Brief Communication

Electronic Structure of Protonic Conductor SrTi$_{0.98}$Sc$_{0.02}$O$_3$ Probed by Soft-X-ray Spectroscopy

Tohru HIGUCHI, Shu YAMAGUCHI[1], Shik SHIN[2,3], Takeshi HATTORI and Takeyo TSUKAMOTO

Department of Applied Physics, Tokyo University of Science, Tokyo 162-8601, Japan
[1]*Department of Materials and Science, University of Tokyo, Tokyo 113-8656, Japan*
[2]*Institute for Solid State Physics, University of Tokyo, Chiba 277-8581, Japan*
[3]*RIKEN, Hyogo 679-5143, Japan*

The electronic structure of a protonic conductor Sc-doped SrTiO$_3$ (SrTi$_{0.98}$Sc$_{0.02}$O$_3$) single crystal has been studied by photoemission spectroscopy and X-ray absorption spectroscopy. The holes and acceptor level are observed at the top of the valence band and just above the Fermi level (E_F), respectively, in dried SrTi$_{0.98}$Sc$_{0.02}$O$_3$. Their intensities are lower in H$_2$-annealed SrTi$_{0.98}$Sc$_{0.02}$O$_3$. The E_F of H$_2$-annealed SrTi$_{0.98}$Sc$_{0.02}$O$_3$ shifts to the conduction band side by approximately 0.4 eV compared with that of a dried sample. These findings indicate that the doped hydrogen compensates the existence of the holes. [DOI: 10.1143/JJAP.44.285]

Perovskite-type compounds such as SrCeO$_3$, CaZrO$_3$ and BaCeO$_3$ show hole conductivity as well as protonic conductivity in a very high temperature region when doped with acceptor ions.[1,2] Protonic conductors are important materials for a wide variety of electrochemical applications such as fuel cells and hydrogen sensors in the renewable energy source industry. A Sc-doped SrTiO$_3$ (SrTi$_{1-x}$Sc$_x$O$_3$) single crystal also exhibits a significantly higher conductivity than the pure one, and the crystal with $x = 0.02$ exhibits a sufficiently higher conductivity than any other crystals.[3,4] The activation energy of the SrTi$_{1-x}$Sc$_x$O$_3$ crystal decreases rapidly with increasing Sc^{3+} concentration at $x \leq 0.02$, and then increases slightly when $x > 0.02$. The microscopic mechanism has been studied by first-principles calculation, neutron diffraction and spectroscopy.[3,5–9] It has been shown that, in a stable ionic configuration, the position of a proton is between two neighboring O ions, and the proton is bound to one O ion with an O–H bond length of about 1.3 Å; this looks like a hydrogen bond.[3,5]

Understanding the electronic structure of a protonic conductor is one of the most important subjects for further applications. We have studied the electronic structures of protonic conductors SrCeO$_3$, CaZrO$_3$ and BaCeO$_3$ by X-ray absorption spectroscopy (XAS) and photoemission spectroscopy (PES).[10–14] For these protonic conductors, the Fermi level (E_F) of H$_2$-annealed samples shifts to the conduction band side, although the E_F of air-annealed samples are located at the valence band side. The holes and acceptor level are observed at the top of the valence band and just above E_F, respectively. These intensities are lower in H$_2$-annealed samples. These findings indicate that the electronic structure of a perovskite-type protonic conductor obeys the rigid-band model.

In this study, the electronic structure of a protonic conductor SrTi$_{0.98}$Sc$_{0.02}$O$_3$ single crystal has been probed using XAS and PES. We report in this paper that the doped hydrogen compensates the presence of the hole at the top of the valence band, as was previously observed in SrCeO$_3$, CaZrO$_3$, and BaCeO$_3$ ceramics.[10–14]

SrTi$_{0.98}$Sc$_{0.02}$O$_3$ samples were prepared by the solid-state reaction of SrTiO$_3$, SrCO$_3$ and Sc$_2$O$_3$ at 1200°C for 12 h, and the single crystals were grown by a floating zone method using a Xe-arc imaging furnace. The single crystals were

grown in O$_2$ atmosphere to prevent the protons from entering the crystals. The prepared crystals were confirmed to be of a single phase with a perovskite structure by powder X-ray diffraction analysis. The H$_2$-annealed samples were kept in an atmosphere of saturated H$_2$O vapor pressure at 20°C.

PES and XAS measurements were carried out at the Photon Factory of the High Energy Accelerator Organization, Tsukuba, Japan. Synchrotron radiation was monochromatized using a varied-line-spacing plane grating whose average groove density is 1000 lines/mm. The PES spectra were measured using an electrostatic hemispherical analyzer whose radius is 100 mm. The XAS spectra were measured using a Si photodiode. The total energy resolutions of PES and XAS were approximately 40 meV and 100 meV, respectively.

