Quantitative analyses of oxidation states for cubic SrMnO_3 and orthorhombic $\text{SrMnO}_{2.5}$ with electron energy loss spectroscopy

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The oxidation state of Mn in cubic SrMnO_3 and orthorhombic $\text{SrMnO}_{2.5}$ was investigated by electron energy loss (EEL) spectroscopy. Change in the oxidation state of Mn produced some spectral changes in the O-K edge as well as in the Mn-L_{2,3} edge EEL spectra. This study demonstrated that the oxidation state of Mn and the amount of oxygen vacancies in cubic SrMnO_3 and orthorhombic $\text{SrMnO}_{2.5}$ could be quantified by analyzing the features of the O-K edge spectrum and the Mn L₃/L₂ ratio in the Mn-L_{2,3} edge spectrum. Our quantitative analysis showed that the spectral changes in the Mn-L_{2,3} edge were mainly caused by the oxidation state of Mn, whereas those in the O-K edge could be sensitive to both the oxidation state of Mn and to lattice distortions.

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I. INTRODUCTION

$\text{SrMnO}_{3-\delta}$ ($\delta=0-0.5$) mainly has three crystal structures: hexagonal SrMnO_3 , pseudocubic $\text{SrMnO}_{3-\delta}$, and cubic SrMnO_3 , depending on oxygen partial pressure and temperature.¹⁻³ Hexagonal SrMnO_3 has a space group of $P6_3/mmc$ and Mn oxidation state 4+. It is the most stable structure in the group of $\text{SrMnO}_{3-\delta}$ ($\delta=0-0.5$) compounds. Hexagonal SrMnO_3 transforms into the pseudocubic $\text{SrMnO}_{3-\delta}$ by introducing oxygen vacancies. The oxygen content in the pseudocubic $\text{SrMnO}_{3-\delta}$ is variable by changing annealing conditions such as oxygen partial pressure and temperature. A final reducing state of $\text{SrMnO}_{3-\delta}$ is $\text{SrMnO}_{2.5}$. $\text{SrMnO}_{2.5}$ has orthorhombic structure with a space group of $Pbma$ ($a=5.523$ Å, $b=10.761$ Å, and $c=3.811$ Å) and Mn oxidation state 3+.⁴ In the range $0<\delta<0.5$, the mixed valence state of Mn appears. At $\delta=0$, SrMnO_3 can have another cubic structure with a space group of $Pm3m$ ($a=3.805$ Å).⁵ To obtain cubic SrMnO_3 , a certain annealing condition of temperature and oxygen partial pressure is necessary in order to avoid the formation of hexagonal SrMnO_3 .⁶ Cubic SrMnO_3 does not contain oxygen vacancies and the linkage of the oxygen octahedrons does not contain distortions, and thus the oxidation state of Mn is 4+. On the other hand, pseudocubic $\text{SrMnO}_{3-\delta}$ and orthorhombic $\text{SrMnO}_{2.5}$ have a distorted linkage of oxygen octahedrons. The manner of the linkage and the distortion of the oxygen octahedrons are varied by the presence of oxygen vacancies.^{4,6,7}

The variation of the Mn oxidation states in $\text{SrMnO}_{3-\delta}$ is very attractive from a viewpoint of mixed valences of manganese oxides. For example, perovskite manganites of $\text{La}_x\text{A}_{1-x}\text{MnO}_3$ (A being a divalent cation) show remarkable properties such as colossal magnetoresistance (CMR) due to the correlation between magnetism and electronic states.⁸ In

the series of perovskite manganites, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSMO) is well known as a CMR materials. The end members of LaMnO_3 (Ref. 9) and cubic SrMnO_3 (Ref. 10) are both antiferromagnetic insulators with Mn valence of 3+ and 4+, respectively. By intermixing LaMnO_3 and SrMnO_3 , mixed valence states of Mn appear. The CMR property partly depends on the Mn oxidation state, which also depends on the La/Sr ratio. $\text{LaMnO}_3/\text{SrMnO}_3$ superlattices use the mixed valence state near the interface between LaMnO_3 and SrMnO_3 .¹¹ The valence state of Mn near the interface is considered to gradually vary from 3+ to 4+ over an area of a few atomic layers.¹²

In order to measure the variations of the Mn oxidation state at the nanoscale, electron energy loss (EEL) spectroscopy with scanning transmission electron microscopy (STEM) is very powerful.^{13,14} It is therefore important to obtain standard EEL spectra from $\text{SrMnO}_{3-\delta}$ ($0\leq\delta\leq0.5$) bulk materials for quantitative analysis of the Mn oxidation states in those manganese oxides. However, there are only a few studies reporting EEL spectra of $\text{SrMnO}_{3-\delta}$ ($0\leq\delta\leq0.5$). In this study, we aim to obtain O-K and Mn-L_{2,3} EEL spectra for a series of $\text{SrMnO}_{3-\delta}$ ($\delta=0$ and 0.5) bulk specimens and discuss the potential of the present method to quantify the oxidation state of Mn and the oxygen vacancy concentration.

