

Electronic structure in the band gap of lightly doped SrTiO₃ by high-resolution x-ray absorption spectroscopy

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The electronic structure of lightly Nb-doped SrTiO₃ has been investigated using high resolution x-ray absorption spectroscopy (XAS). Below the O 1s threshold, XAS spectra show two features due to empty states whose energy positions match with those of the 3d photoemission spectra in the band gap energy region of the parent undoped SrTiO₃. Similar features are also observed in lightly La-doped SrTiO₃. These features exhibit systematic temperature dependence, which is well explained by the Fermi-Dirac distribution function. This indicates that the two features in the band gap are real bulk states such as simple donor states.

I. INTRODUCTION

It is well known that the photoemission spectroscopy (PES) spectra of heavily La-doped SrTiO₃ ($x > 0.5$) show two Ti 3d originated features within the band gap region of the parent SrTiO₃,¹⁻⁴ which are generally believed to be a coherent part at the Fermi level (E_F) and an incoherent part at 1–1.5 eV that is attributed to a remnant of the lower Hubbard band. However, the peak at 1~1.5 eV is also found in the PES spectra of small doping region ($0.05 < x < 0.2$),^{2,5-7} where the electron correlation is believed to play almost no role.⁸⁻¹⁰ Indeed, band structure calculations that assume a rigid-band filling cannot reproduce the peak at 1–1.5 eV, though the shape of O 2p valence band shows a good agreement with experiment.^{1,2} Recently, the same peak has been proposed to be a polaronic feature or a surface structure that is created due to the degree of correlation and disorder in the surface.¹¹ However, the origin of these states in the band gap region has not been settled so far.

In this paper we make an attempt to answer the question. Is the origin of the 1–1.5 eV peak surface or real bulk states? For this purpose, we have performed high-resolution O 1s x-ray absorption spectroscopy (XAS). If the 1–1.5 eV peak is a donor state as expected for a doped semiconductor, we might be able to observe empty states in XAS spectra, which are created by the thermal excitation from the donor state, though it may have very low intensity. However, one might still observe these states by precise XAS measurements. Alternatively, these states are not observed in XAS, it may imply other mechanism for its origin. In this work, we found

two features due to empty states in the O 1s XAS spectra whose energy position matches with the PES spectra within the band gap region. These features exhibit systematic temperature dependence. The results indicate that the 1–1.5 eV peak within the band gap energy region of PES is a real bulk state.

II. EXPERIMENTAL

The single crystals of Nb-doped *n*-type SrTiO₃, which were grown by the Czochralski method, were obtained from Earth Jewelry Co Ltd. The doping concentrations used in this study are 0–5 mol %. As a reference material, the O 1s XAS of La_{0.05}Sr_{0.95}TiO₃ spectrum was also measured.

XAS and PES measurements were carried out at undulator beamline BL-19B at the Photon Factory of the High Energy Accelerator Research Organization, Tsukuba in Japan. Photoelectron energies were measured with a electrostatic hemispherical analyzer whose radius is 100 mm. Synchrotron radiation from the undulator was monochromatized using a grating monochromator. The resolution of the beamline was better than ~0.1 eV at $h\nu = 500$ eV. The XAS spectra were measured using a XUV silicon photodiode.

III. RESULTS AND DISCUSSION

Figure 1 shows the detailed photoemission spectra of SrTi_{1-x}Nb_xO₃. The spectra in the band gap energy region are also shown on an expanded scale. We observe two prominent features *a* and *b* within the band gap, which are

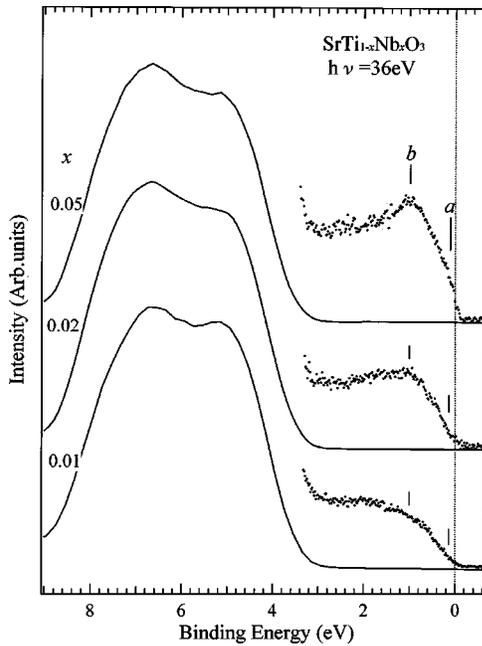


FIG. 1. Photoemission spectra of $\text{SrTi}_{1-x}\text{Nb}_x\text{O}_3$ in the band gap energy region. The spectra near E_F are also plotted on an expanded intensity scale.

