

Direct evidence of p -type SrTiO₃ by high-resolution x-ray absorption spectroscopy

T. Higuchi and T. Tsukamoto

Department of Applied Physics, Tokyo University of Science, Tokyo 162-8601, Japan

K. Kobayashi* and S. Yamaguchi

Department of Materials Science and Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan

Y. Ishiwata

*Institute for Solid State Physics, University of Tokyo, Chiba 277-8581, Japan*N. Sata, K. Hiramoto,[†] and M. Ishigame[‡]*Research Institute of Scientific Measurements, Tohoku University, Sendai 980-8577, Japan*

S. Shin

*Institute for Solid State Physics, University of Tokyo, Chiba 277-8581, Japan**and RIKEN, Hyogo 679-5143, Japan*

(Received 13 June 2001; published 13 December 2001)

We study x-ray absorption spectra below the O 1s threshold in Sc-doped stoichiometric strontium titanate (SrTiO₃). 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 SrTiO₃ is a p -type semiconductor with deep acceptor levels lying in the middle of the band gap.

DOI: 10.1103/PhysRevB.65.033201

PACS number(s): 78.70.Dm, 71.27.+a, 79.60.-i

I. INTRODUCTION

Stoichiometric strontium titanate (SrTiO₃) possesses a cubic perovskite-type structure and is essentially a band insulator with a band gap of about 3.2 eV.¹ It is well known that SrTiO₃ exhibits n -type conductivity on substituting Nb⁵⁺ (or La³⁺) for Tr⁴⁺ (or Sr²⁺) 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 SrTiO₃ has not been confirmed as yet. If its existence were confirmed, p -type SrTiO₃ 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 SrTiO₃ also belong to the series of doped transition-metal compounds, which exhibit superconductivity at low temperature.

The perovskite-type compounds such as SrCeO₃, CaZrO₃, and SrZrO₃ 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 SrTiO₃ also shows protonic conductivity with very low activation energy when Sc³⁺ ions are substituted into Ti⁴⁺ site.⁵ However, there are several mysteries in Sc-doped SrTiO₃. Although perovskite-type protonic conductor is generally re-

alized as p -type sample, p -type SrTiO₃ has not been confirmed so far. Additionally, Sc-doped SrTiO₃ exhibits low conductivity at room temperature. The as-prepared Sc-doped SrTiO₃ 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 SrTi_{0.96}Sc_{0.04}O₃ 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 SrTiO₃ has been studied by absorption spectroscopy in the vacuum ultraviolet region and also by photoemission spectroscopy (PES).⁶⁻⁸ An energy shift of the absorption edge due to Sc doping was observed and the band gap was found to increase with increasing Sc³⁺ ions, indicating the formation of holes at the top of the valence band. Comparing with the PES of Nb-doped n -type SrTiO₃, the Fermi level (E_F) of Sc-doped SrTiO₃ shifts to valence-band side. Furthermore, E_F shifts to valence-band side with increasing Sc³⁺ ions in accord with the rigid-band model. However, the above facts are indirect evidences of p -type SrTiO₃. If Sc-doped SrTiO₃ 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_xO₃ and show how the features found in the band-gap region are related with the p -type electrical conductivity.

