

Unoccupied Electronic State of Lightly La-Doped SrTiO₃ Observed by Inverse-Photoemission Spectroscopy

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The unoccupied electronic state of lightly La³⁺-doped SrTiO₃ has been studied by inverse-photoemission spectroscopy (IPES). The IPES spectra exhibit two features, which correspond to *t*_{2g}- and *e*_g-subbands of the Ti 3*d* state. The peak positions of *t*_{2g}- and *e*_g-subbands are in good agreement with the standard band calculation. The intensity of the *t*_{2g}-subband of the Ti 3*d*-induced conduction band decreases with increasing La³⁺ dopant concentration. This finding is direct evidence that the doped electrons enter the bottom of the Ti 3*d*-induced conduction band. [DOI: 10.1143/JJAP.42.L837]

KEYWORDS: La-doped SrTiO₃ (La_{*x*}Sr_{1-*x*}TiO₃), inverse photoemission spectroscopy (IPES), electronic structure, unoccupied state, rigid-band model, band calculation

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. SrTiO₃ has been extensively used as a substrate for thin-film deposition of superconductors and ferroelectrics because of their similar crystal structures and good lattice matching. It is well known that SrTiO₃ exhibits *n*-type metallic conductivity on substituting La³⁺ for Sr²⁺ and it becomes a superconductor at *T*_c = 0.3 K.¹⁻⁴ The doped SrTiO₃ has also been used in practical applications such as electrodes and as a gas sensor. Therefore, understanding the detailed electronic structure of doped SrTiO₃ is one of the most important subjects for further applications.

In recent years, there has been a renewed interest in the electronic structure of SrTiO₃ doped with a charge carrier. The band structure can be explained by the energy band picture since there are only nominal 3*d* electrons that bring about appreciable correlation interaction.⁵⁻⁷ The top of the valence band is mainly composed of O 2*p* states and the bottom of the conduction band is formed by Ti 3*d* states. When a small number of electrons are chemically doped into SrTiO₃, the doped electrons enter the bottom of the empty Ti 3*d* band. At the limit of the lightly doped concentration, there will be no electron correlation between the doped electrons since the probability of electron-electron scattering is negligible. These findings have been supported from the results of electric transport¹⁻⁴ and a number of spectroscopic studies.⁸⁻¹⁶ On the other hand, the detailed electronic structure in the conduction band of lightly La³⁺-doped SrTiO₃ (La_{*x*}Sr_{1-*x*}TiO₃) has not been clarified by experimental methods such as inverse-photoemission spectroscopy (IPES).

In the present study, we measured the IPES spectra of La_{*x*}Sr_{1-*x*}TiO₃. IPES is a powerful technique for investigating the unoccupied electronic structure in the surface state.^{17,18} However, the number of experimental IPES studies of 3*d* transition metal oxides is very few.¹⁴⁻¹⁶ In this study, we demonstrated that the band structure of the conduction band obeys the rigid band model, as shown in the valence band side.^{9,10,12,16}

Single crystals of La_{*x*}Sr_{1-*x*}TiO₃ were synthesized by melt-quenching stoichiometric mixtures of La₂O₃, TiO₂, and SrO powders in a floating-zone furnace. The dopant concentrations were *x* = 0.05 and 0.10. The crystals were examined by X-ray diffraction.

The IPES measurements were carried out at the Institute for Solid State Physics, University of Tokyo. A filament-cathode-type electron gun was used for the excitation source. The kinetic energy of the electron was calibrated using an electron energy analyzer. The RIPES spectra were measured using a soft-X-ray emission spectrometer, which covers a wide photon-energy range from 15 to 1200 eV.^{17,18} The spectrometer used Rowland circle geometry that consists of a grating with a groove density of 300 lines/mm and a Cs-coated multichannel detector. The single crystals were scraped *in situ* with a diamond file in a vacuum of 2.0 × 10⁻¹⁰ Torr in order to obtain a clean surface. The measurement was carried out at 25 K. The intensity axis was normalized by the electron current and measurement time. The bottom axis was normalized by measuring the Fermi edge of Au film. The total energy resolution of the experimental system was about 0.7 eV at incident electron energy (*E*_k) = 100 eV.

Figure 1(a) shows the IPES spectrum of La_{0.05}Sr_{0.95}TiO₃ measured at *E*_k = 100 eV. The abscissa represents the energy above the Fermi level (*E*_F) that was calibrated by the Fermi edge of Au. The experimentally determined *E*_F is located almost at the bottom of the conduction band because the sample used in this study has *n*-type conductivity. Two prominent features *α* and *β* are found at ~2.0 eV and 4.2 eV, respectively.

Figure 1(b) shows the energy band DOS histogram calculated by Mattheiss *et al.*⁵ Mattheiss calculated the DOS histogram using the augmented plane wave (APW) and Slater-Coster linear combination of atomic-orbitals interpolation method. The solid line shown above the histogram is obtained by convoluting the original DOS with Gaussian broadening functions with widths of 0.7 eV. Compared with the IPES spectrum of Fig. 1(a), the bandwidth and peak positions of *α* and *β* are in good agreement with the calculated energy band DOS.