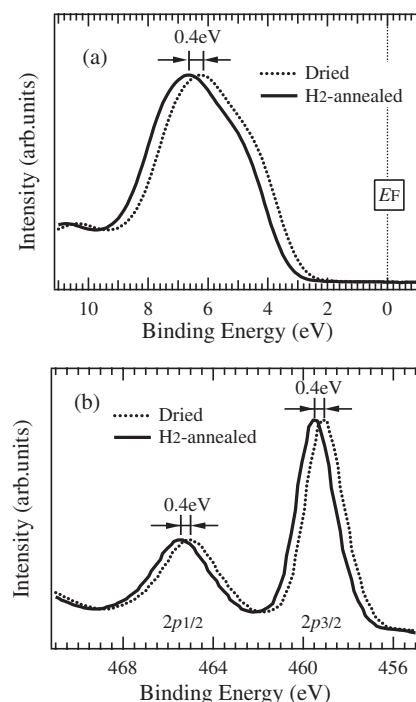Figure 1 shows the PES spectra in the (a) valence band

Fig. 1. Comparisons of the PES spectra in the (a) valence band and (b) Ti 2p core level between dried and H$_2$-annealed SrTi$_{0.98}$Sc$_{0.02}$O$_3$.
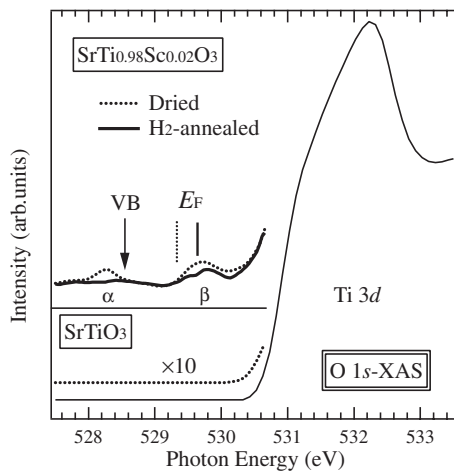
Fig. 2.   O 1*s* XAS spectra of dried and H$_2$-annealed SrTi$_{0.98}$Sc$_{0.02}$O$_3$. As a reference, the O 1*s* XAS spectrum of undoped SrTiO$_3$ is also shown. The intensity of the photon energy region below 530.5 eV is expanded and shown as a thick line.

and (b) Ti 2*p* core level energy regions of dried and H$_2$-annealed SrTi$_{0.98}$Sc$_{0.02}$O$_3$. Dashed and solid lines indicate dried and H$_2$-annealed SrTi$_{0.98}$Sc$_{0.02}$O$_{3-\delta}$, respectively. These PES spectra are normalized using the beam current and measurement time. The positions of the valence band and Ti 2*p* core level are shifted to higher binding energy by 0.4 eV in H$_2$-annealed SrTi$_{0.98}$Sc$_{0.02}$O$_3$. These shifts indicate that E_F becomes higher in H$_2$-annealed SrTi$_{0.98}$Sc$_{0.02}$O$_3$, indicating the effect of the hydrogen doping on the rigid-band model.[11]

Figure 2 shows the O 1*s* XAS spectra of dried and H$_2$-annealed SrTi$_{0.98}$Sc$_{0.02}$O$_3$. From the dipole selection rule, it is understood that the O 1*s* XAS spectra of Ti oxides correspond to transitions from O 1*s* to O 2*p* character.[10] The large band above 530 eV is mainly composed of the O 2*p* state hybridized with the unoccupied Ti 3*d* state. The spectral intensity below the threshold is expanded 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 below E_F correspond to those of the thermally excited structure from the valence band. An arrow shows the top of the valence band (VB). In both samples, the energy separation between E_F and VB correlates with the result shown in Fig. 1(a).

In dried SrTi$_{0.98}$Sc$_{0.02}$O$_3$, two features denoted by the α and β peaks are observed near the band-gap energy region, although there is no structure in the band gap of undoped SrTiO$_3$. The feature α is assigned to holes created by Sc^{3+} doping at the VB, which is mainly composed of nonbonding O 2*p* states in the valence band. In the absorption spectra in the vacuum ultraviolet region, Sata *et al.* have reported that the energy gap of SrTi$_{0.98}$Sc$_{0.02}$O$_3$ increases with increasing Sc^{3+} concentration.[15] The increase in the energy gap indicates an increase in holes at the VB. This finding indicates that the effect of the acceptor on the electronic structure can be explained by the rigid-band model. The feature β near E_F is assigned to the acceptor level, since it lies immediately above E_F. The existences of holes and acceptors have been probed from the temperature depend-ence of O 1*s* XAS spectra.[10]

In H$_2$-annealed SrTi$_{0.98}$Sc$_{0.02}$O$_3$, the holes (α) at the VB disappear, indicating that the doped hydrogen compensates the presence of the holes in the crystal lattice. E_F of H$_2$-annealed SrTi$_{0.98}$Sc$_{0.02}$O$_3$ shifts to the conduction band side by approximately 0.4 eV and the acceptor level (β) splits into two features around E_F. The β peak in the H$_2$-annealed sample below E_F may be contributed by the thermally excited hydrogen. The energy separation between the VB and the bottom of the hydrogen-induced level is approximately 0.4 eV, which corresponds to the activation energy of H$_2$-annealed SrTi$_{0.98}$Sc$_{0.02}$O$_3$ estimated from the electrical conductivity. These findings correlate with the results of XAS and PES studies probed in SrCeO$_3$, CaZrO$_3$, and BaCeO$_3$.[10–14]

In conclusion, we have studied the electronic structure of the protonic conductor SrTi$_{0.98}$Sc$_{0.02}$O$_3$ single crystal by XAS and PES. E_F of H$_2$-annealed SrTi$_{0.98}$Sc$_{0.02}$O$_3$ shifts to the conduction band by 0.4 eV. In dried SrTi$_{0.98}$Sc$_{0.02}$O$_3$, the holes and acceptor level are observed at the top of the valence band and just above E_F, respectively. In H$_2$-annealed SrTi$_{0.98}$Sc$_{0.02}$O$_3$, the holes in the valence band disappear and the intensity of acceptor level decreases, indicating that the doped hydrogen compensates the existence of the holes. These findings show the effect of the hydrogen doping on the rigid-band model.

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