidence of electron beam induced O₂ formation, and points to new methods to activate water splitting or hydrogen/oxygen transportation through the interaction of oxides and water using high-energy electrons, high-energy photons or strong fields. This information is expected to assist in the development of new energy storage devices, hydrogen/oxygen pumps or gas sensors^{21, 22, 24}.

In summary, we have demonstrated that the combined effect of water and e-beam irradiation results in significant oscillatory structural changes inside highly active BSCF catalytic particles.

Increased H₂O pressure or electron dose rate leads to an increase in the frequency of the oscillations, with a corresponding decrease in their amplitude. EELS analysis indicated the formation of gaseous O₂ during these oscillations. The structural oscillations can be explained by the uptake of water into the BSCF and e-beam induced O₂ evolution inside the oxides. In contrast, the structural oscillation is weak or absent in other Co- or Mn-based oxides due to the larger energy gaps between their O 2p-band centers and their Fermi levels, which leads to lower oxygen ion mobility and a higher energy penalty for oxygen vacancy formation, which in turn hinders water uptake. These *in situ* observations provide a thorough understanding of the interaction between water and oxides under e-beam irradiation, and point to new routes to the design of materials with enhanced performance.

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Author contributions

B. H., Y. S.-H. and E. A. S. designed the experiments. B. H. and K. S. prepared the materials. A. D. G., E. A. S., B. H. and V. T. carried the ETEM experiments. B. H. prepared the manuscript

initially. All authors contributed to the discussions and revisions of the manuscript.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints.

Competing financial interests

The authors declare no competing financial interests.

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Figure Legends

Figure 1. TEM images and TED patterns of a BSCF particle (Particle A) a, before and b, after the observed structural oscillations, obtained in HV. TED patterns were collected from the entire

particle. **c**, Images extracted from a video of the structural oscillations, in a mild condition (30 mTorr H₂O, electron dose rate of 1 e/Å²s). A video is available online (Supplementary Movie 1). **d**, Images extracted from a video of the structural oscillations obtained in a harsh condition (50 mTorr H₂O, electron dose of 10 e/Å²s). A video is available online (Supplementary Movie 2). The blue dashed lines in **c** and **d** are guides to help in the comparison of the motion of the particle edges. **e,f**, Quantitative measurements of the changes in bubble size vs. time under the mild and harsh conditions, respectively. Video clips are available online (Supplementary Movie 3 and Supplementary Movie 4, respectively.) **g,h**, TED patterns from BSCF under the mild and harsh conditions, respectively. The number of seconds shown in **c-h** represents the passage of time after the initiation of the environmental stimulus. The faint white-dotted lines superimposed upon the TED patterns in **a**, **b**, **g** and **h** show the expected location of the standard reflections for BSCF.

Figure 2. Oscillation frequency and amplitude when exposed to different water vapor pressures and electron dose rates. **a**, Bubble size (average diameter) evolution of Particle B over time in the presence of an electron dose rate of 40 e/Å²s and a H₂O pressure of 0.4 and 11 mTorr. **b**, Bubble size evolution of Particle C over time in the presence of 10 mTorr H₂O pressure and an electron dose rate of 20 and 100 e/Å²s. **c,d**, The frequency and displacement of the structural oscillations as a function of different electron dose rate and H₂O pressure, as indicated, respectively. Particle A, B, C and D represent different BSCF particles. The numbers under the columns represent the H₂O pressure in the unit of mTorr. The numbers above the columns represent the electron dose rate in units of e/ Å²s. The water partial pressure was always increased from base pressure (high vacuum) to low pressure to high pressure, and then returned to base

pressure, where we always observed the termination of all oscillations to the deflated bubble state.

At each water partial pressure, the electron beam current was changed from either from low to high dose (Particle B: 11 mTorr; Particle C: 10 mTorr; Particle D: 0.11 and 10 mTorr), or from high to low dose (Particle B: 0.4 mTorr; Particle C: 1 mTorr; Particle D: 1.3 mTorr).

