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Observation of acceptor level of p-type $SrTiO_3$ by high-resolution soft-X-ray absorption spectroscopy

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Abstract

The electronic structure of Sc-doped $SrTiO_3$ ($SrTi_{1-x}Sc_xO_3$) has been investigated by soft-X-ray absorption spectroscopy (XAS) in the O 1s core region. Hole states at the top of the valence band and acceptor-induced levels just above the Fermi level are observed below the O 1s threshold. The XAS features and their temperature dependence are in good agreement with electrical conductivity studies on the same samples. These results conclude that $SrTi_{1-x}Sc_xO_3$ is a p-type semiconductor with deep acceptor levels lying in the middle of the band gap.

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1. Introduction

Perovskite-type compounds such as $SrCeO_3$, $CaZrO_3$ and $SrZrO_3$ show hole conductivity as well as protonic conductivity in the very high temperature region when doped with acceptor ions [1–6]. These compounds are expected as the electrochemical applications such as fuel cell, hydrogen sensor. A recent report suggested that $SrTiO_3$ also shows protonic conductivity with very low activation energy when Sc^{3+} ions are substituted into Ti^{4+} site [4]. However, there are several mysteries in Sc-doped $SrTiO_3$ ($SrTi_{1-x}Sc_xO_3$). Although perovskite-type protonic conductor is generally realized as p-type sample, p-type $SrTiO_3$ has not been confirmed so far. Additionally, $SrTi_{1-x}Sc_xO_3$ exhibits low conductivity at room temperature. The as-prepared $SrTi_{1-x}Sc_xO_3$ single crystal is transparent in the visible light region. The electrical conductivity is low and shows a thermal activation-type behavior with activation energy of

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0.4 eV for $SrTi_{0.96}Sc_{0.04}O_3$ in the high temperature region. Therefore, it is very difficult to prove the existence of p-type conductivity by Hall effect or thermoelectric measurements.

In this paper, we present high-resolution X-ray absorption spectroscopy (XAS) spectra and electrical conductivity of $SrTi_{1-x}Sc_xO_3$ and show how the features found in the band gap region are related with the p-type electrical conductivity. If $SrTi_{1-x}Sc_xO_3$ were p-type, the holes at the top of the valence band or acceptor level near E_F, which provide the electrical conductivity, might be observed by careful measurements using high-resolution and high brightness XAS. XAS are related directly to the unoccupied DOS [7]. 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 gives the spectrum relating to the site- and symmetry-selected DOS.

2. Experimental

The samples of $SrTi_{1-x}Sc_xO_3$ were prepared by the solid-state reaction of Sc_2O_3, $SrTiO_3$ and $SrCO_3$ at 1200 °C for about 12 h, and the single crystals were grown by floating-zone method using a Xe-arc imaging furnace. The prepared crystals were transparent. The Sc^{3+} ion is clearly to be doped as an acceptor ion in Ti^{4+} ions site of $SrTiO_3$ as observed by a simple thermoelectromotive force experiment. The dopant concentrations are ranged from $x = 0$ to 0.10. The single crystals were confirmed as being in a single phase with a perovskite structure by powder X-ray diffraction analysis.

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. The revolver undulator covers a wide energy range from 10 to 1200 eV in the first harmonic. High brightness with a high resolution is realized using a varied line-spacing plane grating monochromator. The resolution of about $\Delta E/E = 2 \times 10^{-4}$ at $hv =$ 400 eV and high photon flux of about 10^{12}–10^{13} photons/s is realized with the spot size of 100 μm [8,9]. The XAS spectra were measured by collecting the total fluorescence yield.

3. Results and discussion

Fig. 1 shows the O 1s XAS spectra as a function of Sc doping in $SrTi_{1-x}Sc_xO_3$. From the dipole selection rule, it is understood that the O 1s XAS spectra of $SrTiO_3$ correspond to transitions from O 1s to the O 2p character hybridized with the unoccupied Ti 3d states. The feature around 532 eV is mainly composed of the Ti 3d state hybridized with O 2p states [10–12]. The spectral intensity below the threshold is expanded by 10 times and is shown as a thick line above the XAS spectrum in order to obtain reliable information in the band gap energy region. In this energy region, the

