

## Electronic Structure in the Band-Gap Region of Protonic Conductor $\text{SrZr}_{0.90}\text{Y}_{0.10}\text{O}_{3-\delta}$

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The electronic structure in the band-gap region of protonic conductor  $\text{SrZr}_{0.90}\text{Y}_{0.10}\text{O}_{3-\delta}$  was studied by soft-X-ray absorption spectroscopy (XAS). The O 1s XAS spectrum of air-annealed  $\text{SrZr}_{0.90}\text{Y}_{0.10}\text{O}_{3-\delta}$  exhibits three distinct features, namely, the holes on top of the valence band, acceptor-induced level just above the Fermi level and Zr 4d defect-induced level at the bottom of the conduction band, which are lower in the O 1s XAS spectrum of wet-annealed  $\text{SrZr}_{0.90}\text{Y}_{0.10}\text{O}_{3-\delta}$ . These findings directly indicate that the doped hydrogen compensates the presence of the holes. [DOI: 10.1143/JJAP.43.5419]

KEYWORDS:  $\text{SrZr}_{0.90}\text{Y}_{0.10}\text{O}_{3-\delta}$ , soft-X-ray absorption spectroscopy (XAS), band-gap, electronic structure, holes, acceptor

Perovskite-type oxide  $\text{SrZrO}_3$  in which a trivalent cation is partially substituted for a  $\text{Zr}^{4+}$  site exhibits appreciable proton conduction under hydrogen-containing atmosphere at high temperature.<sup>1–6</sup> Protonic conductivity at high temperature has many promising potential electrochemical applications such as in a fuel cell and hydrogen pump. In particular,  $\text{Y}^{3+}$ -doped  $\text{SrZrO}_3$  ( $\text{SrZr}_{1-x}\text{Y}_x\text{O}_{3-\delta}$ ) is a good protonic conductor that can be used in relatively high temperature. Proton conductivity is referred to as hole conduction; proton transfer numbers decrease at high temperatures above 700°C.<sup>3</sup> Protonic conductivity increases rapidly with increasing  $\text{Y}^{3+}$  concentration and becomes almost constant at  $x > 0.05$ , though the activation energy decreases with increasing  $\text{Y}^{3+}$  concentration. The proton diffusion of  $\text{SrZr}_{0.95}\text{Y}_{0.05}\text{O}_{3-\delta}$  was observed by quasielastic neutron scattering. Sata *et al.*<sup>7</sup> have reported that the temperature dependence of the linewidth of the quasielastic component is well elucidated by thermal-activation-type proton migration with activation energy ( $E_A$ ) of 0.2 eV.

The band structures of perovskite-type protonic conductors have been probed by soft-X-ray absorption spectroscopy (XAS).<sup>8–10</sup> XAS spectra are related directly to the unoccupied density of states (DOS). This optical process is rather local process, because of the localized core state. It is governed by dipole selection rules so that XAS gives the spectrum related to the site- and symmetry-selected DOS. In  $\text{SrCe}_{1-x}\text{Y}_x\text{O}_{3-\delta}$ ,<sup>10</sup> XAS spectra exhibit two empty states, which correspond to the holes at the top of the valence band (VB) and acceptor level just above the Fermi level ( $E_F$ ). The number of holes and acceptor level decrease with hydrogen doping, suggesting that hydrogen compensates the presence of the holes created at the VB by acceptor doping. The hydrogen-induced level is also created at just below  $E_F$ . The energy separation between the holes and hydrogen-induced level coincides with  $E_A$  estimated from transport properties.

In this study, the electronic structure in the band-gap energy region of protonic conductor  $\text{SrZr}_{0.90}\text{Y}_{0.10}\text{O}_{3-\delta}$  was measured by XAS. As references, soft-X-ray emission spectroscopy (SXES) spectra, which reflect the band structure in the valence band region, are also measured.

$\text{SrZr}_{0.90}\text{Y}_{0.10}\text{O}_{3-\delta}$  samples were sintered ceramics prepared by the solid state reaction of  $\text{SrCO}_3$ ,  $\text{ZrO}_2$ , and  $\text{Y}_2\text{O}_3$ , and pressed into cylinders of  $\phi 10 \text{ mm} \times 5 \text{ mm}$ , then sintered

again in air at 1700°C for 10 h. Wet-annealed samples were prepared in an atmosphere of saturated  $\text{H}_2\text{O}$  vapor at 17°C. The prepared ceramics were confirmed to have a single phase with a perovskite structure by powder X-ray diffraction analysis.

