Single-crystal epitaxial thin films of SrFeO$_2$ with FeO$_2$ "infinite layers"

Satoru Inoue,[1] Masanori Kawai,[1] Yuichi Shimakawa,[1,a] Masaichiro Mizumaki,[2]
Naomi Kawamura,[2] Takashi Watanabe,[3] Yoshihiro Tsujimoto,[3] Hiroshi Kageyama,[3] and
Kazuyoshi Yoshimura[3]

[1]*Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan*
[2]*Japan Synchrotron Radiation Research Institute/SPring-8, Sayo, Hyogo 679-5198, Japan*
[3]*Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo, Kyoto 606-8502, Japan*

Single-crystal thin films of SrFeO$_2$, which is an oxygen-deficient perovskite with "infinite layers" of Fe^{2+}O$_2$, were prepared by using CaH$_2$ for low-temperature reduction of epitaxial SrFeO$_{2.5}$ single-crystal films deposited on KTaO$_3$ substrates. This reduction process, removing oxygen ions from the perovskite structure framework and causing rearrangements of oxygen ions, topotactically transforms the brownmillerite SrFeO$_{2.5}$ to the *c*-axis oriented SrFeO$_2$. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2913164]

Strontium and iron form a number of oxygen-deficient perovskite structure oxides: SrFeO$_{3-\delta}$ with δ ranging from 0 to 0.5.[1] SrFeO$_3$ ($\delta=0$) with Fe^{4+}O$_6$ octahedra has been synthesized in bulk form at 400–550 °C under an oxygen partial pressure of 10^5 Torr (Ref. 2) and has also been prepared in a thin film form by pulsed laser deposition (PLD) following *in situ* oxidization with flowing O$_3$.[3,4] This strongly oxidizing atmosphere stabilized the unusually high ionic state of Fe^{4+}. SrFeO$_{2.5}$ ($\delta=0.5$), on the other hand, has been prepared at ambient pressure and its brownmillerite structure consists of alternate layers of Fe^{3+}O$_6$ octahedra and Fe^{3+}O$_4$ tetrahedra [Fig. 1(a)]. However, it was not possible to produce SrFeO$_2$ ($\delta=1.0$), a perovskite with Fe^{2+} ions, by using H$_2$/Ar gas or electrochemical reduction techniques[5] because the perovskite structure was not conserved under those reducing conditions in thermodynamically controlled solid-state reaction processes.[6]

SrFeO$_2$ was recently synthesized by reducing SrFeO$_{2.875}$ (Sr$_8$Fe$_8$O$_{23}$) with CaH$_2$ at 280 °C,[7] a temperature too low for structural rearrangement but high enough that the oxygen ions could change their positions. SrFeO$_2$ is an oxygen-deficient perovskite and is isostructural with the "infinite-layer" cupric oxides used to make high-T_C superconductors.[8] Its crystal structure [Fig. 1(b)] consists of FeO$_2$ planes with corner-sharing square-planar coordinated FeO$_4$ and at room temperature, its tetragonal ($P4/mmm$) lattice constants are $a=3.991$ and $c=3.474$ Å. The lack of apical oxygen in SrFeO$_2$ makes its crystal structure highly anisotropic and makes its magnetism two dimensional, and the high mobility of the oxygen ions in SrFeO$_2$ would make it a useful material for the electrodes in solid-oxide fuel cells and batteries.[9]

Square-planar oxygen coordination around Fe^{2+} is extremely rare because iron ions are favorably tetrahedrally or octahedrally coordinated by oxygen irons. To understand the crystallographic, electronic, and magnetic characteristics of SrFeO$_2$, we need to investigate them in studies with single-crystal samples. In this letter, we report the crystal structure and the ionic state of Fe in single-crystal epitaxial thin films of SrFeO$_2$ prepared by *ex situ* reduction of epitaxially grown brownmillerite SrFeO$_{2.5}$ films.