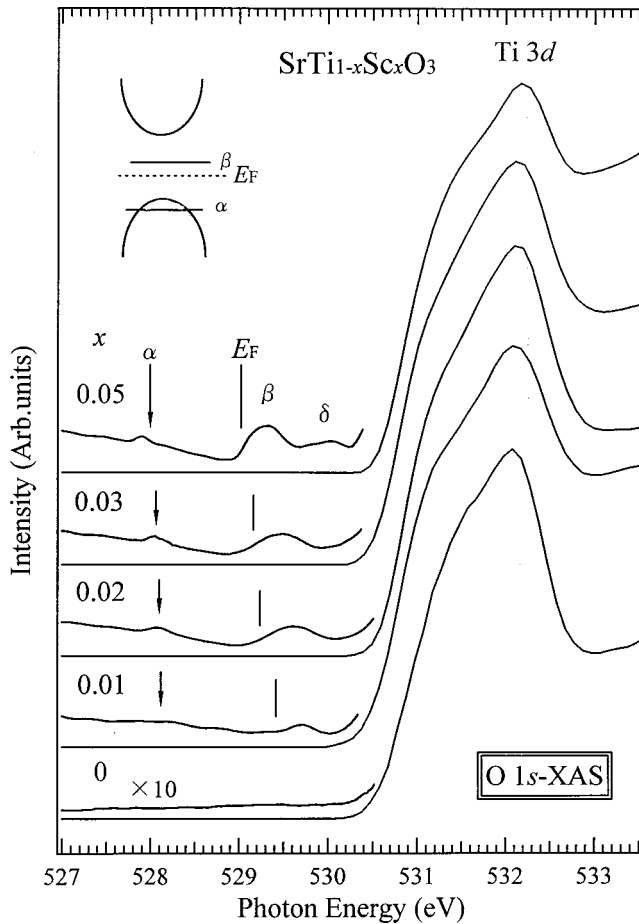


FIG. 1. O 1s XAS spectra of $\text{SrTi}_{1-x}\text{Sc}_x\text{O}_3$. Thick lines show the O 1s XAS spectra on an expanded scale. Vertical bar is the position of E_F determined from the binding energy of the O 1s photoemission peak. Arrows indicate the top of the valence band.

II. EXPERIMENTAL

The single crystal of Sc-doped SrTiO_3 ($\text{SrTi}_{1-x}\text{Sc}_x\text{O}_3$) was grown by the floating-zone method. The crystals were examined using x-ray diffraction. 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 $h\nu = 400$ eV and high photon flux of about $10^{12} \sim 10^{13}$ photons/sec is realized with the spot size of 100 μm .^{10,11} The XAS spectra were measured by collecting the total fluorescence yield.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the O 1s XAS spectra as a function of Sc doping in $\text{SrTi}_{1-x}\text{Sc}_x\text{O}_3$. 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.^{12,13} The O 1s XAS spectra 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.⁸ 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^{2+} ions. In the photoemission study on $\text{SrTi}_{1-x}\text{Sc}_x\text{O}_3$, it is reported that E_F shifts to the valence-band side with increasing Sc^{3+} ions in accord with the rigid-band model.⁸ 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 α and β peaks are observed in the band-gap energy region of $\text{SrTi}_{1-x}\text{Sc}_x\text{O}_3$, though there is no structure in the band gap of nondoped SrTiO_3 . The weak feature δ of $x=0.05$ 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 α and β peaks increase with increasing Sc^{3+} ions. The feature α 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 $\text{SrTi}_{1-x}\text{Sc}_x\text{O}_3$ increases with increasing Sc^{3+} ions.⁶ This fact is consistent with the presence of holes created at the top of the valence band. On the other hand, the feature β 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 α and β , we measured the temperature dependence of O 1s XAS spectra in the band-gap region of $\text{SrTi}_{0.98}\text{Sc}_{0.02}\text{O}_3$, 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 α peak decreases with decreasing temperature. In contrast, the intensity of β peak increases with decreasing temperature. The intensities of α and β peaks are plotted in Fig. 2(b), where $\log(\text{intensity})$ is plotted against $1000/T$ (K^{-1}). The α and β 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 $\log(\text{Intensity})$ scale is not determined by a constant and the slope does not change. These slopes are exponential-like. The slopes of α and β peaks are 0.70 eV and -0.72 eV, which correspond to activation energies (ΔE). The ΔE of α