reported to have Ti 3d character.⁴ The intensities of these features increase with increasing Nb doping. For the feature *a*, the intensity at E_F reflects the result of the electrical conductivity that increases with increasing Nb doping.¹² On the other hand, the feature *b* is located at ~ 1.0 eV below E_F . The photoemission spectra of La-doped SrTiO_3 also show a feature at ~ 1.5 eV, and are discussed later.

Figure 2 shows the O 1s XAS spectra of $\text{SrTi}_{1-x}\text{Nb}_x\text{O}_3$.

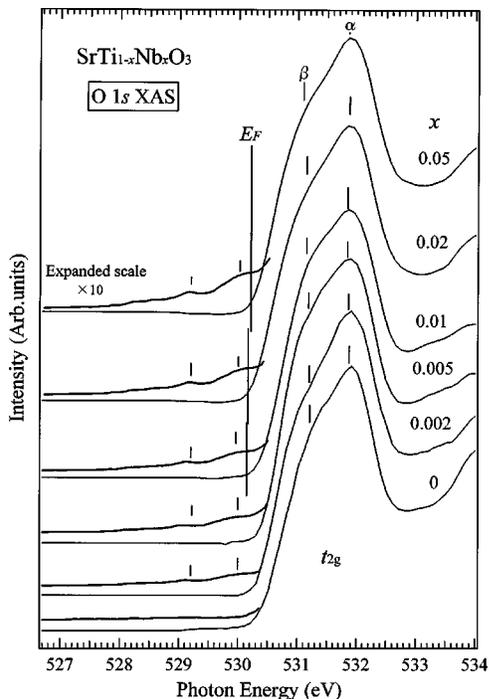


FIG. 2. O 1s XAS spectra of $\text{SrTi}_{1-x}\text{Nb}_x\text{O}_3$. The intensity of the photon energy region below 530.4 eV is expanded and shown as a thick line.

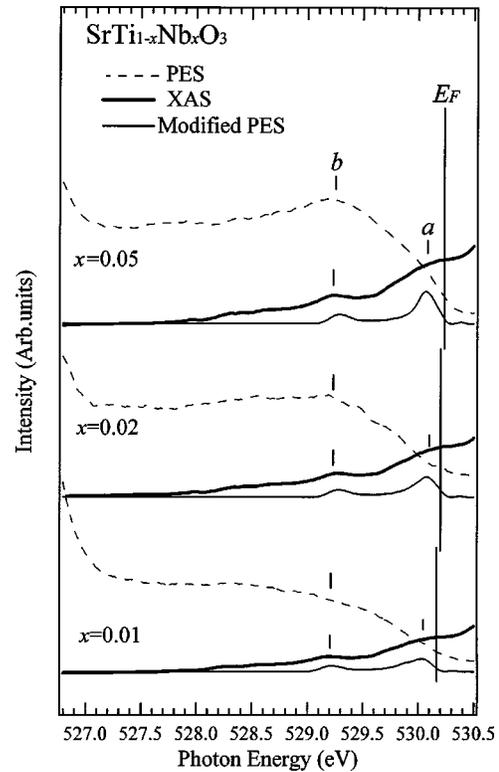


FIG. 3. O 1s XAS spectra in the band gap energy region on an expanded scale. As a reference, the PES spectra of Fig. 1 are also shown as dashed lines. Thin solid lines are the modified PES spectra (see the text), which correspond to the thermally empty states estimated by the PES.

From the dipole selection rule, it is indicated that the O 1s XAS spectra of SrTiO_3 correspond to transitions into O 2p character hybridized into the unoccupied Ti 3d states.¹³ The feature α and β around 531–532 eV reflect the t_{2g} subbands of the Ti 3d states. The shoulder β around 531 eV is observed in this study possibly because of the high resolution of our spectrometer. The E_F marked in Fig. 2 is determined from the binding energy of the O 1s photoemission peak. One can find that E_F is located around the bottom of the conduction band and gradually shifts further into the conduction band with increasing Nb doping. This is consistent with *ab initio* band structure calculations.¹⁴ The thick solid line above each XAS spectrum drawn on an expanded scale in the photon energy region below 530.4 eV correspond to the same spectra in order to detailed the reliable information in the band gap energy region. It is found that two features due to empty states are also observed in the XAS spectra, even below the threshold. The intensities of these empty states increases in accord with the Nb dopant concentration.