The XAS and SXES measurements were carried out at the revolver undulator beamline BL-19B at the Photon Factory of the High Energy Accelerator Organization, Tsukuba, Japan. The XAS spectra were measured using a Si photodiode. The SXES spectra were measured using a soft-X-ray emission spectrometer.

Figure 1 shows the O 1s SXES spectra of air-annealed and wet-annealed  $\text{SrZr}_{0.90}\text{Y}_{0.10}\text{O}_{3-\delta}$ . The clear selection rule of SXES is implemented mainly within the same atomic species, because the core hole is strongly localized. For this reason, the O 1s SXES spectra reflect the O 2p partial density of states in the valence band region.<sup>8</sup> The dashed line at  $\sim 525.8 \text{ eV}$  indicates the position of the VB. The bandwidth and peak position do not differ in either spectrum. The authors have reported that the Zr 4d contribution is more significant on the higher binding energy side of the valence band, where the bonding O 2p states have a larger

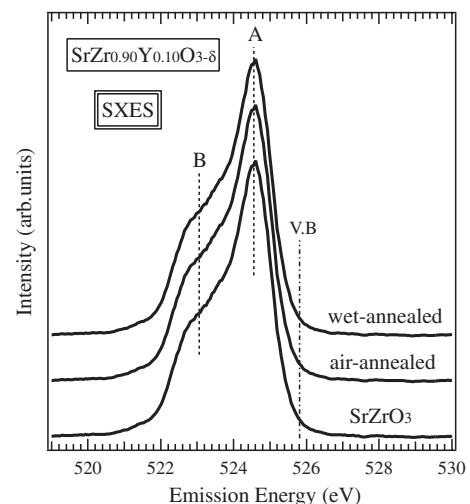


Fig. 1. O 1s SXES spectra of air- and wet-annealed  $\text{SrZr}_{0.90}\text{Y}_{0.10}\text{O}_{3-\delta}$ . As a reference, the spectrum of undoped  $\text{SrZrO}_3$  is also shown.

admixture of Zr 4d states.<sup>9)</sup> For CaZrO<sub>3</sub>, A and B peaks corresponding to those in the SXES spectrum of SrZrO<sub>3</sub> are estimated to represent the nonbonding state and the bonding state that is well mixed with the Zr 4d state, respectively. Such a situation is also expected for SrZrO<sub>3</sub>.

Figure 2 shows the O 1s XAS spectra of air-annealed and wet-annealed SrZr<sub>0.90</sub>Y<sub>0.10</sub>O<sub>3-δ</sub>. From the dipole selection rules, it is understood that the O 1s XAS spectra of Zr oxides correspond to transitions from O 1s to O 2p.<sup>8-10)</sup> The large band around 532.5 eV is mainly composed of the O 2p state hybridized with the unoccupied Zr 4d state. The spectral intensity below the threshold is expanded by ten times and is shown as a thick line above the XAS spectrum in order to show the electronic structure in the band gap energy region. The XAS features correspond to the thermally excited structure from the valence band. Each  $E_F$  is determined from the binding energy of the O 1s photoemission peak.  $E_F$  of air-annealed SrZr<sub>0.90</sub>Y<sub>0.10</sub>O<sub>3-δ</sub> is located at ~0.7 eV on top of the valence band.  $E_F$  of wet-annealed SrZr<sub>0.90</sub>Y<sub>0.10</sub>O<sub>3-δ</sub> shifts to the conduction band side by approximately 0.4 eV. This shift of  $E_F$  expected from the rigid-band model indicates the existence of hydrogen, which acts as a donor in the crystal lattice.

