Overlayer deposition-induced control of oxide ion concentration in SrFe$_{0.5}$Co$_{0.5}$O$_{2.5}$ oxygen sponges†

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Controlling the oxide ion (O$^{2-}$) concentration in oxides is essential to develop advanced ionic devices, i.e. solid oxide fuel cells, smart windows, memory devices, energy storage devices, and so on. Among many oxides several transition metal (TM)-based perovskite oxides show high oxide ion conductivity, and their physical properties show high sensitivity to the change of the oxide ion concentration. Here, the change in the oxide ion concentration is shown through the overlayer deposition on the SrFe$_{0.5}$Co$_{0.5}$O$_{2.5}$ (SFCO) oxygen sponge film. We grew SFCO films followed by the deposition of two kinds of complex oxide films under exactly the same growth conditions, and observed the changes in the crystal structure, valence states, and magnetic ground states. As the NSMO overlayer grows, strong evidence of oxidation at the O K edge is shown. In addition, the Fe$^{4+}$ feature is revealed, and the electron valence state of Co increased from 3 to 3.25. The oxide ion concentration of SFCO changes during layer growth due to oxidation or reduction due to differences in chemical potential. The present results might be useful to develop advanced ionic devices using TM-based perovskite oxides.

1. Introduction

The functional properties of complex metal oxides are influenced by lattice, spin, orbital, charge degrees of freedom, and their interplay.1-7 The functionality is often realized by substrate induced strain, cation doping, and charge doping through interfacial engineering. Another promising method for controlling such functionality in complex metal oxides is to manipulate oxide ion concentration in the oxides.8-13 Due to the known high oxide ion conductivity and excellent catalytic activity without triple phase boundaries, perovskite and perovskite-like structures are suitable choices for ion-driven technology.13,14 The oxide ion-driven technology is important for ion conduction, the center of many energy storages such as magnetic memory devices,15,16 fuel cells,13,17 smart windows,18 and sensor technology.19

Typically, functional devices, i.e. neuromorphic devices, solid oxide fuel cells, and etc., are designed as a stack of several layers. It is often found that functional properties of each layer in the stack are deviated from those of its bulk-form.20-21 For example, due to modulation of interfacial chemistry, when certain oxides form heterostructures, reduced spin transport in La$_{1-x}$Sr$_x$MnO$_3$-based tunneling devices and unconventional transport behavior in LaNiO$_3$ due to unidirectional oxygen diode effect are observed.22,23 In addition, heterointerface design is crucial for performance and longevity of electrochemical devices from the example of an oxide getter for detoxicating contaminated air and enhanced oxygen surface exchange kinetics in fuel cell applications.24,25 Therefore, it is indispensable to understand chemistry at the interface between the two oxides and track the changes in oxide ion concentration along depth direction.

Fig. 1 Schematic illustration of overlayer deposition-induced oxide ion concentration control in SFCO film. When STO is deposited on BM-SFCO film, reduction occurs. On the other hand, when NSMO is deposited on BM-SFCO, oxidation occurs and the crystal structure changes to perovskite.

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In this report, we studied modulation of interfacial chemistry of oxygen sponge SrFe$_{2.5}$Co$_{0.5}$O$_{2.5}$ (SFCO), which is a solid solution of SrFeO$_{2.5-δ}$ and SrCoO$_{2.5+δ}$. The crystal structure of the oxygen sponges can be reversibly converted between brownmillerite/perovskite upon redox reactions with various ways. Brownmillerite structure is $ABO_{3-δ}$, where A and B are cations and O is oxygen in chemical formula. It consists of alternate stacks of an octahedral layer and an oxygen deficient tetrahedral layer. A simple deposition of an overlayer on an SFCO oxygen sponge film changes the oxide ion concentration (Fig. 1). We fabricated SFCO films following the deposition of two different complex oxides, i.e. SrTiO$_3$ and Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ films under exactly the same growth condition. We tracked the changes in the crystal structure, valence state, and magnetic ground state. As a result of these observations, the oxide ion concentration of SFCO readily changed during layer growth due to oxidation or reduction due to changes in chemical potentials. The results of this study on the interface of complex oxides can provide opportunities to improve the design and performance of new devices.