There is no structure in the band gap of non doped SrTiO_3 . Figure 3 shows the comparison between the PES and XAS. It is striking that the energy position of both structures *a* and *b* are the same below E_F . From the temperature dependence of Hall measurements, the Hall coefficient is negative (electron-type), and the existence of the positive carrier due to the hole has not been found.⁸ Here, we estimate the thermally excited empty states to compare with XAS spectra, on the assumption that these two states are the simple donor states. The modified PES spectrum of Fig. 3 is

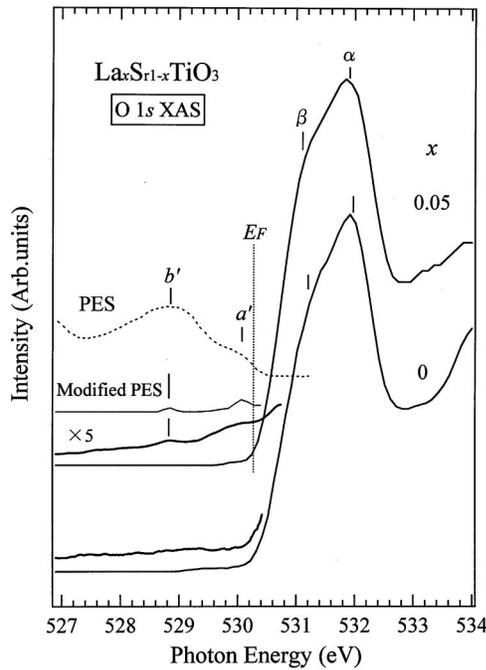


FIG. 4. O 1s XAS spectra of $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ ($x=0.0$ and 0.05) together with the PES spectrum near the Fermi level in the band gap of $\text{La}_{0.05}\text{Sr}_{0.95}\text{TiO}_3$. Thin solid lines are the modified PES spectra (see the text), which correspond to the thermally empty states estimated by the PES.

obtained by the following expression:¹⁵

$$(\text{modified PES}) = (\text{PES}) \times [1 - 1/\{\exp(E/k_B T) + 1\}], \quad (1)$$

where E is the binding energy, $1/[\exp(E/k_B T) + 1]$ is the Fermi-Dirac (FD) function, and k_B, T are Boltzmann constant, temperature. The thin solid lines in Fig. 3 show the thermally excited empty states, which is convoluted by the experimental resolution. It is clear that the two features appearing in XAS spectra are well reproduced by the empty states estimated from PES. Furthermore, the Nb doping dependence of their intensities resemble with that of the O 1s XAS spectra. These facts suggest that the contribution by thermal excitation is significant and that the lightly doped SrTiO_3 system is a degeneratelike semiconductor.

In Fig. 4, we show the O 1s XAS spectra of $\text{La}_{0.05}\text{Sr}_{0.95}\text{TiO}_3$ together with the PES spectrum. The binding energy of b state in $\text{La}_{0.05}\text{Sr}_{0.95}\text{TiO}_3$ is different from that of $\text{SrTi}_{1-x}\text{Nb}_x\text{O}_3$. One clearly finds two features in the XAS spectrum and their position matches with those of the features in the PES spectrum. Thus, one finds that the two states within the band gap region, which correspond to the PES features, are not unique to the Nb doped system. Recently, Kajuter *et al.*¹¹ proposed that the peak position of bulk states is different from that of surface states since the degree of correlation and disorder is larger in the surface than in the bulk. The present results indicate that the 1–1.5 eV peak of carrier-doped SrTiO_3 also consists of a bulk state since escape depth of XAS is of the order of thousand Å and longer than that of PES as well as surface states.