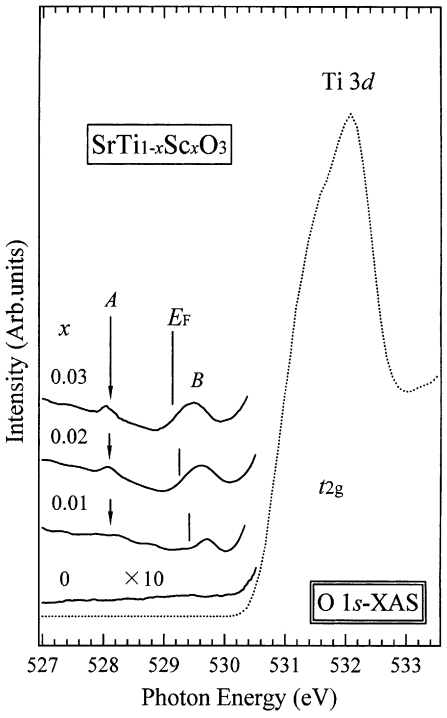

Fig. 1. O 1s XAS spectra as a function of Sc^{3+} doping of $SrTi_{1-x}Sc_xO_3$. Thick lines show the O 1s XAS spectra on an expanded scale. Vertical bar is the position of E_F determined from the O 1s photoemission peak. Arrows indicate the top of the valence band.

electronic structure related with the p-type conductivity should be realized. Arrow shows the top of the valence band. The Fermi level (E_F) is determined from the binding energy of the O 1s photoemission peak. One can find that E_F is located between the valence band and conduction band and gradually shifts to the valence band side with increasing Sc^{3+} ions. In the photoemission study on $SrTi_{1-x}Sc_xO_3$, it is reported that E_F shifts to the valence band side with increasing Sc^{3+} ions in accord with the rigid-band model [13,14]. However, the shift does not quantitatively follow the shift in XAS by about 0.2–0.5 eV, the discrepancy possibly originates in surface effects due to difference of the mean free path of XAS and photoemission spectroscopy.

It is striking that two features corresponding to A and B peaks are observed in the band gap energy region of $SrTi_{1-x}Sc_xO_3$ though there is no structure in the band gap of non-doped $SrTiO_3$. The intensities of A and B peaks increase with increasing Sc^{3+} ions. The feature A might be assigned to holes created by Sc doping at the top of the valence band, which is mainly composed of non-bonding O 2p states in the valence band. In the absorption spectra of vacuum ultraviolet region, it has been clarified that the band gap of $SrTi_{1-x}Sc_xO_3$ increases with increasing Sc^{3+} ions [15]. This fact is consistent with the presence of holes created at the top of the valence band. On the other hand, the feature B at or near E_F might be assigned to the acceptor level, since it lies just above E_F.

In order to confirm these assignments for A and B, we measured the temperature dependence of O 1s XAS spectra in the band gap region of $SrTi_{0.98}Sc_{0.02}O_3$, as shown by Fig. 2. The spectra are measured from 300 to 80 K. To make sure of the reproducibility of the spectra, the measurements were carried out on decreasing temperature from 300 to 80 K and for increasing temperatures from 80 to 300 K. The intensity of A peak decreases with decreasing temperature. In contrast, the intensity of B peak increases with decreasing temperature. The intensities of A and B peaks are plotted in Fig. 3, where log (intensity) is plotted against $1000/T$ (K^{-1}). The A and B peak intensities are obtained by the subtraction of a linear or a

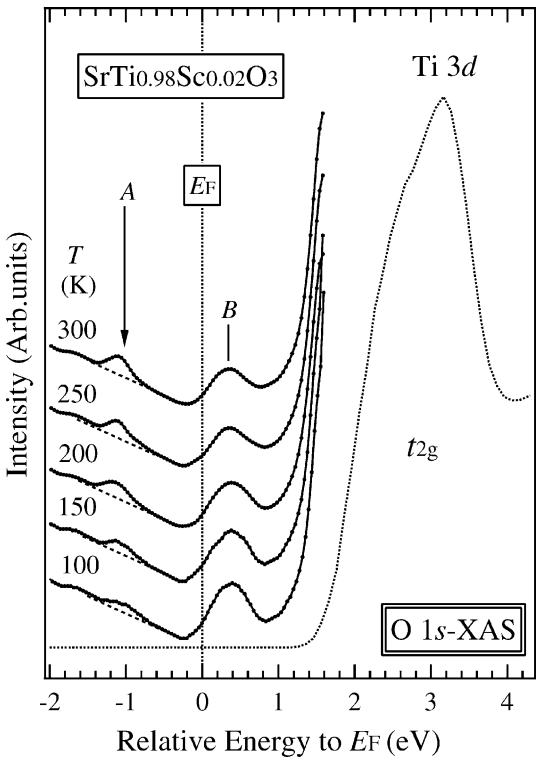

Fig. 2. O 1s XAS spectra as a function of temperature of $SrTi_{0.98}Sc_{0.02}O_3$.

