

Electronic Structures of $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ and $\text{Bi}_4\text{Zr}_x\text{Ti}_{3-x}\text{O}_{12}$ Single Crystals Studied by Soft-X-Ray Spectroscopy

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The electronic structures of La-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$) and Zr-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($\text{Bi}_4\text{Zr}_x\text{Ti}_{3-x}\text{O}_{12}$) single crystals have been studied by X-ray absorption spectroscopy (XAS) and soft-X-ray emission spectroscopy (SXES). In both $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ and $\text{Bi}_4\text{Ti}_{3-x}\text{Zr}_x\text{O}_{12}$, the Ti 3*d* and O 2*p* partial densities of states (PDOS) in the valence band region were observed in O 1*s* and Ti 2*p* SXES spectra. The energy position of the Ti 3*d* state overlapped with that of the O 2*p* state, indicating the occurrence of the hybridization effect between the Ti 3*d* and O 2*p* states. The hybridization effect of $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ increases with increasing La dopant concentration, although that of $\text{Bi}_4\text{Ti}_{3-x}\text{Zr}_x\text{O}_{12}$ does not depend on Zr dopant concentration. This finding indicates that the hybridization effect is closely related to the change in the bond length between Ti and O ions. [DOI: 10.1143/JJAP.42.6226]

KEYWORDS: $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$, $\text{Bi}_4\text{Ti}_{3-x}\text{Zr}_x\text{O}_{12}$, single crystal, electronic structure, soft-X-ray emission spectroscopy (SXES), X-ray absorption spectroscopy (XAS), Ti-O hybridization effect, lattice constant

1. Introduction

Ferroelectric thin films have attracted considerable attention because of their use in ferroelectric random access memories (FeRAMs). Most attention has been focused on bismuth-layer-structured ferroelectrics, such as $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT) and $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT).^{1–3} However, the poor fatigue characteristic and the same remanent polarization of these ferroelectrics are viewed as the major problem in their FeRAM applications. Therefore, La-doped BIT ($\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$) has been reported as a promising material for solving such problems. The $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ thin film prepared at a low temperature of 650°C exhibits a relatively large remanent polarization and superior fatigue endurance.^{4–6} Such a significant improvement in ferroelectricity has been observed only for $(\text{Bi}_{4-x}\text{La}_x)(\text{Ti}_{3-y}\text{V}_y)\text{O}_{12}$ and $\text{Bi}_4\text{Ti}_{3-y}\text{V}_y\text{O}_{12}$ films. This selective control of each site is called “site engineering”. The site engineering effect on BIT has been extensively studied by Watanabe *et al.* and Tokumitsu *et al.*^{7–10} They reported that the major contribution of site engineering to BIT is to the adjustment of the Curie temperature and the suppression of domain pinning. However, fundamental knowledge of the site-engineering effect for BIT is lacking. Therefore, understanding the electronic structure of BIT is also one of the most important considerations for its further applications.

In this research, the electronic structure of $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ single crystals has been studied by absorption spectroscopy (XAS) and emission spectroscopy (SXES) in the soft-X-ray region. As reference, the XAS and SXES spectra of $\text{Bi}_4\text{Ti}_{3-x}\text{Zr}_x\text{O}_{12}$ single crystals were also measured. XAS is related directly to the unoccupied density of state (DOS).^{11,12} This optical process is a local process, because of the localized core state. It is governed by the dipole selection rules so that XAS provides the spectrum related to the site- and symmetry-selected DOS. On the other hand, SXES is related directly to the occupied DOS.^{13–15} The partial DOS (PDOS) localized at an atom can be

obtained from SXES spectra because SXES has a clear selection rule regarding the angular momentum due to dipole selection. In order to study the doping site and hybridization effect, we measured the XAS and SXES spectra in the energy regions of Ti 2*p* and O 1*s* excitation thresholds.

