DEVELOPMENT OF IN SITU SOFT X-RAY ABSORPTION SPECTROSCOPIC TECHNIQUE UNDER HIGH TEMPERATURE AND CONTROLLED ATMOSPHERE

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Abstract

In this study, *in situ* soft X-ray absorption spectroscopy (soft XAS) technique, which enables us to analyze electronic structures of oxides at elevated temperatures while controlling atmospheric conditions, was developed. The technique was applied to investigate the electronic structures of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$. X-ray absorption spectra at the Co *L*-edges and the O

K-edge were measured in the temperature range from room temperature to 873 K and the $p(\text{O}_2)$ range from 10^{-4} to 10^{-2} bar. The developed *in situ* soft XAS technique is found to be effective for evaluating electronic structures of oxides under controlled temperature and $p(\text{O}_2)$.

Keywords: Soft X-ray, X-ray absorption spectroscopy, *in situ*, high temperature

1. Introduction

Ion/electron conducting oxides are widely utilized in electrochemical devices such as solid oxide fuel cells (SOFCs), lithium-ion secondary batteries and so on. In order to improve the device performance, it is essential to understand electronic structures of the components, which are often related deeply to their electrical and electrochemical properties. For the analysis of electronic structures of oxides, X-ray absorption spectroscopy (XAS) is frequently applied. XAS is a spectroscopic analytical technique detecting the excitation of core electrons by the X-ray irradiation, and is available to examine unoccupied orbitals of materials. In the case of 3d transition metal oxides, hybrid orbitals between the transition metal 3d and oxygen 2p orbitals are known to be responsible for their electronic properties. When XAS is applied to investigate electronic states of those orbitals, it is required to measure X-ray absorption at the 3d transition metal L_{II} - and L_{III} -edges and the O *K*-edge, which give us information on electronic structures of the transition metal 3d and oxygen 2p orbitals, respectively.

Energies of above absorption edges range between 500 and 900 eV, *i.e.* in the soft X-ray region. Since soft X-ray is easily absorbed even by gases such as N₂, O₂, H₂O and so on, it is difficult for X-ray to penetrate the long distance in atmospheres containing above gases. Thus, in general, soft XAS measurements are carried out in high vacuum conditions. However, measurements in high vacuum conditions are not desirable for the analysis of oxides, because oxides can change their oxygen nonstoichiometry and electronic structures depending on atmospheric $p(\text{O}_2)$ [1].

In order to avoid such problems, in this work, we developed *in situ* soft XAS technique which can be used under desired temperature and atmospheric conditions. $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ having the perovskite-type structure was chosen as a model oxide. $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ is a candidate of SOFC cathode materials because of their high electronic/ionic conductivity and high catalytic activity for the reduction of oxygen gas [2, 3]. XAS spectra at the Co L_{II} - and L_{III} -edges and the O K -edge were measured under $p(\text{O}_2) = 10^{-4} - 10^{-2}$ bar at RT - 873 K, and validity of the developed technique was confirmed.

2. Experimental

2.1 Sample preparation

For the preparation of a dense compact of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$, the commercially available powder (AGC SEIMI CHEMICAL Co., Ltd.) was uniaxially pressed in a cylindrical shape, and was sintered at 1473 K for 4 hours. The relative density of the obtained compact

was higher than 92%. The compact was cut into a plate shape of $5 \times 3 \times 0.8$ mm and polished with the diamond paste of 3 μm . Before XAS measurements, the $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ compact was annealed at 973 K for 2 hours and slowly cooled down to 473 K for 4 days under 1% O_2 -Ar gas.

2.2 Soft X-ray absorption spectroscopy

Soft XAS measurements were performed at the beam line of BL27SU at SPring-8, JASRI, Japan. The system for soft XAS under controlled atmosphere at elevated temperature was developed based on the differential pumping system for soft XAS under normal atmospheric conditions by Tamenori [4]. In order to control partial gas pressures while ensuring the sufficient incident X-ray, the sample chamber was separated from the optical upstream part with an Si_3N_4 thin film window of 500 nm. To achieve *in-situ* soft XAS measurements at elevated temperature, a special sample holder was designed and fabricated. In this holder, the Pt-Ir electric furnace was used to heat the sample and the sample was placed inside the furnace to reduce the thermal noises from the furnace as much as possible. The specimen was tilted at a 45 degrees angle to the incidence X-ray and the fluorescence X-ray detector, so that the incident X-ray could be delivered to wider area on the sample surface and the exited fluorescence X-ray was detected efficiently. Inside the sample chamber, the mixture of He and O_2 gases was flowed to control $p(\text{O}_2)$ around the sample. In order to minimize the X-ray absorption by gases, the light passes in the sample chamber were designed to be as short as

possible.

In this work, soft XAS measurements of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ at Co L_{II} - (~795 eV) and L_{III} -edge (~780 eV) and O K -edge (~530 eV) were performed with the fluorescence mode by using a photodiode as a detector. Temperature was controlled from room temperature to 873 K. Oxygen partial pressure was controlled from 10^{-4} to 10^{-2} bar, and was monitored by a zirconia oxygen sensor at the outlet from the sample chamber.

