

## Ti–O Hybridization Effect of Lightly La-doped SrTiO<sub>3</sub> Observed by Resonant-Photoemission Spectroscopy

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The electronic structure of lightly La-doped SrTiO<sub>3</sub> (La<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub>) has been investigated by resonant-photoemission spectroscopy (RPES). The RPES spectra show that the Ti 3d partial density of states in the valence band decreases with increasing La dopant concentration. This finding indicates that the hybridization effect between the Ti 3d and O 2p states decreases with La<sup>3+</sup> dopant concentration. [DOI: 10.1143/JJAP.41.5674]

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Perovskite-type oxide SrTiO<sub>3</sub> exhibits *n*-type conductivity with Nb<sup>5+</sup> substitution at the Ti<sup>4+</sup> site and it becomes a superconductor at  $T_c = 0.3$  K.<sup>1,2)</sup> Nb-doped SrTiO<sub>3</sub> (SrTi<sub>1-x</sub>Nb<sub>x</sub>O<sub>3</sub>) is used as a substrate for the thin film deposition of ferroelectrics and superconductors because of their similar crystal structures and good lattice matching. Such doping can also be achieved by altering either of the two sublattices Sr<sup>2+</sup> and O<sup>2-</sup>. In particular, La<sup>3+</sup> substitution at the Sr<sup>2+</sup> site (La<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub>) has been extensively studied because this system shows the insulator-to-metal transition as well as superconductivity.<sup>3-5)</sup> In the small dopant region, the electrical conductivity of La<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub> resembles with that of SrTi<sub>1-x</sub>Nb<sub>x</sub>O<sub>3</sub>.<sup>2)</sup> For this reason, La<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub> might also be used as a substrate for thin film deposition. Therefore, understanding the electronic structure of La<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub> ( $x \leq 0.05$ ) is also important in terms of the science and technology of materials.

The electronic structure of SrTiO<sub>3</sub> has been extensively studied over many years.<sup>6-16)</sup> The electronic structure can be explained from the energy band picture since there are only a few 3d electrons that bring about an appreciable correlation effect. It is well known that the valence band mainly consists of the O 2p state which strongly hybridizes with Ti 3d states, and the conduction band is formed by the Ti 3d states. This leads to a situation in which nonvanishing 3d electrons exist in the ground state. In the resonant-photoemission (RPES) study on SrTi<sub>1-x</sub>Nb<sub>x</sub>O<sub>3</sub>, it was reported that the Ti 3d partial density of states (PDOS) in the valence band increases with increasing Nb<sup>5+</sup> dopant concentration.<sup>11,16)</sup> This result implies that the hybridization effect between the Ti 3d state and the O 2p state becomes more extensive with increasing Nb<sup>5+</sup> dopant concentration, indicating the change of the effective charges of Ti<sup>4+</sup> and O<sup>2-</sup>. Such a situation might also be expected in small doping region ( $x \leq 0.05$ ) of La<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub>.

In this study, the hybridization effect of La<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub> ( $x = 0.01$  and 0.05) has been investigated by RPES. We discuss how the hybridization effect is related to the lattice parameter of La<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub>.

Single crystals of La<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub> were synthesized by melt-quenching stoichiometric mixtures of La<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and SrO powders in a floating-zone furnace. The dopant concentrations were  $x = 0.01$ , 0.05. The crystals were examined by X-ray diffraction. RPES measurements were

carried out at the revolving undulator beamline BL-19B at the Photon Factory (PF) of the High Energy Accelerator Organization (KEK), Tsukuba, Japan. Photoelectron energies were measured with an electrostatic hemispherical analyzer with a radius of 100 mm. The total energy resolution was approximately 40 meV. The samples were scraped *in situ* with a diamond file in a vacuum of  $2.0 \times 10^{-10}$  Torr in order to obtain a clean surface.

Figure 1(a) shows the constant final state (CFS) spectrum of La<sub>0.05</sub>Sr<sub>0.95</sub>TiO<sub>3</sub> measured at the kinetic energy where the secondary electron has a maximum intensity. This spectrum is regarded as the approximate absorption spectrum of Ti 3p → 3d. The CFS spectrum shows a broad maximum at approximately 47 eV.

Figure 1(b) shows the RPES spectra in the valence band region of La<sub>0.05</sub>Sr<sub>0.95</sub>TiO<sub>3</sub> measured at various photon energies. The valence band has two features, indicated by

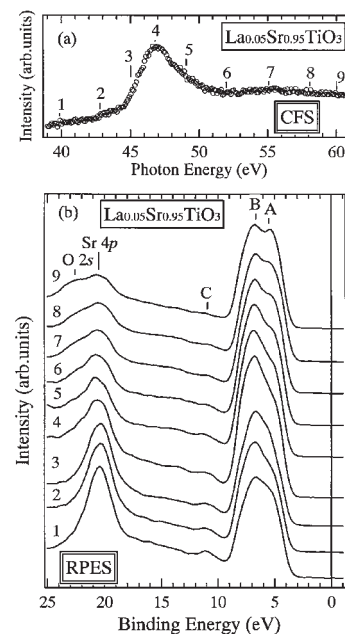


Fig. 1. (a) CFS spectrum of La<sub>0.05</sub>Sr<sub>0.95</sub>TiO<sub>3</sub>, corresponding to the Ti 3p → 3d absorption spectrum. The numbers indicate the photon energies at which the RPES spectra were measured. (b) RPES spectra in the valence band region of La<sub>0.05</sub>Sr<sub>0.95</sub>TiO<sub>3</sub> excited at various photon energies.