2. Experimental

$\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ single crystals were grown by a conventional flux method using Bi_2O_3 as a flux. A mixture of Bi_2O_3 , TiO_2 , and La_2O_3 was heated to 1200°C, maintained for 10 h, and then slowly cooled to 100°C at a rate of 5°C/min. Residual flux was removed using 20% HCl solution. The single crystals were confirmed to be in a single phase with a BLT structure by powder X-ray diffraction analysis. The La dopant concentrations were $x = 0–1.5$. These electrical and structural properties have been reported in refs. 16 and 17.

The $\text{Bi}_4\text{Ti}_{3-x}\text{Zr}_x\text{O}_{12}$ samples were prepared by the solid-state reaction of Bi_2O_3 , TiO_2 , and ZrO_2 at 1200°C for approximately 4 h, and the single crystals were grown by a floating-zone method using a halogen-arc imaging furnace. The single crystals were confirmed to be in a single phase with a BIT structure by powder X-ray diffraction analysis. The Zr dopant concentrations were $x = 0–0.40$. The detailed electrical and structural properties will be published elsewhere.¹⁸

XAS and SXES spectra were measured using a soft-X-ray spectrometer installed at the undulator beamline BL-19B (in Photon Factory) at the High Energy Accelerator Organization, in Tsukuba, Japan. Synchrotron radiation was monochromatized using a varied-line spacing plain grating whose average groove density is 1000 lines/mm. The spectra were measured in a polarization configuration. The energy resolution of XAS was about 0.1 eV at $h\nu = 450$ eV. The energy resolution of SXES was about 0.5 eV at $h\nu = 500$ eV. The bottom axis was calibrated by measuring the 4*f* core level of the Au film.

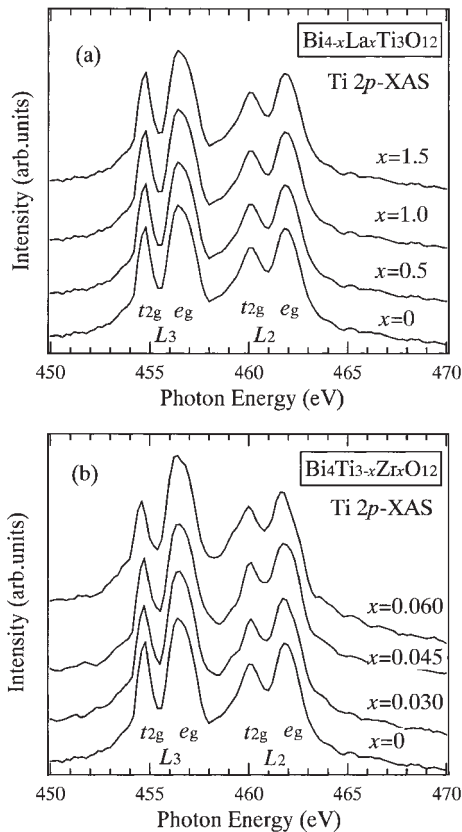


Fig. 1. (a) Ti 2*p* XAS spectra as a function of La dopant concentration in $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ single crystals. (b) Ti 2*p* XAS spectra as a function of Zr dopant concentration in $\text{Bi}_4\text{Ti}_{3-x}\text{Zr}_x\text{O}_{12}$ single crystals.

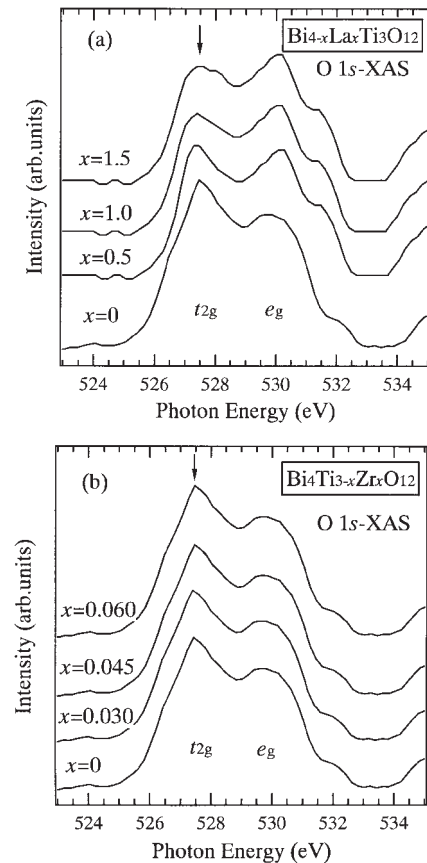


Fig. 2. (a) O 1*s* XAS spectra as a function of La dopant concentration in $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ single crystals. (b) O 1*s* XAS spectra as a function of Zr dopant concentration in $\text{Bi}_4\text{Ti}_{3-x}\text{Zr}_x\text{O}_{12}$ single crystals.