In air-annealed SrZr<sub>0.90</sub>Y<sub>0.10</sub>O<sub>3-δ</sub>, three features denoted by the  $\alpha$ ,  $\beta$ , and  $\delta$  peaks are observed in the band-gap energy region, though there is no structure in the band gap of undoped SrZrO<sub>3</sub>. The distinct feature  $\delta$  is considered to be a defect-induced level of the Zr 4d state, since the feature is located at the bottom of the Zr 4d conduction band. A similar defect-induced level has been reported in In<sup>3+</sup>-doped CaZrO<sub>3</sub>.<sup>10)</sup> The feature  $\alpha$  is assigned to holes created by Y<sup>3+</sup> doping at the VB, which is mainly composed of nonbonding O 2p states in the valence band. In the absorption spectra of the vacuum ultraviolet region, Sata *et al.* reported that the band gap of SrZr<sub>1-x</sub>Y<sub>x</sub>O<sub>3-δ</sub> increases with increasing Y<sup>3+</sup> concentration.<sup>11)</sup> The increase in band gap contributes to the presence of holes created at the VB. This finding indicates that the filling of the acceptor is rigid-band-like. The feature

$\beta$  at  $E_F$  is assigned to the acceptor level, since it lies immediately above  $E_F$ .

In wet-annealed SrZr<sub>0.90</sub>Y<sub>0.10</sub>O<sub>3-δ</sub>, the holes ( $\alpha$ ) at the VB disappear and the intensity of the Zr 4d defect-induced level ( $\delta$ ) decreases. These behaviors indicate that the doped hydrogen compensates the presence of the holes and vacancies in the crystal lattice.  $E_F$  of hydrogen-doped SrZr<sub>0.90</sub>Y<sub>0.10</sub>O<sub>3-δ</sub> shifts to the conduction band side by approximately 0.4 eV and the acceptor level ( $\beta$ ) splits into two features around  $E_F$ . The feature  $\beta$  below  $E_F$  contributes to the presence of the thermally excited hydrogen from the VB, since the energy separation between the VB and the bottom of the hydrogen-induced level is approximately 0.6 eV, which corresponds to  $E_A$  of wet-annealed SrZr<sub>0.90</sub>Y<sub>0.10</sub>O<sub>3-δ</sub>. This value is near the activation energy estimated from the electrical conductivity and the potential barrier for proton hopping in hydrogen bonding systems calculated by Islam<sup>12)</sup> and Yoshino *et al.*<sup>13)</sup>

In conclusion, we have studied the electronic structure in the band gap energy region of the protonic conductor SrZr<sub>0.90</sub>Y<sub>0.10</sub>O<sub>3-δ</sub> by XAS and SXES. The valence band is mainly composed of O 2p states. The O 1s XAS spectra of air-annealed SrZr<sub>0.90</sub>Y<sub>0.10</sub>O<sub>3-δ</sub> exhibit three distinct features, namely, the holes on top of VB, acceptor level just above  $E_F$ , and Zr 4d defect-induced level at the bottom of the conduction band, which are lower in wet-annealed SrZr<sub>0.90</sub>Y<sub>0.10</sub>O<sub>3-δ</sub>. This indicates that the doped hydrogen compensates the presence of the holes and vacancies. The energy separation between the holes and the bottom of the proton-induced level is in agreement with  $E_A$  estimated from the conductivity measurement.

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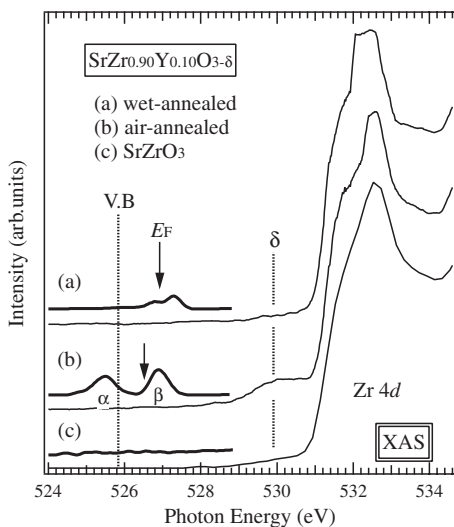


Fig. 2. O 1s XAS spectra of air- and wet-annealed SrZr<sub>0.90</sub>Y<sub>0.10</sub>O<sub>3-δ</sub>. As a reference, the spectrum of undoped SrZrO<sub>3</sub> is also shown. The dashed line indicates the top of the valence band (VB) estimated from Fig. 1.

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