A and B, which mainly consist of O 2*p* states mixed with Ti 3*d* states. It is well known that feature A and corresponds to the nonbonding state and feature B corresponds to the bonding state which is well mixed with Ti 3*d* states. The intensity of the bonding state is enhanced at  $h\nu = 47$  eV, which corresponds to the Ti 3*p* → 3*d* absorption edge. Feature C is due to the oxygen defects at the surface.<sup>6,11)</sup> The doublet structures at approximately 20 eV are the O 2*s* and Sr 4*p* core levels. The intensity of Sr 4*p* peaks at ~23 eV increases with decreasing excitation energy. This is evidently due to the excitation energy dependence of the ionization cross section of the Sr 4*p* electron.

Figure 2(a) shows the on- and off-resonance spectra of the valence band of  $\text{La}_{1-x}\text{Sr}_x\text{TiO}_3$  measured at  $h\nu = 60$  eV. Comparing the off-resonance spectra, the intensity of the nonbonding state is lower in  $x = 0.01$ . In both on-resonance spectra, the intensities of peaks A and B are resonantly enhanced by the Ti 3*p* → 3*d* excitation. The resonance effect is stronger in  $x = 0.01$ .

Figure 2(b) shows the difference spectra by subtracting the off-resonance from the on-resonance spectra. The difference spectra correspond to the Ti 3*d* PDOS in the valence band. Comparing the difference spectra, the Ti 3*d* PDOS is larger in the case of  $x = 0.01$ . This fact implies that the hybridization effect between the Ti 3*d* state and O 2*p* state becomes more extensive with  $\text{La}^{3+}$  dopant concentration, indicating that the bond length between  $\text{Ti}^{4+}$  and  $\text{O}^{2-}$  ions or the symmetry changes with a small amount of doping cations.

In terms of the crystal structure, it is reported that the lattice parameters increase linearly with increasing  $\text{La}^{3+}$  dopant concentration.<sup>5)</sup> The ionic radius of  $\text{La}^{3+}$  is slightly less than that of  $\text{Sr}^{2+}$ , i.e.,  $\text{La}^{3+}$ : 0.123 nm and  $\text{Sr}^{2+}$ : 0.125 nm for 12-fold coordination. The ionic radius of  $\text{Ti}^{3+}$ , which formed for the charge compensation, is larger than that of  $\text{Ti}^{4+}$ , i.e.,  $\text{Ti}^{3+}$ : 0.076 nm and  $\text{Ti}^{4+}$ : 0.068 nm for 6-

fold coordination. The  $\text{Ti}^{3+}$  constant was approximately equal to the nominal La content for any composition based on the weight gain after the oxidation. Accordingly, the increase in lattice parameters is attributed to the increase in  $\text{Ti}^{3+}$  content of the crystal. This fact has been confirmed in the X-ray photoemission (XPS) spectra of  $\text{Y}_x\text{Ca}_{1-x}\text{TiO}_3$ . The band structure of  $\text{Y}_x\text{Ca}_{1-x}\text{TiO}_3$  resembles with that of  $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ . In the XPS spectra in the Ti 2*p*<sub>3/2</sub> core region,  $\text{Ti}^{4+}$  and  $\text{Ti}^{3+}$  peaks are found at ~460 eV and ~462 eV, respectively.<sup>17)</sup> The peak intensities of the  $\text{Ti}^{4+}$  and  $\text{Ti}^{3+}$  peaks vary systematically with  $\text{Y}^{3+}$  dopant concentration. This phenomenon is also expected for  $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ . The doped electrons enter the bottom of the empty state 3*d* band and the Ti 3*d*-originated-DOS ( $\text{Ti}^{3+}$  component) exists in the band-gap energy region.<sup>10-14)</sup> Thus, the decrease in the hybridization effect between the Ti 3*d* and O 2*p* states with La doping can be explained by the decrease in the effective charges of  $\text{Ti}^{4+}$  and  $\text{O}^{2-}$  ions.

In conclusion, we measured the RPES spectra on  $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$  using synchrotron radiation. The RPES spectra show that the hybridization effect between the Ti 3*d* and O 2*p* states decreases with increasing  $\text{La}^{3+}$  dopant concentration. This finding indicates that the effective charge of  $\text{Ti}^{4+}$  and  $\text{O}^{2-}$  ions decreases with  $\text{La}^{3+}$  dopant concentration.

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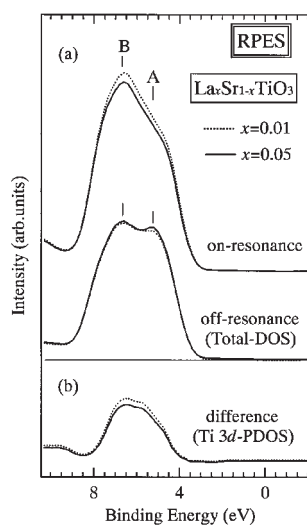


Fig. 2. RPES spectra as a function of La doping of  $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$  ( $x = 0.01$  and  $0.05$ ). (a) On-resonance spectra measured at  $h\nu = 47$  eV and off-resonance spectra measured at  $h\nu = 60$  eV. (b) Difference spectra obtained by subtracting the off-resonance spectra from the on-resonance spectra.

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