The SrFeO$_{2.5}$ precursor ceramic target was first prepared in a solid-state reaction under an oxygen partial pressure of 10^{-4} Torr. The SrFeO$_{2.5}$ precursor was deposited on a KTaO$_3$ substrate by PLD using a KrF excimer laser pulse with an energy density of 0.4 J/cm^2. KTaO$_3$ single-crystal substrates were used in this study because the cubic lattice constant of KTaO$_3$, 3.988 Å, is quite close to the *a* lattice constant of SrFeO$_2$. The obtained SrFeO$_{2.5}$ film samples were treated in a way similar to that in which the bulk samples described in Ref. 7 were treated. The bulk samples were treated with CaH$_2$ in a mixed compressed disk, whereas each of the present 5 mm square SrFeO$_{2.5}$ film samples was embedded with about 0.2 g of CaH$_2$ in an evacuated Pyrex tube in an Ar-filled glove box. The tube was sealed in vacuum and then kept at 280 °C for 24 h. The residual products, including CaH$_2$, on the film surface were removed by washing with 2-butanone. The crystal structure of the resultant material was examined by 2θ-θ x-ray diffraction (XRD) measurement with Cu $K\alpha$ radiation. The XRD intensity map in (H,L) reciprocal lattice space was also measured with a
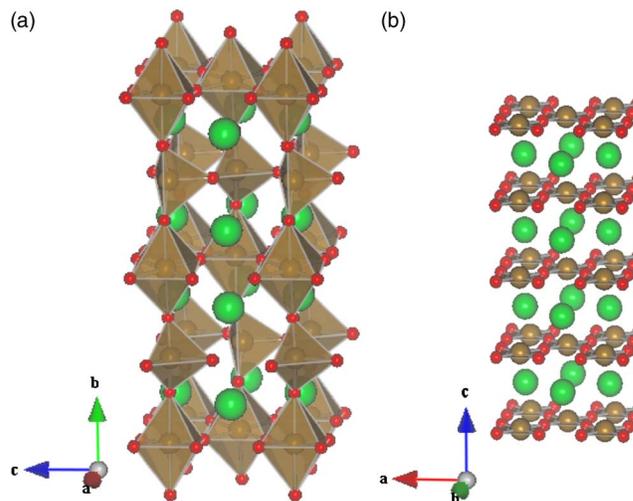
FIG. 1. (Color online) (a) SrFeO$_{2.5}$ brownmillerite structure consisting of alternate layers of FeO$_6$ octahedra and FeO$_4$ tetrahedra. (b) SrFeO$_2$ infinite-layer structure consisting of corner-sharing planar FeO$_4$ and Sr. Note that the *b* axis of SrFeO$_{2.5}$ and the *c* axis of SrFeO$_2$ are perpendicular to the film plane.

a)Electronic mail: shimak@scl.kyoto-u.ac.jp.
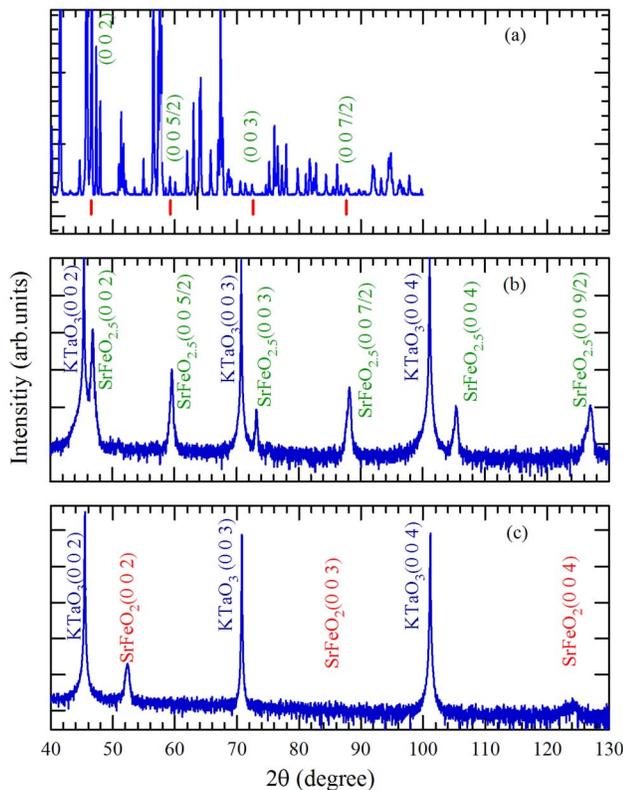
FIG. 2. (Color online) XRD patterns of (a) $SrFeO_{2.5}$ target (linear scale), (b) $SrFeO_{2.5}$ film grown on $KTaO_3$ (logarithmic scale), and (c) reduced $SrFeO_2$ film (logarithmic scale).

