

Electronic Structure in the Band Gap of Protonic Conductor $\text{Sr}[\text{Ce}_x\text{Zr}_{1-x}]_{0.95}\text{Yb}_{0.05}\text{O}_3$ Thin Film

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The electronic structure in the band gap of protonic conductor $\text{Sr}[\text{Ce}_x\text{Zr}_{1-x}]_{0.95}\text{Yb}_{0.05}\text{O}_3$ thin film has been studied by soft-X-ray absorption spectroscopy (XAS). Below the O 1s threshold, the XAS spectra show two features whose energy positions match with the holes state at the top of the valence band and acceptor or proton-induced levels just above the Fermi level (E_F). The energy separation between the holes state and E_F agrees with the activation energy estimated from the electrical conductivity. [DOI: 10.1143/JJAP.42.5696]

KEYWORDS: $\text{Sr}[\text{Ce}_x\text{Zr}_{1-x}]_{0.95}\text{Yb}_{0.05}\text{O}_3$, protonic conductor, electronic structure, soft-X-ray absorption spectroscopy (XAS), hole, proton-induced level

Perovskite-type oxides, such as SrCeO_3 and SrZrO_3 , exhibit high protonic conductivity at sufficiently high temperature region when they are doped with acceptor ions.^{1–8)} These protonic conductors are important materials for a wide range of electrochemical applications, such as fuel cells, hydrogen sensors and so on. Many theoretical and experimental investigations into the mechanism have been reported in the case of ceramic and single crystal samples.^{1–10)} It has been clarified that the local lattice distortion due to acceptor-doping plays an important role in the proton migration mechanism in these protonic conductors. Sata and coworkers attempted to fabricate a locally distorted thin film of proton conductors by the pulsed laser ablation (PLD) method and found that the lattice distortion and the proton conductivity depends on the thickness ratio of $\text{SrZr}_{0.95}\text{Yb}_{0.05}\text{O}_3$ to $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$.^{11–13)}

In recent years, the electronic structure of perovskite-type protonic conductor has been investigated by X-ray absorption spectroscopy (XAS).^{8,14–17)} In Sc-doped SrTiO_3 , the XAS spectra show the holes state at the top of the valence band and acceptor-induced level just above the Fermi level (E_F). The authors have reported that the XAS features and their temperature dependence reflect the activation energy estimated from the electrical conductivity studies.^{14–17)} Similar results are obtained in In-doped CaZrO_3 and Sc-doped SrZrO_3 .^{8,17)} Such a situation might also be expected for $\text{Sr}[\text{Ce}_x\text{Zr}_{1-x}]_{0.95}\text{Yb}_{0.05}\text{O}_3$ thin film.

In this study, the electronic structure of protonic conductor $\text{Sr}[\text{Ce}_x\text{Zr}_{1-x}]_{0.95}\text{Yb}_{0.05}\text{O}_3$ thin film has been investigated by the XAS technique. The XAS is related directly to the unoccupied density-of-state (DOS).¹⁴⁾ This optical process is a rather local process, because of the localized core state. It is governed by the dipole selection rules so that XAS yields the spectrum relating to the site- and symmetry-selected DOS. Therefore, the holes at the top of the valence band or proton-induced level near E_F , which provide the electrical conductivity, might be observed by careful measurements using high-resolution and high-brightness XAS. In this paper, we present high-resolution XAS spectra of $\text{Sr}[\text{Ce}_x\text{Zr}_{1-x}]_{0.95}\text{Yb}_{0.05}\text{O}_3$ thin film and show how the features found in the band gap region are related to the protonic conductivity.

$\text{Sr}[\text{Ce}_x\text{Zr}_{1-x}]_{0.95}\text{Yb}_{0.05}\text{O}_3$ thin film was prepared by the

PLD method using an ArF excimer laser ($\lambda = 193$ nm). Sintered ceramics of $\text{SrZr}_{0.95}\text{Yb}_{0.05}\text{O}_3$ and $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ were used for ablation targets. The Ce concentration was $x = 0.8$ and 1.0. A single crystal of Si (111) was used as the substrate. The substrate temperature during deposition was about 700°C. The ablation chamber was evacuated to 10^{-7} Pa and then 0.5 Pa oxygen gas was introduced into the chamber only after deposition started to avoid oxidation of the Si substrate. The film thickness was about 400 nm in the case of all the thin films. For $\text{Sr}[\text{Ce}_{0.8}\text{Zr}_{0.2}]_{0.95}\text{Yb}_{0.05}\text{O}_3$ thin film, the film thicknesses of $\text{SrZr}_{0.95}\text{Yb}_{0.05}\text{O}_3$ and $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ were 320 nm and 80 nm, respectively. The prepared thin films were annealed at 800°C for 6 h in wet air moisturized by bubbling of H_2O at 60°C. Then, the electrical conductivity was $4.5 \times 10^{-6} \text{ cm}^{-1} \Omega^{-1}$.^{9,10)}

The XAS measurements were carried out at the revolver undulator beamline BL-19B at the Photon Factory (PF) of the High Energy Accelerator Organization (KEK), Tsukuba in Japan. Synchrotron radiation from the undulator was monochromatized using a grating monochromator. High brightness with high resolution is realized using a varied line spacing plane grating monochromator. The resolution of about $\Delta E/E = 2 \times 10^{-4}$ at $h\nu = 400$ eV and high photon flux of about 10^{12} – 10^{13} photons/s is realized with the spot size of 100 μm . The XAS spectra were measured by collecting the total fluorescence yield. The incidence angle of X-ray was about 90° against the surface in order to avoid the surface effect.