2. Experimental

2.1 Sample preparation

Brownmillerite SFCO (space group $icmm$, $a = 5.6243$ Å, $b = 15.6515$ Å, $c = 5.5017$ Å (ref. 31)) thin films (three samples) were grown on (001) (LaAlO$_3$)$_{0.3}$-(SrAl$_{0.5}$Ta$_{0.5}$O$_3$)$_{0.7}$ (LSAT) substrates by pulsed laser deposition (PLD). A Q-switched 3μm:YAG ($λ = 355$ nm) laser was used to ablate the ceramic targets. The laser fluence and repetition rate were kept as 0.75 J cm$^{-2}$ and 4 Hz, respectively. Optimal growth conditions were selected by the growth condition. We tracked the changes in the crystal structure, valence state, and magnetic ground state. As a result of these observations, the oxide ion concentration of SFCO readily changed during layer growth due to oxidation or reduction due to differences in chemical potentials. The results of this study on the interface of complex oxides can provide opportunities to improve the design and performance of new devices.

2.2 Characterization

2.2.1 X-ray diffraction. Before studying the interface between the two layers, non-contact atomic force microscopy observation (AFM, SPA 400, Seiko) was performed to ensure that each layer was deposited flat. The root mean square roughness of the as-grown SFCO is 0.4 nm, and the roughness values of the overlayered SFCOs were 0.7 nm or less as shown in Fig. S1.† We conducted X-ray diffraction (XRD, D8 discover, Bruker, Cu Kα1, $λ = 1.5406$ Å) to analyze the crystal structure of each sample. We could calculate the changes in the lattice constant through the $2θ$–$ω$ scan and reciprocal space mapping (RSM) around (103) Bragg reflection of LSAT substrates depending on the overlayers.

2.2.2 X-ray absorption. X-ray absorption spectroscopy (XAS) with total electron yield (TEY) mode was performed to determine the valence states of SFCO thin films at 300 K and under $10^{-3}$ torr at the 2A beamline of the Pohang Accelerator Laboratory. The probing depth of TEY mode is about 5 to 10 nm, so the spectrum comes out completely from the top of the film. Surface-sensitive XAS mode was chosen, since the overlayer thickness is four unit cells. In addition, the beam incidence angle was set to 45° to observe the valence state changes in the buried oxygen sponge SFCO.

2.2.3 Magnetization. Magnetization versus temperature ($M$–$T$) curves were measured to identify possible magnetic phase transition due to the overlayers using a superconducting quantum interference device magnetometer (SQUID, MPMS3, Quantum Design Inc). In SQUID, the $M$–$T$ curve shows weak ferromagnetism below 160 K. Element-specific X-ray magnetic circular dichroism (XMCD) measurements were performed to analyze the element-specific magnetism at 130 K, where ferromagnetism was confirmed through the bulk magnetometer.

3. Results and discussion

3.1 Crystallographic analyses

To identify the crystal structure, we measured out-of-plane XRD patterns of the samples (Fig. 2a and S2†). In the XRD pattern of as-grown SFCO (navy), diffraction peaks of 001 SrTiO$_3$ (STO) or Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ (NSMO) was deposited on each SFCO sample under the same PLD condition without breaking vacuum. Then, these two samples, i.e. NSMO/SFCO and STO/SFCO, were cooled below 50 °C under the same $P_O$, after the film growth. In order to exclude other influences during the deposition of the overlayer, the target was rotated and replaced while maintaining the same deposition state after the growth of the SFCO. Only the overlayer deposition induced a phase transition from brownmillerite to perovskite structure. A detailed discussion of phase transitions will be provided later. The deposition time was adjusted to control the thickness of each layer. After depositing individual SFCO, STO, and NSMO thin films, the thickness and deposition rate were determined by the X-ray reflectivity followed by the simulation/fitting analysis. Through the deposition rate obtained through analysis, SFCO was controlled to be eight unit cells in brownmillerite notation, while STO and NSMO were controlled to be four unit cells.