3. Results and Discussion

X-ray absorption spectra of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ at the Co L -edges and O K -edge were measured under $p(\text{O}_2) = 10^{-4} - 10^{-1}$ bar at various temperatures. Fig. 1 shows the absorption spectra of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ at the Co L -edges under $p(\text{O}_2) = 10^{-4} - 10^{-1}$ bar at room temperature. The spectra were normalized by the peak height at 780 eV. Absorption spectra were clearly observed under $p(\text{O}_2) = 10^{-4} - 10^{-2}$ bar. On the other hand, spectra could not be observed under $p(\text{O}_2) = 10^{-1}$ bar. In the case of X-ray of 780 eV, if we assume 5 cm of the light pass, approximately 55 % of X-ray can penetrate under 1 % O_2 -He mixed gas. However, only 0.3 % of X-ray can penetrate through 5 cm under 10 % O_2 -He mixed gas. It is thought that such a difference in the penetrating power of soft X-ray against oxygen gas decides the $p(\text{O}_2)$ limit for *in situ* soft XAS measurements in our setup. Normalized absorption spectra of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ at the Co L -edges under $p(\text{O}_2) = 10^{-4}$ bar at various temperatures were shown in Fig. 2. At 873 K, soft XAS measurements were performed two times and X-ray absorption

spectrum was averaged in order to minimize the influence of the thermal noises. Absorption spectra were clearly observed at temperatures lower than 873 K, while spectra could not be obtained at above 873 K. This is possibly because radiation from the furnace became significant with increasing temperature. From the results given in Figs. 1 and 2, it was demonstrated that the *in situ* XAS technique developed in this work enables us to measure absorption spectra in soft X-ray region while controlling temperature lower than 873 K and $p(\text{O}_2)$ lower than 10^{-1} bar.

In the absorption spectra of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ at L_{III} -edge shown in Figs. 1 and 2, a shoulder at the lower energy side of the main peak was observed. The absorption of incident X-ray is caused by the transition of the core orbital electron to the unoccupied levels. This means that XAS spectra reflect the spin state and the valence state of the investigated atom. In the case of Co L_{II} - and L_{III} -edges, XAS spectra were associated with the transition of electrons from the Co 2p to the 3d state. In $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$, the mean valence of cobalt ions is considered as higher than 3. As temperature increases, the mean valence decreases even under the constant oxygen partial pressure, because of the formation of oxygen vacancies[1]. However, in this study, the spectrum shape did not change apparently. The reason for this is possibly because the variation in the mean valence of cobalt ions were negligible, because the amount of formed oxygen vacancies is small under the experimental conditions [5]. Another possible explanation is that the change in the oxygen nonstoichiometry did not considerably affect the

electronic structures in the Co 3d band because the Co 3d band is strongly hybridized with the O 2p band [6].

Fig.3 show the absorption spectra of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ at the O *K*-edge under $p(\text{O}_2) = 10^{-4}$ bar at various temperatures. The spectra were normalized to equalize the peak heights at 527 eV.

At 873 K, soft XAS measurements were performed three times and X-ray absorption spectrum was averaged. The absorption spectra at the O *K*-edge were associated with the transition of electrons from the O 1s core level to the unoccupied states in the O 2p level, hybridized with the orbitals of bonding cations. According to Abbatte *et al.*, peaks around 527 eV are assigned to the unoccupied orbitals of O 2p orbital hybridized with Co 3d orbital [7].

Since the X-ray energy for XAS measurements at the O *K*-edge is much lower than that at the Co *L*-edge, the absorption of X-ray by atmospheric gases is considered more significant. Nevertheless, it was found that O *K*-edge absorption spectra could be observed below 773 K by using *in situ* XAS system developed in this work. XAS measurement was carried out under atmosphere containing oxygen gas. Thus, absorption spectra at the O *K*-edge would include signals from not only oxide ions in $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ but also oxygen gas and moisture in atmosphere. A small peak at around 530 eV, shown by an open triangle, is assigned to oxygen gas, and small peaks at around 533 – 538 eV, shown by closed triangles, are attributed to H_2O gas [8]. However, as shown in Fig. 3, the absorption peaks due to the oxide and the gases were

separately observed. In particular, the absorption peaks assigned to the hybridized orbitals with the Co 3d band, which are strongly related to electronic properties, did not overlap with those assigned to the atmospheric gases. This indicated that the developed technique is applicable for examining electronic structures of oxides, especially functional oxides for high temperature uses.

4. Conclusions

Novel *in situ* soft X-ray absorption spectroscopy technique was developed in this study and applied to investigate electronic structures of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ under controlled temperature and $p(\text{O}_2)$. It was found out that the developed system enabled us to measure X-ray absorption spectra in the soft X-ray region, e.g. 500 –900 eV, under $p(\text{O}_2)$ lower than 10^{-2} bar and at temperatures up to 873 K. The developed technique can be a powerful tool to evaluate electronic structures of functional oxides for high temperature electrochemical devices.

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Figure Captions

Fig. 1: X-ray absorption spectra of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ at Co L_{II} - and L_{III} -edges under $p(\text{O}_2) = 10^{-4} - 10^{-1}$ bar at room temperature.

Fig. 2: X-ray absorption spectra of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ at Co L_{II} - and L_{III} -edges under $p(\text{O}_2) = 10^{-4}$ bar at various temperatures.

Fig. 3: X-ray absorption spectra of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ at O K -edge under $p(\text{O}_2) = 10^{-4}$ bar at various temperatures.

Figure 1

Figure 2

Figure(3)