II. EXPERIMENTAL

Polycrystalline samples of cubic SrMnO_3 and orthorhombic $\text{SrMnO}_{2.5}$ were prepared by solid-state sintering. At first, hexagonal SrMnO_3 powder was prepared by a conventional solid-state reaction method. The powder mixtures with appropriate molar quantities of SrCO_3 and $\text{Mn}(\text{NO}_3)_2\cdot6\text{H}_2\text{O}$ were calcined at 1300 °C for 5 h in air, and were confirmed to have hexagonal SrMnO_3 structure by x-ray diffractometry (XRD). After that, orthorhombic $\text{SrMnO}_{2.5}$ was obtained by heating the pellets made of the calcined powder at 1240 °C

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FIG. 1. (Color online) X-ray powder diffraction patterns of (a) cubic SrMnO_3 and (b) orthorhombic $\text{SrMnO}_{2.5}$, respectively. X-ray powder diffraction patterns previously reported are shown by the red lines (Refs. 1 and 15).

for 12 h in a vacuum with a back pressure of $\sim 3 \times 10^{-3}$ Torr and quenched into oil. As for cubic SrMnO_3 , the quenched sinters were annealed again at 350 °C for 24 h in air to reduce oxygen vacancies. This annealing condition does not induce a transformation from cubic SrMnO_3 to hexagonal SrMnO_3 .⁶

The prepared samples were characterized by XRD with Cu $K\alpha$ radiation ($\lambda = 1.5406$ Å). O-K and Mn- $L_{2,3}$ edge EEL spectra were obtained with crushed polycrystalline particles supported on holey carbon films by an EEL spectrometer (EELS, Model 766 Enfina, Gatan Inc.) attached to a STEM (JEM-2100F, JEOL Ltd.), which was operated at 200 kV. EEL spectra of O-K and Mn- $L_{2,3}$ edge were acquired from a relatively thin region at the same time. The backgrounds of these EEL spectra were removed by power law fitting. The dispersion of each channel, acquisition time, and energy spread of the electron beam (full width at half maximum of zero-loss peak) were 0.2 eV/ch, 15 s, and 1.0 eV, respectively.

III. RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of the synthesized cubic SrMnO_3 and orthorhombic $\text{SrMnO}_{2.5}$. The lattice parameters obtained in this study exhibit good agreement with those of previous reports, as shown with the red lines.^{1,15} The lattice parameters of cubic SrMnO_3 and orthorhombic $\text{SrMnO}_{2.5}$ obtained in this study were $a = 3.805$ Å and $a = 5.52$ Å, $b = 10.78$ Å, $c = 3.81$ Å, respectively. This confirms that cubic SrMnO_3 and orthorhombic $\text{SrMnO}_{2.5}$ specimens were obtained.

Figure 2 shows O-K and Mn- $L_{2,3}$ edges obtained from SrMnO_3 and $\text{SrMnO}_{2.5}$. In the figures, the onset of the O-K edge from SrMnO_3 was shifted to align with that from $\text{SrMnO}_{2.5}$. The Mn- $L_{2,3}$ edge was also shifted in the same way. Commonly for both specimens, the O-K edge consists

FIG. 2. (Color online) (a) O-K and (b) Mn- $L_{2,3}$ edge EEL spectra obtained from SrMnO_3 (red line) and $\text{SrMnO}_{2.5}$ (blue line).

of three main peaks (**a**, **b**, and **c**),¹⁴ and also a small peak (**a***) (Refs. 16 and 17) which appears between the peaks **a** and **b**. Detailed inspection reveals some differences in the O-K edge from the two specimens. The intensity of **a** and the energy difference (ΔE) between **a** and **b** increase as the Mn nominal oxidation state increases, and peak **a*** shifts to the higher energy side in the lower oxidation state (Mn^{3+}). In the Mn- $L_{2,3}$ edge, a chemical shift and a change in the Mn L_3/L_2 ratio are observed. The Mn- $L_{2,3}$ edge from SrMnO_3 is located 2.5 eV lower in energy than that from $\text{SrMnO}_{2.5}$, and the Mn L_3/L_2 ratio is smaller in SrMnO_3 . These spectral differences between the two samples must be related to the Mn oxidation states and, hence, the variation of oxygen vacancy content.

According to a previous report, the three major peaks **a**, **b**, and **c** in the O-K edge are caused by hybridizations of unoccupied O $2p$ orbitals with Mn $3d$, Sr $4d$, and Mn $4sp$ orbitals, respectively.^{16–20} Since oxygen vacancy formation results in the increase in the number of the Mn $3d$ electrons, the intensity and the position of **a** can be sensitive to the oxidation state of Mn and the oxygen vacancy content. In addition, it was also reported that the small peak **a*** in the O-K edge is due to hybridization with the Mn $3d$ t_{2g} band, which gives us information about the crystal-field t_{2g}/e_g splitting.^{16,17} On the other hand, since the $L_{2,3}$ edges of a transition metal oxide originate from the electron transition from $2p_{3/2}$ and $2p_{1/2}$ states to unoccupied $3d$ bands, the peak positions and Mn L_3/L_2 ratio are related to the Mn oxidation state. Hence, in order to precisely understand the oxidation states of Mn, it is necessary to discuss the variation of peaks (**a** and **a***) and ΔE in the O-K edge and the Mn L_3/L_2 ratio in the Mn- $L_{2,3}$ edge systematically.