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reduced by depositing an STO overlayer, whereas SFCO is oxidized by depositing an NSMO overlayer.

### 3.2 Valence state

Changes in oxide ion concentration through the overlayer enable not only structural changes but also electronic structural changes in the SFCO. Due to oxide ion movement, XAS was performed to determine the valence state of the transition metals and qualitative oxide ion concentration. Fig. 3 shows the O K edge spectra of SFCO, STO/SFCO and NSMO/SFCO. Additionally, we measured XAS spectra of single layered STO and NSMO thin films to identify the origin of peaks in O K edge spectra from SFCO, STO and NSMO/SFCO. Fig. 3a shows an O K edge spectrum of as-grown SFCO thin film in brownmillerite. As the overlayer changes, the shapes of signals show a clear change. Fig. 3b shows an O K edge spectrum of STO/SFCO. We added XAS spectra from individual SFCO and STO thin films. There is no drastic change in the O K edge spectrum of STO/SFCO. However, peaks that were not present in that of SFCO are clearly seen at 531 and 533 eV in STO/SFCO. From the comparison with that of an STO film, they are mainly contributed from STO. Lastly, in Fig. 3c, a large peak at the pre-edge region of O K edge (vertical black dotted line at about 528 eV) from the spectrum of NSMO/SFCO was observed. The pre-edge peak from O K edge spectra is related to O 2p–TM 3d hybridization, and the intensity is related to the strength of hybridization.

In order to clarify the change of the O K edge spectrum due to the overlayer, the O K edge spectra of the SFCO, STO and NSMO are indicated by dotted lines. In NSMO/SFCO, the hybridization of TM 3d–O 2p was increased.
found at around 528 eV, which shows an increase in oxygen content. A decrease in peak intensity in the O K edge spectrum of STO/SFCO indicates the removal of oxide ions in SFCO. Changes in oxygen ion concentration are shown by comparing the O K edges of each sample. When two complex metal oxides form an interface through overlayer deposition, the oxygen ion concentration changes rather than simply having two layers.

Fig. 4a shows XAS spectra around Fe L edge. The peak position of Fe L$_3$ edge of the SFCO is located at 709.15 eV. The peak of the STO/SFCO is located at 709.20 eV, close to that of the SFCO. However, the peak of the NSMO/SFCO is located at 709.30 eV, where 0.15 eV higher than that of the SFCO. The 0.15 eV difference seen in the NSMO/SFCO suggests an increase in Fe valence state. It also shows the broadening of the peak in the high energy side of the Fe L$_2$ edge, which means an increase in the Fe$^{4+}$ state in the Fe valence state. In addition, changes in the relative intensities in two peaks at Fe L$_2$ edge can be considered as the increase of Fe valency in the NSMO/SFCO. The shape of the Fe L$_2$ edge is similar to the previously reported SrFeO$_3$. The increase in the peak position through Fe L$_3$ edge and broadening of the peak in the high energy side of the Fe L$_2$ edge show that the NSMO overlayer increases the valence state of Fe.

Fig. 4b shows XAS spectra around Co L edge. Oxide ion concentration can be inferred from valence states of TMs. The Co L$_3$ edge of SFCO is located at 779.20 eV. Although there is no difference between the SFCO and STO/SFCO, the Co L$_3$ edge of the NSMO/SFCO locates a higher energy side (779.45 eV), clearly indicating that NSMO overlayer oxidized SFCO. Next, in order to

![Fig. 4](image_url)  
**Fig. 4** (a) XAS of Fe L edge and (b) Co L edge in SFCO, STO/SFCO and NSMO/SFCO. Fe L edge spectra shows an increase in Fe$^{3+}$ in NSMO/SFCO. The spectral centroid for comparing the Co L edge are included in the inset of (b). The valence of TM is lowered through the STO overlayer and increased through the NSMO overlayer.