To further investigate the two structures observed in XAS spectra, we have measured temperature dependence of O 1s XAS spectra in $\text{SrTi}_{0.98}\text{Nb}_{0.02}\text{O}_3$ (Fig. 5). The spectra have

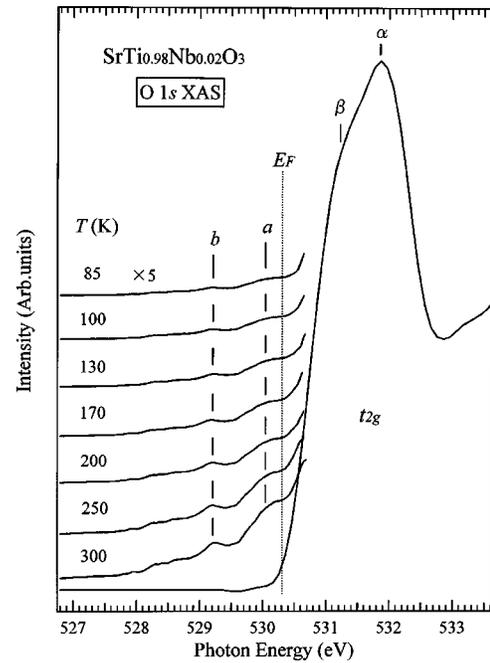


FIG. 5. Temperature dependence of O 1s XAS spectra of $\text{SrTi}_{0.98}\text{Nb}_{0.02}\text{O}_3$.

been measured in the temperature region from 300 to 80 K. To make sure of the reproducibility of the spectra, the measurement was carried out for both, decreasing temperatures from 300 K and increasing temperatures from 80 K. The intensity of a and b peaks decrease with the decreasing of temperature. The intensities of a and b peaks are shown in Fig. 6, where $\log(\text{Intensity})$ is plotted against $1000/T$ (K^{-1}). Open and closed triangle marks superimposed on the intensities of a and b peaks in modified PES are expected ones from Eq. (1). The slopes of both a and b peaks are exponential-like and is in good agreement with the slopes of the intensities of modified PES. The activation energy (ΔE), which estimated from the slope of modified PES, is 0.1 eV for a peak and 0.8 eV for b peak. They are of the same order

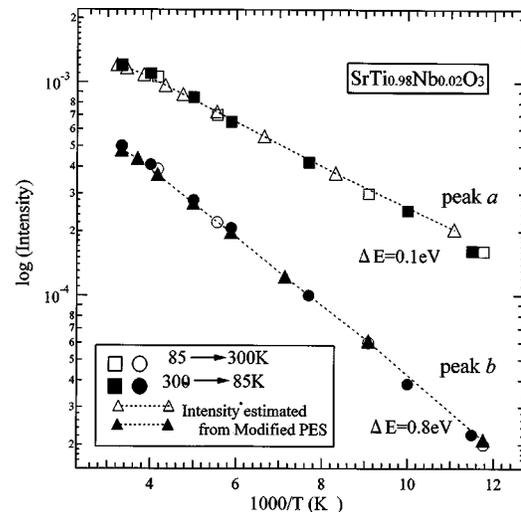


FIG. 6. The plot of intensities of a and b peaks of O 1s XAS spectra shown in Fig. 5. Open and closed triangles are the intensities of a and b peaks obtained from modified PES.

as that of binding energies for PES features. This result indicates that the two features due to empty states in the XAS spectra are due to the thermal excitation from the two features that are found in the PES spectra. The estimated activation energy is larger than that obtained from the electrical conductivity measurement in Nb-doped SrTiO₃.¹² Because the feature *a* has a bandwidth, it is supposed that the lower energy side of the feature *a* contributes to the electron conductivity.

A PES peak at 1–1.5 eV below E_F has been observed in many d^0 transition-metal compounds such as CaTiO₃ (Ref. 16) as well as SrTiO₃ (Refs. 1–7) when lightly doped with extra electrons. For the La_{*x*}Sr_{1–*x*}TiO₃ system with $x < 0.5$, it has been reported that the peak at 1–1.5 eV is incompatible with the rigid-band behavior or Hubbard model.^{1,2} In our experimental results, the electronic states in the band gap energy region seem to be the simple donor states, which are independent of the photoelectron excitation process.

IV. CONCLUSION

In conclusion, we studied the electronic structure in the band gap region of carrier-doped SrTiO₃ using XAS. The O 1*s* XAS spectrum shows two empty features, corresponding to two features observed in photoemission spectra. These states show apparent temperature dependence, which are well explained by calculation using FD distribution. This indicates that the peak at 1–1.5 eV of lightly carrier-doped SrTiO₃ is not due to surface states but a real bulk state such as a donor state.

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