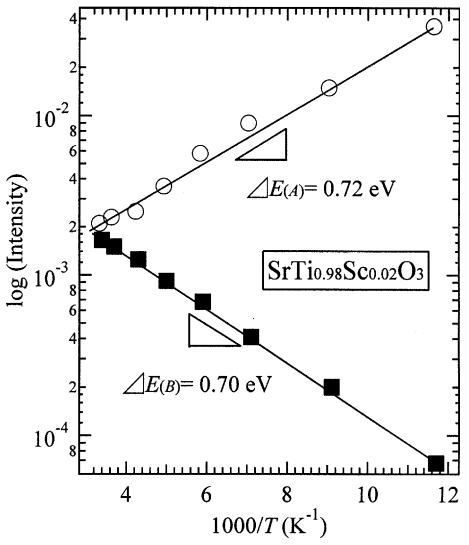

Fig. 3. The plot of intensity of A peak (open circles) and B peak (closed square) of O 1s XAS spectra shown in Fig. 2. Solid lines indicate the activation energy ($\Delta E_{(A)}, \Delta E_{(B)}$) for the A and B peaks of $SrTi_{0.98}Sc_{0.02}O_3$.

polynomial smooth background. The peak intensity is in arbitrary unit, so that the log (intensity) scale is not determined by a constant and the slope does not change. These slopes are exponential-like. The slopes of A and B peaks are 0.70 and −0.72 eV, which correspond to activation energies (ΔE). The $\Delta E_{(A)}$ peak is in good agreement with $\Delta E_{(B)}$. This fact indicates that the electrons occupying the hole level (A peak) are excited thermally to the acceptor levels (B peak). Thus, we can assign A to be the hole states at the top of the valence band and B corresponds to the acceptor levels.

Fig. 4 shows the comparison of ΔE as a function of Sc^{3+} doping from the XAS data (Figs. 2 and 3) and the slope of the Arrhenius plot. The ΔE from the Arrhenius plot, which is obtained from [11], rapidly decreases to 0.62 eV at $x = 0.02$ and then slowly increases for $x > 0.02$. For Sc doping dependence, the behavior of E_A from the Arrhenius plot is in good agreement with that obtained from XAS, although the energy difference of ΔE between Arrhenius plot and XAS is about ~0.1 eV.

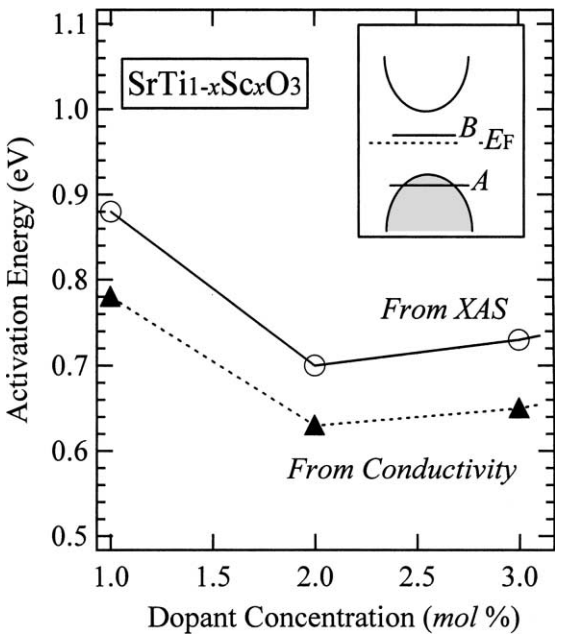

Fig. 4. ΔE as a function of doping of $SrTi_{1-x}Sc_xO_3$ obtained from O 1s XAS (open circle) and Arrhenius plot of the electrical conductivity (closed triangle mark). The ΔE from the electrical conductivity is obtained from [11].

The energy difference may be due to the difference between the experimental accuracies. The estimation of the intensity in XAS may bring about an error of ~0.1 eV because the total resolution of the experimental system used in this study is about 0.1 eV for XAS. If the electrical conductivity is attributed to holes, the E_A should be related with the energy separation between the high energy side of the hole (A) and the low energy side of the acceptor level (B), as shown in the inset of Fig. 4.

4. Conclusion

We have studied the electronic structure in the band gap energy region of $SrTi_{1-x}Sc_xO_3$ using XAS. The O 1s XAS spectrum shows two empty states, which correspond to acceptor level near E_F and hole states created at the top of the valence band. The activation energies obtained by XAS is in good agreement with those obtained by electrical conductivity. These facts prove that $SrTi_{1-x}Sc_xO_3$ exhibits p-type conductivity.

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