The values estimated from the present data are shown in

FIG. 3. (Color online) The quantitative analysis of EEL spectra from experimental O-K and Mn- $L_{2,3}$ edges with Mn nominal oxidation state in (a) the normalized prepeak intensity of O-K edge, (b) the energy distance between the positions of prepeaks and second peaks, and (c) the Mn L_3/L_2 ratio. The linear fit to the data is shown by black lines. For comparison of results, the previous report of quantitative analysis and linear fit about the series of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ are shown with open squares and dashed lines (Ref. 14).

Fig. 3. Estimation of the values was performed in a similar way to the previous report.¹⁴ In the estimation, the spectral profiles of the peaks **a** and **b** in the O-K edge were fitted by a Gaussian function with DIGITAL MICROGRAPH (Gatan Inc.) software. As for the Mn L_3/L_2 ratio, in order to extract the white line integrated intensities, a Hartree–Slater function was used as a step function. The integrated areas were within the energy loss range of ± 10 eV from the energy loss at a minimum intensity between the L_2 and L_3 peaks, and a scaling window of 4 eV from the terminated position of the L_2 edge integration was used.

As seen in Fig. 3, when the Mn oxidation state increases, the intensity of **a** and ΔE increase while the Mn L_3/L_2 ratio decreases. In addition, the peak **a*** shifts to the lower energy side for the lower oxidation state (Mn^{3+}). It is also found that the three parameters show a linear relationship with the Mn oxidation state.

The increase in the peak **a** intensity in Mn^{4+} is explained by the less occupied Mn $3d$ orbital, and the decrease in the Mn L_3/L_2 ratio is caused by the decrease in the hybridization between the L_3 and L_2 edges.²⁰ The shift in the peak **a*** is accounted for by the fact that the t_{2g}/e_g splitting becomes larger by the presence of one more electron for Mn^{3+} than for Mn^{4+} . These spectral changes are similar to that reported for $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ (LCMO).¹⁴ The results in LCMO are compared with that in $\text{SrMnO}_{3-\delta}$ ($\delta=0$ and 0.5) in the same figure. By comparing those different compounds, it is seen

that the changes of the Mn L_3/L_2 ratio are almost identical to each other [Fig. 3(c)], whereas the peak **a** intensity and ΔE in the O-K edge are more sensitively changed in $\text{SrMnO}_{3-\delta}$ ($\delta=0$ and 0.5) than LCMO [Figs. 3(a) and 3(b)]. These different behaviors can be ascribed to the bond length changes induced by cation doping or oxygen vacancies. In the case of LCMO, the difference of lattice parameters for LaMnO_3 (Ref. 21) and CaMnO_3 (Ref. 22) is $0.21 \text{ \AA}$. On the other hand, the difference between the lattice parameter for $\text{SrMnO}_{2.5}$ (Ref. 4) and SrMnO_3 (Ref. 7) is $0.05 \text{ \AA}$. Here, these lattice parameters were calculated for a pseudocubic or cubic structure. Namely, $\text{SrMnO}_{3-\delta}$ ($\delta=0$ and 0.5) can change Mn oxidation state with only a small change in the lattice. As mentioned above, the Mn- $L_{2,3}$ edge is caused by the electron transition from the Mn $2p$ to Mn $3d$ orbitals, both of which are commonly localized. On the other hand, although the O-K edge has similar information to the Mn- $L_{2,3}$ edge, the O-K edge has relatively delocalized information because it originates from the O $2p$ orbitals hybridized with the Mn $3d$ orbitals. Thus, the spectral changes in the Mn- $L_{2,3}$ edge are less sensitive to the lattice changes, whereas those in the O-K edge can be sensitive to both the Mn oxidation state and to the lattice distortion.

This result indicates that the oxidation state of Mn and the amount of oxygen vacancies, which would cause lattice distortions, can in perovskite manganese oxides be quantified by analyzing those spectral changes in the O-K and Mn- $L_{2,3}$ edge spectra.

IV. SUMMARY

Quantitative analysis of Mn oxidation states was performed by EEL spectroscopy for cubic SrMnO_3 and orthorhombic $\text{SrMnO}_{2.5}$, whose Mn oxidation states are $4+$ and $3+$, respectively. It was found that the intensity of peak **a**, the position of peak **a*** and the ΔE value of the O-K edge, and the Mn L_3/L_2 ratio of the Mn- $L_{2,3}$ edge all depend on the Mn oxidation state. The spectral changes in the Mn- $L_{2,3}$ edge are less sensitive to lattice changes, whereas those in the O-K edge can be sensitive to both the Mn oxidation state and lattice distortions. We think that these results can be used as a reference for the investigation of Mn oxidation states and, hence, the oxygen vacancy content in manganese perovskite oxide family materials.

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