![Fig. 5](image_url)  
**Fig. 5** (a) Magnetization vs. temperature graph of SFCO, STO/SFCO, and NSMO/SFCO. NSMO/SFCO shows ferromagnetism below 160 K. To find the origin of the ferromagnetism of NSMO/SFCO, elementspecific XMCD of (b) Fe and (c) Co L edges was measured.
clearly see the differences in the Co L\textsubscript{3} edge peak position of SFCO and STO/SFCO in detail, we compared the spectral centroid value of the Co L\textsubscript{3} edge (inset of Fig. 4b). The spectral centroid of Co L\textsubscript{3} edge of STO/SFCO shows 0.01 eV reduction compared to SFCO, indicating an oxygen reduction of SFCO occurred by depositing STO overlayer, most likely due to STO extracts oxide ion from SFCO. From the Co L edge spectra, it can be seen that the STO overlayer reduces SFCO while the NSMO overlayer oxidizes SFCO.

### 3.3 Magnetism

SFCO system shows change in the magnetic properties from antiferromagnetic to ferromagnetic upon structural transition from brownmillerite to perovskite.\textsuperscript{35-39} We measured the magnetic properties at low temperatures (Fig. 5). The M–T curve of the NSMO/SFCO shows a clear upturn around 160 K (Fig. 5a), indicating ferromagnetic properties, though the SFCO and the STO/SFCO do not show any phase transition in the range of temperature we measured.

Since the noise level of the M–T curves is quite large, we further measured grazing angle XMCD spectra at 130 K with 0.5 T (Fig. 5b and c) to confirm the ferromagnetism of the NSMO/SFCO. Ferromagnetic XMCD signals from Fe L edge and Co L edge are clearly seen. Note we also measured XMCD of Mn L edge and O K edge, however no XMCD signals were detected (Fig. S3f). The XMCD features of Fe L edge and Co L edge are similar in shape, meaning spin polarization direction are parallel. The signals from Fe L edge and Co L edge clearly demonstrate that the NSMO/SFCO shows weak ferromagnetism.

### 3.4 Discussion

Here we would like to discuss the mechanism of the reduction/oxidation of SFCOs by the overlayer deposition. We focused on the oxygen vacancy formation energy (E\textsubscript{OV}) because E\textsubscript{OV} represents the energy required to form oxygen vacancy. E\textsubscript{OV} of NSMO is 1.78 eV (ref. 42) while that of STO is 5.54 eV (ref. 43 and 44). STO is known as an oxide ion getter material that extracts oxide ion from SFCO. From the Co L\textsubscript{3} edge of STO/SFCO shows 0.01 eV reduction compared to SFCO, indicating an oxygen reduction of SFCO occurred by depositing STO overlayer while brownmillerite structure was kept when STO was deposited. We showed spectroscopic evidence of redox activity through bilayer interfaces, which supported by the energy difference. Due to the difference in E\textsubscript{OVs}, oxygen vacancies in SFCO are easily generated in STO/SFCO (\(\Delta E_{\text{OV}} \sim -2.59\) eV), while oxygen absorption from NSMO occurs in NSMO/SFCO (\(\Delta E_{\text{OV}} \sim 1.17\) eV). Further, the NSMO/SFCO showed weak ferromagnetism. From these observations, the oxide ion concentration in SFCO is changed during the overlayer growth due to oxidation or reduction originated from the difference in the chemical potential. The present results might be useful to design advanced ionic devices using TM-based perovskite oxides.

### Conflicts of interest

There are no conflicts to declare.

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