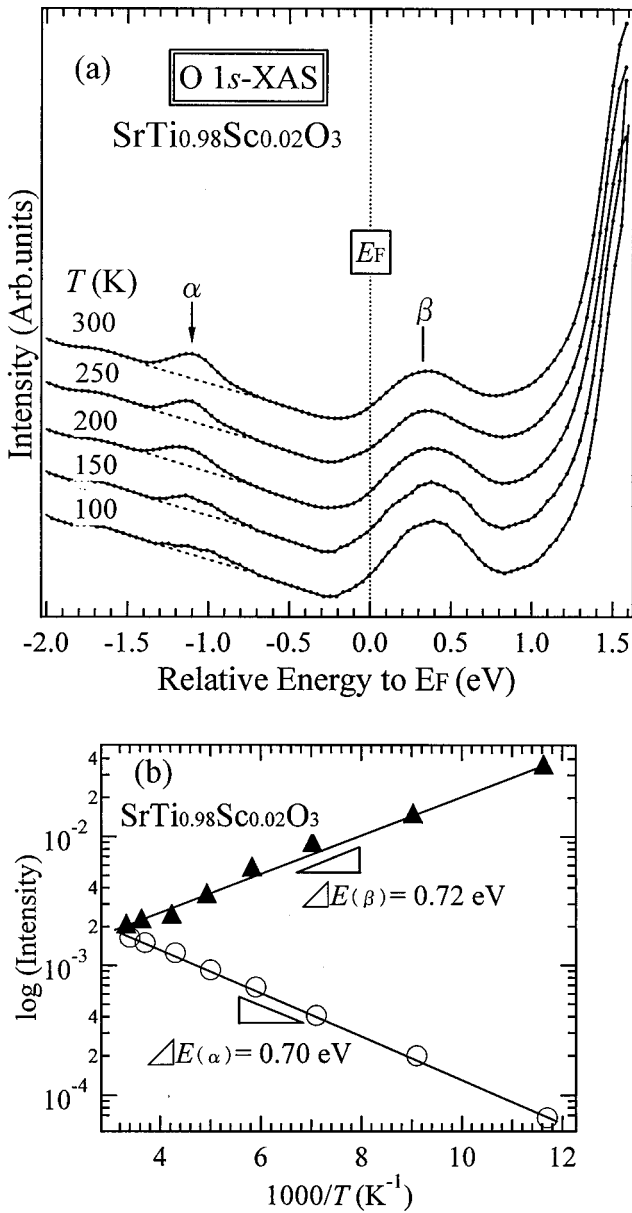


FIG. 2. (a) Temperature dependence of O 1s XAS spectra of $\text{SrTi}_{0.98}\text{Sc}_{0.02}\text{O}_3$. (b) The plot of intensity of α peak (open circles) and β peak (closed circle) of O 1s XAS spectra shown in (a). Solid lines indicate the activation energy [$\Delta E_{(\alpha)}$, $\Delta E_{(\beta)}$] for the α and β peaks of $\text{SrTi}_{0.98}\text{Sc}_{0.02}\text{O}_3$.

peak is in good agreement with that of β peak. This fact indicates that the electrons occupying the hole level (α peak) are excited thermally to the acceptor levels (β peak). Thus, we can assign α to be the hole states at the top of the valence band and β corresponds to the acceptor levels.

Figure 3 shows the Arrhenius plot as a function of doping of the conductivity of $\text{SrTi}_{1-x}\text{Sc}_x\text{O}_3$ measured in dry air. Complex impedance was measured by HP4275A LCR meter from room temperature to 900 °C. The electrical conductivity is determined by the Cole-Cole complex impedance plot at each temperature. As a reference, SrTiO_3 ($x=0$) is also measured as shown in the figure. It is clear that the conductivity of $x=0$ is different compared to the case of Sc doping. The

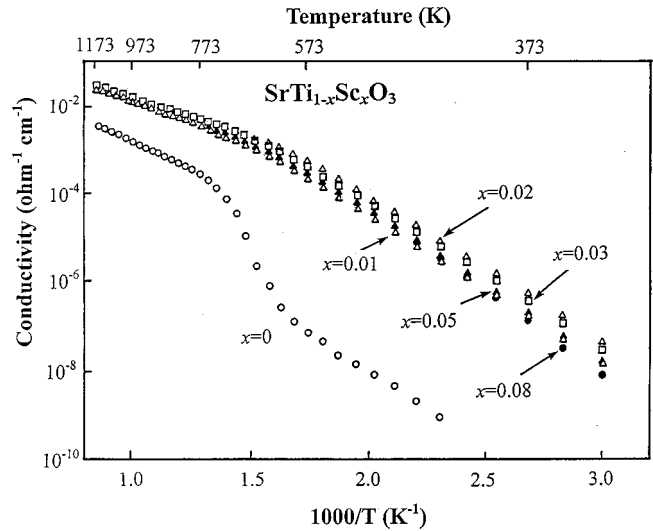


FIG. 3. Arrhenius plots as a function of doping of electrical conductivities of $\text{SrTi}_{1-x}\text{Sc}_x\text{O}_3$ in dry air. As a reference, SrTiO_3 ($x=0$) is also shown.