3. Results and Discussion

Figure 1(a) shows Ti 2*p* XAS spectra as a function of La dopant concentration in $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ single crystals. The Ti 2*p* XAS spectra correspond to the transition from the Ti 2*p* core level to the unoccupied Ti 3*d* state. The spectra are derived from the two parts of L_3 ($2p_{3/2}$) and L_2 ($2p_{1/2}$). They are split into the t_{2g} - and e_g -subbands by the octahedral ligand field.¹³ Comparing both spectra, the intensities of four peaks do not depend much on La dopant concentration. This result indicates that the dopant La ions do not enter the Ti^{4+} site of BIT.

Figure 1(b) shows Ti 2*p* XAS spectra as a function of Zr dopant concentration in $\text{Bi}_4\text{Ti}_{3-x}\text{Zr}_x\text{O}_{12}$ single crystals. The overall profiles of these spectra in $\text{Bi}_4\text{Ti}_{3-x}\text{Zr}_x\text{O}_{12}$ accord with those in $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$. However, the intensity of the t_{2g} -subband decreases with increasing Zr dopant concentration, indicating that the dopant Zr^{4+} ions enter the Ti^{4+} site of BIT.

Figure 2(a) shows the O 1*s* XAS spectra as a function of La dopant concentration in $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ single crystals. From the dipole selection rules, it is understood that the O 1*s* XAS spectra of Ti oxides correspond to transitions from the O 1*s* character to the O 2*p* character hybridized with the unoccupied Ti 3*d* and Bi 6*s* states.^{11–14} The O 1*s* XAS spectra are normalized by measurement time and beam current. The spectra are derived from the two parts of the t_{2g} - and e_g -subbands of the Ti 3*d* state. The energy separation between the t_{2g} - and e_g -subbands is in good agreement with

that in Fig. 1. The intensity of the t_{2g} -subband in the O 1*s* XAS decreases with increasing La dopant concentration. However, the intensity of the t_{2g} -subband in the Ti 2*p* XAS spectra does not depend on La dopant concentration. This discrepancy could be attributed to the existence of the Bi 6*s* state in the unoccupied state, because the La ions are doped into the Bi site of BIT. On the other hand, the O 1*s* XAS spectra of $\text{Bi}_4\text{Ti}_{3-x}\text{Zr}_x\text{O}_{12}$ single crystals do not depend on Zr dopant concentration, as shown in Fig. 2(b).

Figure 3 shows the O 1*s* and Ti 2*p* SXES spectra in the valence band region of $\text{Bi}_{3.5}\text{La}_{0.5}\text{Ti}_3\text{O}_{12}$ single crystals. The O 1*s* SXES spectrum measured at $h\nu = 500$ eV reflects the O 2*p* PDOS. The Ti 2*p* SXES spectrum measured at $h\nu = 550$ eV reflects the Ti 3*d* PDOS. One can find that the energy position of the O 2*p* state overlaps with that of the Ti 3*d* state in the valence band. The valence band has two peaks, A and B, at -5.2 eV and -7.5 eV, respectively. Comparing both SXES spectra the Ti 3*d* contribution is more significant on the higher energy side (peak B), where the O 2*p* states have a larger admixture of the Ti 3*d* state. On the other hand, the valence band derived from the O 2*p* states are hybridizes with the Ti 3*d* states. Therefore, we can conclude that peak A corresponds to the nonbonding state and peak B corresponds to the bonding state that is well mixed with the Ti 3*d* state.^{14,15}

