Electronic Structures of Bi$_{4-x}$La$_x$Ti$_3$O$_{12}$ and Bi$_4$Zr$_x$Ti$_{3-x}$O$_{12}$ Single Crystals 

Studied by Soft-X-Ray Spectroscopy

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The electronic structures of La-doped Bi$_{4-x}$La$_x$Ti$_3$O$_{12}$ (Bi$_{4-x}$La$_x$Ti$_3$O$_{12}$) and Zr-doped Bi$_4$Ti$_3$O$_{12}$ (Bi$_4$Zr$_x$Ti$_{3-x}$O$_{12}$) single crystals have been studied by X-ray absorption spectroscopy (XAS) and soft-X-ray emission spectroscopy (SXES). In both Bi$_{4-x}$La$_x$Ti$_3$O$_{12}$ and Bi$_4$Zr$_x$Ti$_{3-x}$O$_{12}$, the Ti 3d and O 2p partial densities of states (PDOS) in the valence band region were observed in O 1s and Ti 2p SXES spectra. The energy position of the Ti 3d state overlapped with that of the O 2p state, indicating the occurrence of the hybridization effect between the Ti 3d and O 2p states. The hybridization effect of Bi$_{4-x}$La$_x$Ti$_3$O$_{12}$ increases with increasing La dopant concentration, although that of Bi$_4$Zr$_x$Ti$_{3-x}$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: Bi$_{4-x}$La$_x$Ti$_3$O$_{12}$, Bi$_4$Zr$_x$Ti$_{3-x}$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 Bi$_4$Ti$_3$O$_{12}$ (BIT) and SrBi$_2$Ta$_2$O$_6$ (SBT).$^{1–3}$ However, the poor fatigue characteristic and the same remanent polarization of these ferroelectrics are viewed as the major problem in their ferroelectric thin films. This selective control of each site is 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 2p and O 1s excitation thresholds.

2. Experimental

Bi$_{4-x}$La$_x$Ti$_3$O$_{12}$ single crystals were grown by a conventional flux method using Bi$_2$O$_3$ as a flux. A mixture of Bi$_2$O$_3$, TiO$_2$, and La$_2$O$_3$ was heated to 1200°C, maintained for 10h, 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 Bi$_4$Zr$_x$Ti$_{3-x}$O$_{12}$ samples were prepared by the solid-state reaction of Bi$_2$O$_3$, TiO$_2$, and ZrO$_2$ at 1200°C for approximately 4h, 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 (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.
3. Results and Discussion

Figure 1(a) shows Ti 2p XAS spectra as a function of La dopant concentration in Bi_{4-x}La_xTi_3O_{12} single crystals. The Ti 2p XAS spectra correspond to the transition from the Ti 2p core level to the unoccupied Ti 3d 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. 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 2p XAS spectra as a function of Zr dopant concentration in Bi_{4-x}La_xTi_3O_{12} single crystals. The overall profiles of these spectra in Bi_{4-x}La_xTi_3O_{12} accord with those in Bi_{4-x}La_xTi_3O_{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 1s XAS spectra as a function of La dopant concentration in Bi_{4-x}La_xTi_3O_{12} single crystals. From the dipole selection rules, it is understood that the O 1s XAS spectra of Ti oxides correspond to transitions from the O 1s character to the O 2p character hybridized with the unoccupied Ti 3d and Bi 6s states. The O 1s 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 3d 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 1s XAS decreases with increasing La dopant concentration. However, the intensity of the t_{2g}^-subband in the Ti 2p XAS spectra does not depend on La dopant concentration. This discrepancy could be attributed to the existence of the Bi 6s state in the unoccupied state, because the La ions are doped into the Bi site of BIT. On the other hand, the O 1s XAS spectra of Bi_{4-x}La_xTi_3O_{12} single crystals do not depend on Zr dopant concentration, as shown in Fig. 2(b).

Figure 3 shows the O 1s and Ti 2p SXES spectra in the valence band region of Bi_{3.5}La_{0.5}Ti_3O_{12} single crystals. The O 1s SXES spectrum measured at hv = 500 eV reflects the O 2p PDOS. The Ti 2p SXES spectrum measured at hv = 550 eV reflects the Ti 3d PDOS. One can find that the energy position of the O 2p state overlaps with that of the Ti 3d 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 3d contribution is more significant on the higher energy side (peak B), where the O 2p states have a larger admixture of the Ti 3d state. On the other hand, the valence band derived from the O 2p states are hybridized with the Ti 3d 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 3d state.

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
using local density approximation (LDA) were performed using the \textit{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 \( \text{O}^2p \) PDOS has four peaks, which correspond to \( \Gamma, X, P, \) and \( N \) points in the tetragonal Brillouin zone.\(^{15} \) Although the \( \text{O}^1s \) 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 \( \text{Ti}^2p \) and \( \text{O}^2s \) SXES spectra.

Figure 4(a) shows \( \text{O}^1s \) and \( \text{Ti}^2p \) 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 that of the 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.\(^{10} \) 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 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.\(^{10} \) 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

![Fig. 3](image-url)  
**Fig. 3.** \( \text{O}^1s \) and \( \text{Ti}^2p \) SXES spectra of \( \text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12} \) single crystal. For reference, the calculated band PDOS is also shown under each SXES spectrum.

![Fig. 4](image-url)  
**Fig. 4.** (a) \( \text{O}^1s \) and \( \text{Ti}^2p \) 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) \( \text{O}^1s \) and \( \text{Ti}^2p \) 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.
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 Bi$_{4-x}$La$_x$Ti$_3$O$_{12}$ and Bi$_{4}$Ti$_3$-$x$Zr$_x$O$_{12}$ single crystals by XAS and SXES. The O $1s$ XAS spectra of Bi$_{4-x}$La$_x$Ti$_3$O$_{12}$ single crystals show that the dopant La ions enter the Bi site of BIT. The Ti $2p$ XAS spectra of Bi$_{4}$Ti$_3$-$x$Zr$_x$O$_{12}$ single crystals show that the dopant Zr ions enter the Ti site of BIT. In the SXES spectra of both Bi$_{4-x}$La$_x$Ti$_3$O$_{12}$ and Bi$_4$Ti$_3$-$x$Zr$_x$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 Bi$_{4-x}$La$_x$Ti$_3$O$_{12}$ single crystals increases with increasing La dopant concentration, although that of Bi$_4$Ti$_3$-$x$Zr$_x$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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