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

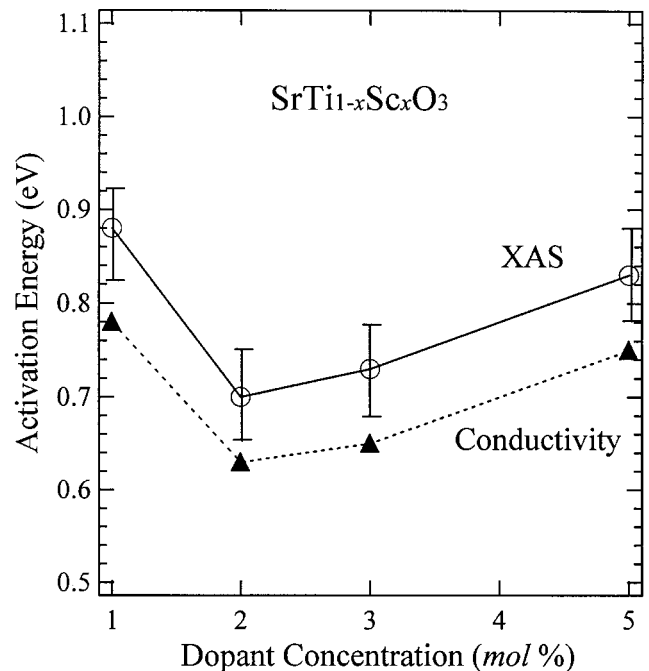


FIG. 4. Activation energies as a function of doping of $\text{SrTi}_{1-x}\text{Sc}_x\text{O}_3$ obtained from O 1s XAS (open circle) and Arrhenius plot of the electrical conductivity (closed triangle mark).

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 (α) and the low energy side of the acceptor level (β). If we pay attention to the position of the holes (α peak) in Fig. 2, the dashed line of background actually intersects hemline of the hole structure at about 0.65 \sim 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.^{14,15} The holes in p -type SrTiO_3 are expected to migrate as a small polaron that exist in the oxygen ions. It is probable that the change of the E_A with Sc dopant concentration is affected 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 $\text{SrTi}_{1-x}\text{Sc}_x\text{O}_3$ 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 $\text{SrTi}_{1-x}\text{Sc}_x\text{O}_3$ 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.

ACKNOWLEDGMENTS

We would like to thank Dr. T. Yokoya and Dr. A. Chainani for their valuable discussions. We also would like to thank A. Fukushima for her technical support in performing XAS measurement. This work was partially supported by Foundation for Material Science and Technology of Japan (MST Foundation), the Grant-In-Aid for Science Research (No. 13740191) from the Ministry of Education, Culture, and Science of Japan.

*Present address: National Institute of Advanced Industrial Science and Technology, Tsukuba 305-8565, Japan.

[†]Present address: Central Research Laboratory, Hitachi Co. Ltd., Tokyo 185, Japan.

[‡]Present address: Akita Technical College, Akita 011-0923, Japan.

¹M. Cardona, Phys. Rev. **140**, 651 (1965).

²H. Iwahara, T. Esaka, and H. Uchida, Solid State Ionics **3/4**, 359 (1981).

³S. Shin, H. H. Huang, M. Ishigame, and H. Iwahara, Solid State Ionics **40/41**, 910 (1990).

⁴H. H. Huang, S. Shin, and M. Ishigame, Solid State Ionics **47**, 251 (1991).

⁵N. Sata, K. Hiramoto, M. Ishigame, S. Hosoya, N. Niimura, and S. Shin, Phys. Rev. B **54**, 15 795 (1996).

⁶N. Sata, M. Ishigame, and S. Shin, Solid State Ionics **86**, 629 (1996).

⁷T. Higuchi, T. Tsukamoto, N. Sata, M. Ishigame, Y. Tezuka, and S. Shin, Phys. Rev. B **57**, 6978 (1998).

⁸T. Higuchi, T. Tsukamoto, N. Sata, M. Ishigame, Y. Tezuka, and

S. Shin, Solid State Ionics **108**, 349 (1998).

⁹J. C. Fuggle and J. E. Inglesfield, *Unoccupied Electronic States* (Springer-Verlag, Berlin, 1991).

¹⁰S. Shin, A. Agui, M. Fujisawa, Y. Tezuka, T. Ishii, and N. Hirai, Rev. Sci. Instrum. **66**, 1584 (1995).

¹¹M. Fujisawa, A. Harasawa, A. Agui, M. Watnabe, A. Kakizaki, S. Shin, T. Ishii, T. Kita, T. Harada, Y. Saitoh, and S. Suga, Rev. Sci. Instrum. **67**, 345 (1996).

¹²M. Abbate, F. M. F. de Groot, J. C. Fuggle, A. Fujimori, Y. Fujishima, Y. Tokura, J. van Elp, G. A. Sawatzky, O. Strebel, M. Domke, G. Kaindl, M. Sacci, and N. Tsuda, Phys. Rev. B **44**, 5419 (1991).

¹³T. Higuchi, T. Tsukamoto, K. Kobayashi, Y. Ishiwata, M. Fujisawa, T. Yokoya, S. Yamaguchi, and S. Shin, Phys. Rev. B **61**, 12 860 (2000).

¹⁴E. K. Kudinov, D. N. Mirlin, and Y. A. Firsov, Sov. Phys. Solid State **11**, 2257 (1970).

¹⁵D. Adler, in *Solid State Chemistry*, edited by N. B. Hannay (Plenum, New York, 1967), Vol. 2.