In Fig. 3, the PDOS histogram calculated in undoped BIT is also shown under each SXES spectrum. The electronic structure calculations based on the density functional theory

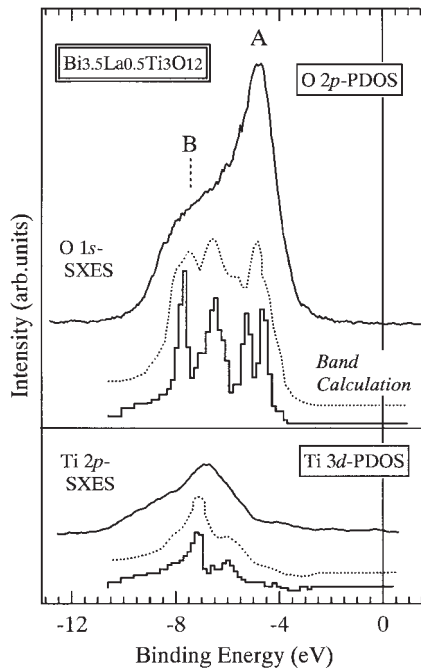


Fig. 3. O 1s and Ti 2p SXES spectra of $\text{Bi}_{3.5}\text{La}_{0.5}\text{Ti}_3\text{O}_{12}$ single crystal. For reference, the calculated band DOS is also shown under each SXES spectrum.

using local density approximation (LDA) were performed using the *ab-initio* calculation program. In order to calculate the electronic structure, we optimized the bases sets with effective core potential. A dashed curve above each calculated PDOS histogram is obtained by convoluting the original PDOS with Gaussian broadening functions with a width of 0.5 eV, which reflects the total resolution of the experimental system. The calculated O 2p PDOS has four peaks, which correspond to Γ , X, P, and N points in the tetragonal Brillouin zone.¹⁵⁾ Although the O 1s SXES spectrum has only two peaks, this is considered to be due to the poor resolution of the experimental system. However, the bandwidths of the calculated PDOS are in good agreement with those of the Ti 2p and O 1s SXES spectra.

Figure 4(a) shows O 1s and Ti 2p SXES spectra as functions of La dopant concentration in $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ single crystals. The intensities of the SXES spectra are normalized by the intensity of the elastic scattering, although the elastic scattering peak is not shown in this figure. At all dopant concentrations, it is clear that the O 2p state hybridizes with the Ti 3d state in the valence band, as shown in the case of the $\text{Bi}_{3.5}\text{La}_{0.5}\text{Ti}_3\text{O}_{12}$ single crystal in Fig. 3. Furthermore, the bandwidths of O 2p and Ti 3d states in the $\text{Bi}_{3.5}\text{La}_{0.5}\text{Ti}_3\text{O}_{12}$ single crystal are in good agreement with those in $\text{Bi}_{3.0}\text{La}_{1.0}\text{Ti}_3\text{O}_{12}$ and $\text{Bi}_{2.5}\text{La}_{1.5}\text{Ti}_3\text{O}_{12}$ single crystals. It is notable that the intensity of Ti 3d PDOS increases with increasing La dopant concentration. This finding indicates that the hybridization effect between the Ti 3d and O 2p state decreases with increasing La dopant concentration. On the other hand, the hybridization effect of $\text{Bi}_4\text{Ti}_{3-x}\text{Zr}_x\text{O}_{12}$ single crystals does not depend on Zr dopant concentration, as shown in Fig. 4(b). The difference in the hybridization effect between $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ and $\text{Bi}_4\text{Ti}_{3-x}\text{Zr}_x\text{O}_{12}$ is considered to be due to the change in lattice constant or Ti-O bond length upon the site engineer-