Figure 1 shows the O 1s XAS spectra of $\text{Sr}[\text{Ce}_x\text{Zr}_{1-x}]_{0.95}\text{Yb}_{0.05}\text{O}_3$ thin films. As a reference, the O 1s XAS spectrum of undoped SrCeO_3 thin film is also shown in this figure. From the dipole selection rule, it is understood that the O 1s XAS spectra of Ce or Zr oxides correspond to the transition from O 1s character to O 2p character hybridized with unoccupied Ce 4f and Zr 4d states.^{14–17)} The O 1s XAS spectra are normalized by the Sr 4d peak of the conduction band, though the peak is not shown in this figure. The feature around ~534 eV is considered to be composed of the Ce 4f and Zr 4d states hybridized with the O 2p state. The spectral intensity below the threshold is magnified ten times and is shown as a thick line above each XAS spectrum in order to obtain reliable information of the band gap energy region. In this energy region, the electronic

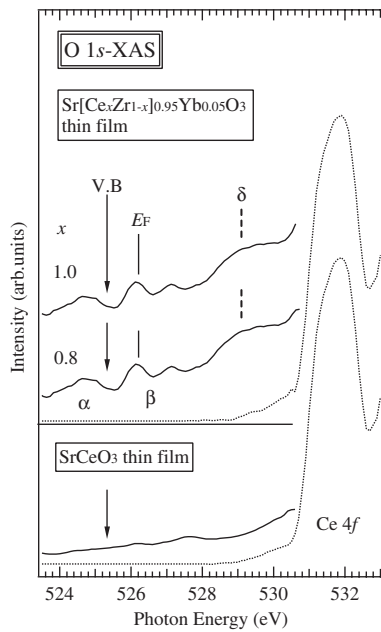


Fig. 1. O 1s XAS spectra as a function of Ce concentration of $\text{Sr}[\text{Ce}_x\text{Zr}_{1-x}]_{0.95}\text{Yb}_{0.05}\text{O}_3$ thin films. As a reference, the O 1s XAS spectrum of undoped SrCeO_3 thin film is also shown. Thick lines show the O 1s XAS spectra on an expanded scale. The vertical bar is the position of E_F estimated from the binding energy of O 1s photoemission peak. Arrow (V.B) indicates the top of the valence band.

structure related to the proton conductivity can be elucidated. The arrow shows the top of the valence band. The E_F is determined from the binding energy of the O 1s photoemission peak.

It is striking that three features corresponding to α , β and δ peaks are observed in the band gap energy region of $\text{Sr}[\text{Ce}_x\text{Zr}_{1-x}]_{0.95}\text{Yb}_{0.05}\text{O}_3$ thin films, though there is no structure in the band gap of nondoped SrCeO_3 thin film. Similar features have been reported in $\text{SrCe}_{1-x}\text{Y}_x\text{O}_{3-\delta}$ ceramics.¹⁵ The large feature δ is considered to be defect-induced levels of the Ce 4*f* and Zr 4*d* states, since the feature is located at the bottom of the conduction band. The feature α may be assigned to holes created by Yb^{3+} doping at the top of the valence band, since the intensity of α does not depend on the Ce concentration. This fact indicates that the doped acceptor is introduced into the top of the valence band, which consists of the O 2*p* nonbonding state. On the other hand, the feature β at or near E_F splits into two structures, which may be assigned to the acceptor and proton-induced levels, as expected from the rigid-band model. The energy separation between the hole state and E_F is about 0.7 eV. This value is near the activation energy estimated from the electrical conductivity.^{11–13}

It has been reported that the electrical conductivity increases slightly with increasing Ce concentration, and the thin film with $x = 0.8$ exhibits sufficiently higher conductivity than any other.^{11–13} This result indicates that the proton concentration is the largest at $x = 0.8$, though the

E_A is almost the same in this Ce content region. In the infrared absorption spectra of O–H stretching,¹¹ five absorption bands, which correspond to five different sites of protons, are observed in the wave number range from 2000 to 3500 cm^{-1} . The intensity of the absorption band at the high-energy side ($\sim 3200 \text{ cm}^{-1}$), which is assigned to the proton site accompanying a dopant cation, is the highest at $x = 0.8$. These facts indicate that the protonic conduction is controlled by local lattice distortion. Therefore, the electronic structure with the lattice distortion has to be clarified in future studies.

In conclusion, we studied the electronic structure in the band gap energy region of protonic conductor $\text{Sr}[\text{Ce}_x\text{Zr}_{1-x}]_{0.95}\text{Yb}_{0.05}\text{O}_3$ thin films using high-resolution XAS. The O 1s XAS spectra show two features, corresponding to acceptor level near E_F and hole states created at the top of the valence band. The energy separation between E_F and hole state reflects E_A estimated from the electrical conductivity.

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