Direct evidence of $p$-type SrTiO$_3$ by high-resolution x-ray absorption spectroscopy

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We study x-ray absorption spectra below the O 1s threshold in Sc-doped stoichiometric strontium titanate (SrTiO$_3$). We find hole states at the top of the valence band and acceptor-induced levels just above the Fermi level. The x-ray absorption spectra features and their temperature dependence are in good agreement with electrical-conductivity studies on the same samples. It is concluded that Sc-doped SrTiO$_3$ is a $p$-type semiconductor with deep acceptor levels lying in the middle of the band gap.

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I. INTRODUCTION

Stoichiometric strontium titanate (SrTiO$_3$) possesses a cubic perovskite-type structure and is essentially a band insulator with a band gap of about 3.2 eV. It is well known that SrTiO$_3$ exhibits $n$-type conductivity on substituting Nb$^{5+}$ (or La$^{3+}$) for Ti$^{4+}$ (or Sr$^{2+}$) and it becomes a superconductor at $T_C=0.3$ K. The doped systems have been used in practical applications such as electrodes and as a gas sensor. On the other hand, the existence of $p$-type SrTiO$_3$ has not been confirmed as yet. If its existence were confirmed, $p$-type SrTiO$_3$ would be a very promising material. First, it would become a wide-gap semiconductor diode in blue-light region and would be highly valued in the semiconductor industry. Second, it is well known that $p$-type doping in perovskite structure accommodates protonic conductivity.$^{2–4}$ The protonic conductors are important materials for a wide variety of electrochemical applications such as fuel cell and hydrogen sensor in the renewable energy-source industry. Third, doped transition-metal compounds show a wide variety of interesting electrical properties, such as high $T_C$ superconductivity. Doped SrTiO$_3$ also belong to the series of doped transition-metal compounds, which exhibit superconductivity at low temperature.

The 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.$^{2–4}$ 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.$^5$ However, there are several mysteries in Sc-doped SrTiO$_3$. Although perovskite-type protonic conductor is generally re-alized as $p$-type sample, $p$-type SrTiO$_3$ has not been confirmed so far. Additionally, Sc-doped SrTiO$_3$ exhibits low conductivity at room temperature. The as-prepared Sc-doped SrTiO$_3$ 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 0.4 eV for Sr$_{1.00}$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.