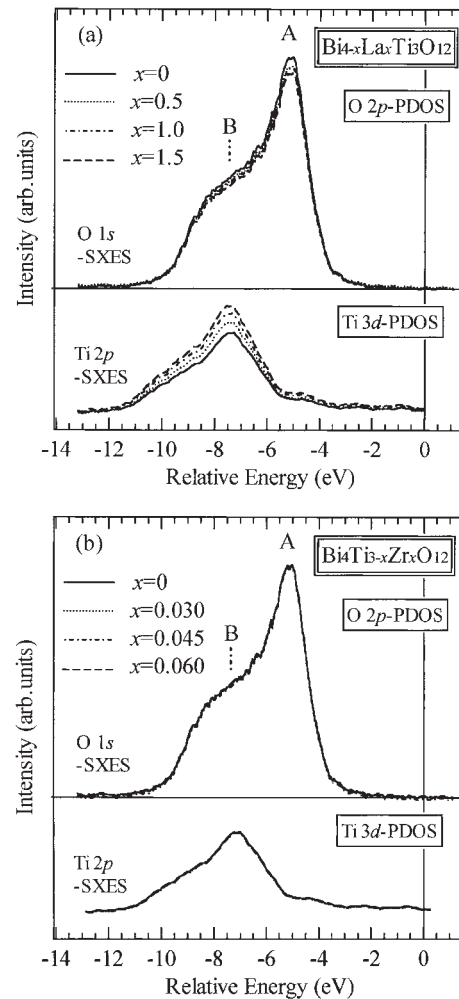


Fig. 4. (a) O 1s and Ti 2p SXES spectra as functions of La dopant concentration in $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ single crystal. (b) O 1s and Ti 2p SXES spectra as a function of La dopant concentration in $\text{Bi}_4\text{Ti}_{3-x}\text{Zr}_x\text{O}_{12}$ single crystals.

ing of BIT, as reported in BaTiO_3 .¹⁹⁾

In this experimental system, the incident angle of the soft-X-ray was about 70° in order to avoid the self-absorption effect. The SXES and XAS spectra were measured in a polarized configuration. The polarization vector of the emitted photon rotates by 90° from the polarization vector of an incident photon. When the SXES spectra are measured in the polarization configuration, the polarization vector of the emitted photon contains the same polarization vector as that of the incident photon. Therefore, the SXES spectra measured in the polarization configuration reflect the electronic structure within the *a-b* plane; the detailed description has been reported in ref. 15. Thus, the change in the hybridization effect of $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ reflects the change in the electronic structure within the *a-b* plane. In terms of crystal structure, the lattice constant of the *a*-axis in $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ decreases rapidly from 5.45 Å to 5.42 Å at $0 \leq x \leq 1.0$, although that of the *b*-axis does not depend on La dopant concentration.¹⁶⁾ In other words, the bond length between Ti and O ions within the *a-b* plane decreases with increasing La dopant concentration. On the other hand, the lattice constants of the *a*- and *b*-axes in $\text{Bi}_4\text{Ti}_{3-x}\text{Zr}_x\text{O}_{12}$ do not depend on Zr dopant concentration.¹⁸⁾ The above results

conclude that the hybridization effect of BIT is closely related to the lattice constant or the bond length between Ti and O ions.

4. Conclusions

We have studied the electronic structures of $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ and $\text{Bi}_4\text{Ti}_{3-x}\text{Zr}_x\text{O}_{12}$ single crystals by XAS and SXES. The O $1s$ XAS spectra of $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ single crystals show that the dopant La ions enter the Bi site of BIT. The Ti $2p$ XAS spectra of $\text{Bi}_4\text{Ti}_{3-x}\text{Zr}_x\text{O}_{12}$ single crystals show that the dopant Zr ions enter the Ti site of BIT. In the SXES spectra of both $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ and $\text{Bi}_4\text{Ti}_{3-x}\text{Zr}_x\text{O}_{12}$ single crystals, the O $2p$ state hybridizes with the Ti $3d$ state in the valence band. The hybridization effect between the Ti $3d$ and O $2p$ states of $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ single crystals increases with increasing La dopant concentration, although that of $\text{Bi}_4\text{Ti}_{3-x}\text{Zr}_x\text{O}_{12}$ does not depend on Zr dopant concentration. These findings conclude that the hybridization effect of BIT fabricated using the site engineering technique is closely related to the lattice constant or bond length between Ti and O ions within the a - b plane.

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