Figure 3. EELS of BSCF before (“BSCF in HV”) and during the structural oscillations (“BSCF in H₂O”), in the energy ranges associated with **a**, the O K-edge, and **b**, the H K-edge / O₂ low loss region, respectively. All EELS data were collected in diffraction mode, with an electron dose rate of $\sim 200 \text{ e}/\text{\AA}^2\text{s}$. The “BSCF in HV” spectra were collected in 10^{-3} mTorr HV, while the “BSCF in H₂O” spectra were collected in 10 mTorr H₂O. The sample region from which this EELS data was collected is shown in Supplementary Fig. S3a. The reference spectra of the O₂ gas (“O₂”) and H₂O vapor (“H₂O”) were also collected in 10 mTorr O₂ and 30 mTorr H₂O, respectively. The characteristic peaks of BSCF, O₂, H₂O and carbonate are labeled in black, red, blue and green, respectively.

Figure 4. Structural oscillation mechanism and modeling. **a**, A schematic of water incorporation accompanied by water splitting within BSCF particles, which leads to structural oscillations observed on BSCF in H₂O vapor under e-beam. **b**, A plot of the square of the bubble size (d^2) versus the time (t) during the first inflation process (solid) and the first deflation process (open) of Particle A (data points from Fig. 1e). The red lines are a linear fit of the inflation and deflation processes, with R^2 values of 0.98 and 0.99, respectively.

Figure 5. Comparison of structural oscillations in BSCF to the lack thereof for other oxides in H₂O and under e-beam. The axis indicates the location of the O 2p-band centers (relative to the Fermi level), E_{vac} , and oxygen tracer diffusion coefficient (D , measured at 900 °C under 0.2-1 atm of O₂), taken or estimated from previous studies^{26, 30, 47, 48, 49}. The water vapor pressures and electron dose rates for each oxide samples are listed above the corresponding TEM images. The number of seconds shown on each TEM image represents the passage of time after the initiation of the environmental stimulus. Video is available online (BSCF: Supplementary Movie 9; SCO: Supplementary Movie 11; LSC: Supplementary Movie 12; LCO: Supplementary Movie 13).

Methods

Material Preparation. BSCF, LCO, SCO, LSC and LMO were synthesized using the nitrate combustion method as reported previously³. Metal nitrates (>99.998%, Sigma-Aldrich) with correct molar ratios were added to deionized water (>18.2 MΩ, Millipore) at the concentration of 0.2 M. Thereafter, 0.1 M Glycine (>99%, Sigma-Aldrich) was added, and the mixture was heated until most of the water had evaporated and sparks were observed. After the sparking ceased, the powder was annealed at 1100 °C in air for 24 h. The structure and lattice parameter of the oxides powders are shown in the Supplementary Table S1. In Ba_{0.5}Sr_{0.5}Co_xFe_{1-x}O_{3-δ}, δ is around 0.4 according to a previous study⁵⁰. The powder was then mortar-milled and directly placed onto the lacey carbon or SiN TEM grid in powder form – the samples were not dispersed in any liquid medium during TEM sample preparation.

ETEM and EELS. The HRTEM images, TED patterns and related videos shown in this work

were collected using an aberration corrected, Schottky field emission gun transmission electron microscope (FEI Titan 80-300 kV S/TEM) operated at 80 kV, with the phase field tuned to ~20 mRad. The microscope base pressure at the HV condition was 10^{-6} Torr. During the experimentation up to 100 mTorr of H₂O vapor was introduced into the ETEM. The *in situ* videos (HRTEM images, bright field images and TED patterns) were acquired using the video capture mode embedded in the FEI TEM Imaging & Analysis (TIA) software. All videos are presented at the frame rates at which they were acquired (real time). The average diameter of the most obvious (usually the largest) bubble structure in each movie was measured frame-by-frame to track oscillation parameters vs. time. EELS was performed in diffraction mode for BSCF, using a Gatan Tridiem post-column energy filter. The energy axis was calibrated using the zero loss peak. The energy resolution was ~ 1 eV, measured as the full width at half height of the zero loss peak. EELS spectra were acquired from an approximately circular area ~ 50 nm in diameter with an acquisition time of 5 min. The e-beam intensities indicated were measured using the e-beam current reading from the phosphor viewing screen. All of the oxide particles were studied first in high vacuum to confirm they were stable and crystalline under electron beam irradiation before introducing any H₂O into the TEM chamber. At least three particles were tested and observed for each oxide to check the repeatability of the oscillation observations.

Reference of Methods

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