The electronic structure of Sc-doped SrTiO$_3$ has been studied by absorption spectroscopy in the vacuum ultraviolet region and also by photoemission spectroscopy (PES).$^{5–8}$ An energy shift of the absorption edge due to Sc doping was observed and the band gap was found to increase with increasing Sc$^{3+}$ ions, indicating the formation of holes at the top of the valence band. Comparing with the PES of Nb-doped $n$-type SrTiO$_3$, the Fermi level ($E_F$) of Sc-doped SrTiO$_3$ shifts to valence-band side. Furthermore, $E_F$ shifts to valence-band side with increasing Sc$^{3+}$ ions in accord with the rigid-band model. However, the above facts are indirect evidences of $p$-type SrTiO$_3$. If Sc-doped SrTiO$_3$ 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 x-ray absorption spectroscopy (XAS). XAS are related directly to the unoccupied density of states (DOS).$^9$ 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. In this paper, we present high-resolution XAS spectra and electrical conductivity of SrTi$_{1-x}$Sc$_x$O$_3$ and show how the features found in the band-gap region are related with the $p$-type electrical conductivity.
The single crystal of Sc-doped SrTiO$_3$ (SrTi$_{1-x}$Sc$_x$O$_3$) was grown by the floating-zone method. The crystals were examined using x-ray diffraction. XAS measurements were carried out on decreasing temperature from 300 to 80 K. The intensities of $\alpha$ and $\beta$ peaks are plotted in Fig. 2(b), where log (intensity) is plotted against $1000/T$ (K$^{-1}$). The $\alpha$ and $\beta$ peak intensities are obtained by the subtraction of a linear or a polynomial smooth background. The peak intensity is in arbitrary unit, so that the log scale is not determined by a constant and the slope does not change. These slopes are exponential-like. The slopes of $\alpha$ and $\beta$ are normalized by Sr 4d peak of the conduction band, though the peak is not shown in this figure. The feature around 532 eV is mainly composed of the Ti 3d state hybridized with O 2p state. The spectral intensity depends on Sc dopant concentration. The change is believed to originate in the difference of hybridization between Ti 3d and O 2p states by doping Sc ions, as indicated from a recent resonant photoemission study. 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 obtain reliable information in the band-gap energy region. In this energy region, the 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. The photoemission study on SrTi$_{1-x}$Sc$_x$O$_3$, it is reported that $E_F$ shifts to the valence-band side with increasing Sc$^{3+}$ ions in accord with the rigid-band model. 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 $\alpha$ and $\beta$ peaks are observed in the band-gap energy region of SrTi$_{1-x}$Sc$_x$O$_3$, though there is no structure in the band gap of nondoped SrTiO$_3$. The weak feature at $x=0.05$ is considered to be a defect-induced level of Ti 3d state, since the Sc dopant concentration is more than the solubility limit in SrTiO$_3$. The intensities of $\alpha$ and $\beta$ peaks increase with increasing Sc$^{3+}$ ions. The feature $\alpha$ might be assigned to holes created by Sc doping at the top of the valence band, which is mainly composed of nonbonding 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$_x$O$_3$ increases with increasing Sc$^{3+}$ ions. This fact is consistent with the presence of holes created at the top of the valence band. On the other hand, the feature $\beta$ 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 $\alpha$ and $\beta$, 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(a). 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 $\alpha$ peak decreases with decreasing temperature. In contrast, the intensity of $\beta$ peak increases with decreasing temperature. The intensities of $\alpha$ and $\beta$ peaks are plotted in Fig. 2(b), where log (intensity) is plotted against $1000/T$ (K$^{-1}$). The $\alpha$ and $\beta$ peak intensities are obtained by the subtraction of a linear or a 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 $\alpha$ and $\beta$ peaks are 0.70 eV and --0.72 eV, which correspond to activation energies ($\Delta E$). The $\Delta E$ of $\alpha$
peak is in good agreement with that of $\beta$ peak. This fact indicates that the electrons occupying the hole level ($\alpha$ peak) are excited thermally to the acceptor levels ($\beta$ peak). Thus, we can assign $\alpha$ to be the hole states at the top of the valence band and $\beta$ corresponds to the acceptor levels.

Figure 3 shows the Arrhenius plot as a function of doping of the conductivity of SrTi$_{1-x}$Sc$_x$O$_3$ measured in dry air. As a reference, SrTiO$_3$ ($x=0$) is also shown.

The conductivity doped with Sc$^{3+}$ ions shows a thermal activation-type behavior. At high temperatures, above 673 K, the conductivity does not depend on Sc dopant concentration, indicating that oxygen ion conductivity is more dominant than hole conductivity. At low temperatures, below 673 K, the conductivity depends on Sc dopant concentration and the magnitude is the highest in $x=0.02$ and the lowest in $x=0.01$.

Figure 4 shows Sc doping dependence of the $E_A$ estimated from the XAS data (Fig. 2) and $E_A$ estimated from the electrical conductivity.
slope of the Arrhenius plot. The $E_A$ from the Arrhenius plot 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 $E_A$ between Arrhenius plot and XAS is about $-0.1$ eV. 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 ($\alpha$) and the low energy side of the acceptor level ($\beta$). If we pay attention to the position of the holes ($\alpha$ peak) in Fig. 2, the dashed line of background actually intersects hemline of the hole structure at about 0.65–0.70 eV from $E_F$.

The above results indicate that the charge of dopant Sc$^{3+}$ ion is compensated by the holes at the top of the valence band in low-temperature region below 673 K in addition to the O$^{2-}$ vacancy. The hole in ionic crystal forms a polaron, in general, which brings about a lattice distortion. The ratio between the high energy side of the hole structure and the O$^{2-}$ band in low-temperature region below 673 K is determined by the delicate balance between the amount of holes and that of oxygen vacancy in the system.

**IV. CONCLUSION**

We have studied the electronic structure in the band-gap energy region of SrTi$_{1-x}$Sc$_x$O$_3$ using XAS. The O 1s XAS spectrum shows two empty states, corresponding 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$_x$O$_3$ exhibits $p$-type conductivity, which was not confirmed so far. High-energy absorption spectroscopy is found to be a powerful tool for the study of electronic structure in the band gap and to relate it to the transport properties.

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