FIG. 3. (Color online) Logarithmic x-ray intensity reciprocal space maps around the (1 0 3) Bragg reflection of (a) $SrFeO_{2.5}$ and (b) the $SrFeO_2$ thin films.

four-circle diffractometer. Here, the reciprocal-space coordinates correspond to those of the cubic $KTaO_3$ substrate, and thus, $H=1.0$ and $L=1.0$ correspond to $1/a$ ($KTaO_3$) $=1/3.988$ Å^{-1}. The x-ray absorption spectra (XAS) near the Fe K edge were examined at the BL39XU beamline of SPring-8 in order to see the change in Fe oxidation state. They were recorded at room temperature with a fluorescence mode.

The $SrFeO_{2.5}$ precursor ceramic was confirmed to have the brownmillerite structure by powder XRD [Fig. 2(a)]. The deposition with the $SrFeO_{2.5}$ precursor target under an oxygen pressure of 10^{-5} Torr at 700 °C yielded *b*-axis oriented epitaxial $SrFeO_{2.5}$ thin films. X-ray reflectivity revealed that the films deposited were typically 170–200 Å thick. In the 2θ-θ XRD pattern shown in Fig. 2(b), one sees the (0 0 *l*) reflections of the perovskite structure and the (0 0 *l*/2) two-fold superstructure reflections due to the ordering of the oxygen defects in the $SrFeO_{2.5}$ brownmillerite structure. Note here that the indices are based on the primitive cubic perovskite cell ($a \sim 3.9$ Å) and the original *b* axis of the brownmillerite structure (the stacking direction of the layered structure) is converted to the *c* axis. An XRD logarithmic intensity map in the reciprocal lattice space around the (1 0 3) Bragg reflection of the $KTaO_3$ perovskite structure is shown in Fig. 3(a), where both the $KTaO_3$ Bragg reflection at $(H,L)=(1.00, 3.00)$ and a diffraction peak from the film at $(H,L) \approx (1.00, 3.08)$ are evident. Since the peak positions along the H and L directions give information on the in-plane and out-of-plane lattices, respectively, the data indicate that the in-plane lattice constant of the $SrFeO_{2.5}$ film is comparable to the $KTaO_3$ cubic lattice and that the out-of-plane lattice constant of the film is smaller than that of the $KTaO_3$
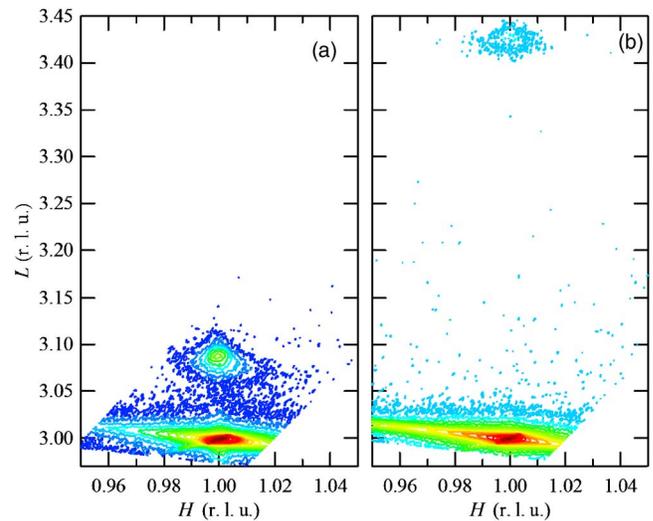
substrate. Therefore, these XRD results clearly show that the growth of the pseudo-tetragonal brownmillerite $SrFeO_{2.5}$ film on the $KTaO_3$ substrate was epitaxial.

A 2θ-θ XRD pattern of the CaH_2-treated film is shown in Fig. 2(c). None of the diffraction peaks originating from $SrFeO_{2.5}$ are evident but the peaks corresponding to $d=1.75$ and 0.87 Å ($2\theta \approx 52°$ and 123°, respectively) are evident. The positions of these peaks are close to those of the (0 0 2) and (0 0 4) reflections of the bulk $SrFeO_2$. The intensities for the infinite-layer $SrFeO_2$ structure that were calculated by the XRD intensity simulation program RIETAN-2000, $I_{002}:I_{003}:I_{004}=10\,361:29:1874$ $=1.0:0.0028:0.18$, agree well with the observed intensities: $I_{002}:I_{003}:I_{004} \approx 1:0:0.14$. Figure 3(b) shows a reciprocal lattice map of the reduced thin film sample. In addition to the (1 0 3) Bragg reflection of the cubic $KTaO_3$ substrate, there is a peak at $(H,L) \approx (1.00, 3.42)$. The lattice constants obtained from the diffraction data were $a=3.988$ and $c=3.493$ Å, which are consistent with those reported for powder samples of $SrFeO_2$.[7]