Figure 1(c) shows the O 1*s* X-ray absorption (XAS)

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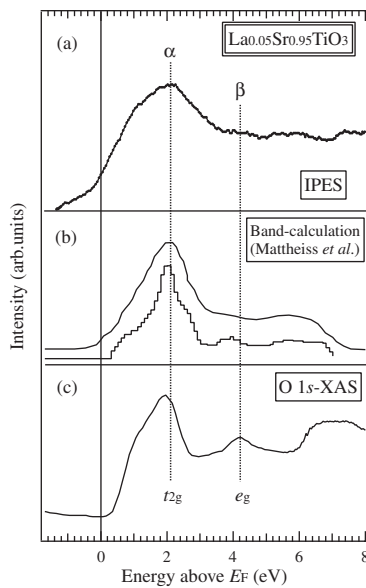


Fig. 1. (a) IPES spectrum of $\text{La}_{0.05}\text{Sr}_{0.95}\text{TiO}_3$ measured at $E_K = 100$ eV. (b) Energy band DOS calculated by Mattheiss *et al.*⁵⁾ (c) O 1s XAS spectrum of SrTiO_3 .

spectrum of SrTiO_3 . The dipole selection rule indicates that the O 1s XAS spectrum of SrTiO_3 corresponds to transitions into O 2p character hybridized with the unoccupied Ti 3d states.¹²⁾ The E_F of the XAS spectrum is determined from the binding energy of the O 1s photoemission peak. Two features at ~ 2.0 eV and 4.2 eV of the O 1s XAS spectrum reflect the t_{2g} - and e_g -subbands of the Ti 3d states. The energy separation between the t_{2g} - and e_g -subbands (crystal-field splitting) accords with the Ti 2p XAS spectrum¹¹⁾ and the band calculation for the O 1s XAS spectrum by Fujimori *et al.*⁸⁻¹⁰⁾ It is striking that the energy positions of the t_{2g} - and e_g -subbands of the O 1s XAS spectrum are in good agreement with features α and β of the IPES spectrum, as shown by two vertical dashed lines.

Figure 2(a) shows the IPES spectra as a function of La^{3+} dopant concentration of $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ ($x = 0.05$ and 0.10)

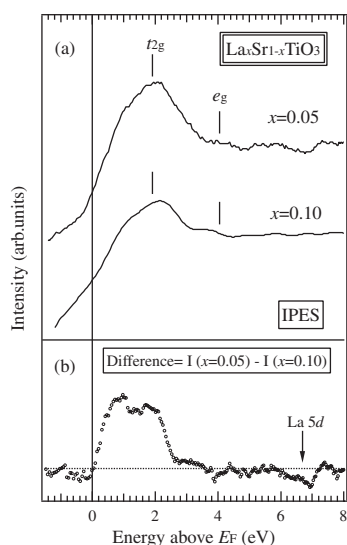


Fig. 2. (a) IPES spectra as a function of La doping of $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ ($x = 0.05, 0.10$) measured at $E_K = 100$ eV. (b) Difference spectrum obtained by subtracting the IPES spectrum of $x = 0.05$ from that of $x = 0.10$.

measured at $E_K = 100$ eV. The IPES spectra are normalized by measurement time and beam current. The peak positions of t_{2g} - and e_g -subbands do not depend on La^{3+} dopant concentration. The intensity of the t_{2g} -subband is lower in $x = 0.10$, indicating that the doped electrons enter the Ti 3d conduction band.

Figure 2(b) shows the difference spectrum by subtracting the IPES spectrum of $x = 0.10$ from that of $x = 0.05$. This difference spectrum reflects the contribution of the Ti 3d conduction band by La^{3+} doping. The intensity at ~ 6.8 eV is negative since the La^{3+} dopant concentration doped into the Sr^{2+} site is lower in $x = 0.05$, indicating the existence of the La 5d state. The intensity at the e_g -subband does not depend on La^{3+} dopant concentration. However, an apparent distribution of difference spectrum is observed in the energy region from E_F to 2.5 eV. This distribution indicates the change of Ti 3d electron number with La^{3+} doping. On one hand, the above result demonstrates that the doped electrons enter the bottom of the empty Ti 3d conduction band. Here, the discrepancy between the spectral area at ~ 6.8 eV and the spectral area of the energy region from E_F to 2.5 eV is considered to be due to the difference of the ionization cross section between La 5d and Ti 3d states.¹⁹⁾

In recent years, the band structure in the conduction band region of the lightly-doped SrTiO_3 has been calculated by Sarma *et al.*¹⁵⁾ They used the linear muffin orbital (LMTO) method within the atomic-sphere approximation. From the second-order perturbation applied to the DOS obtained from the LMTO supercell calculation, a correlation-induced satellite and surface-induced state appear outside the one-electron bandwidth in the unoccupied states. This calculation indicates that the band structure of doped SrTiO_3 does not obey the rigid-band model. However, our results are in good agreement with the one-electron band calculation. The doped electrons enter the bottom of the Ti 3d conduction band and form the impurity state at E_F . The existence of the impurity state has been observed in the photoemission and XAS studies.^{9,10,12)} Thus, the band structure of lightly-doped SrTiO_3 can be explained by the rigid-band model.

In conclusion, we have studied the unoccupied electronic state of $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ in the lightly doping region using IPES. The IPES spectra show two features, which correspond to the t_{2g} - and e_g -subbands of the O 1s XAS spectrum. The peak positions of t_{2g} - and e_g -subbands are in good agreement with the one-electron band calculation. The intensity of the bottom of the conduction band observed in the IPES spectrum decreases with increasing La dopant concentration, indicating that the doped electrons enter the bottom of the empty Ti 3d conduction band. These findings indicate that the band structure of lightly-doped SrTiO_3 obeys the rigid-band model.

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