XAS spectra near the Fe K edge are shown in Fig. 4 for the $SrFeO_{2.5}$ precursor and CaH_2-treated thin film samples. The difference in the shape of their XAS spectra is due to the changes in the electronic states and local structure of Fe ions.[10] The Fe K absorption edge energy of the reduced thin film was about 1.5 eV lower than that of the $SrFeO_{2.5}$ precursor thin film. This chemical shift indicates that the Fe oxidation state in the CaH_2-treated thin film sample was reduced to that close to Fe^{2+}, and all of the XRD and XAS results indicate that the epitaxial $SrFeO_{2.5}$ thin film was reduced to one of $SrFeO_2$. We can therefore conclude that the reduced thin film obtained is single-crystal $SrFeO_2$ with the infinite-layer structure. The pre-edge structures shown in the inset of Fig. 4 have never been observed in any iron oxides, and thus, they appear to originate from the characteristic square-planar coordination of Fe^{2+} ions. The details of the analysis will be published elsewhere.[11]

The low-temperature reduction used in this study moved oxygen ions in the perovskite structure framework and removed some from the framework. This process caused the *b*-axis oriented single-crystal $SrFeO_{2.5}$ brownmillerite thin
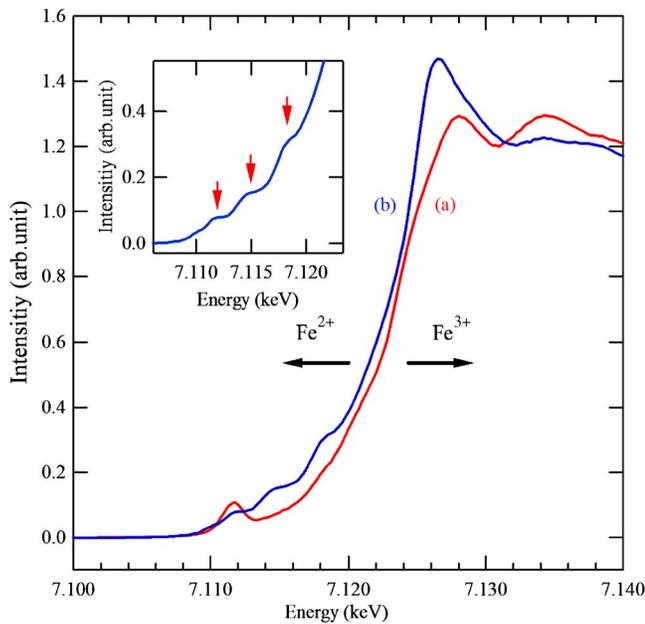
FIG. 4. (Color online) X-ray absorption spectra near the Fe K edge of (a) $SrFeO_{2.5}$ and (b) $SrFeO_2$ thin films. The inset shows the pre-edge spectrum of $SrFeO_2$.

film to topotactically change into the c-axis oriented $SrFeO_2$ infinite-ayer single crystal, which has an out-of-plane lattice constant of 9.8% smaller than that of $SrFeO_{2.5}$ but has almost the same in-plane lattice structure. In the single-crystal thin film sample, the crystal lattice is under strain due to the lattice mismatch to the substrate $KTaO_3$ lattice. Indeed, the in-plane a lattice constant of the single-crystal $SrFeO_2$ (3.988 Å) is slightly smaller than that of bulk $SrFeO_2$ (3.991 Å). As a result, the observed out-of-plane lattice constant of the single-crystal $SrFeO_2$ (3.493 Å) is a bit larger than that of the bulk material (3.474 Å). This strain should play an important role in the conversion of single-crystal $SrFeO_{2.5}$ to single-crystal $SrFeO_2$.

In conclusion, we prepared single-crystal $SrFeO_2$ thin films by low-temperature reduction of single-crystal $SrFeO_{2.5}$ with CaH_2. XRD and XAS results show that the obtained $SrFeO_2$ sample is an oxygen-deficient perovskite with infinite layers of $Fe^{2+}O_2$. The present results demonstrate that this low-temperature reduction process and the lattice strain of the thin film remove some oxygen ions from the perovskite structure and rearrange the others, leading to the topotactic change from $SrFeO_{2.5}$ to $SrFeO_2$.

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