

CORRELATION BETWEEN LOCAL STRUCTURES AND PARTIAL ELECTRONIC BAND STATES IN FERROELECTRIC $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$; $0.0 \leq x \leq 1.46$

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Submitted June 2, 2008; accepted March 23, 2009

Keywords: Ferroelectric thin film; $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$; EXAFS; XANES

The local structures and the partial band states near a Fermi level (E_F) have been studied at room temperature in the ferroelectric phase of $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ (BLT) with $0.00 \leq x \leq 1.46$ by means of X-ray absorption spectra (XAS) including EXAFS and XANES. The EXAFS spectra suggest that, as increasing the substituted La ions, the local structures around Ti and Bi ions in perovskite-blocks of $(\text{Bi}_{2-x}\text{La}_x\text{Ti}_3\text{O}_{10})^{-2}$ are gradually deformed till $x = 0.85$, and are largely changed by a structural phase transition occurring between $x = 0.85$ and 1.20. The XANES spectra suggest that there is a strong hybridization between Ti-3d(t_{2g}) and O-2p bands and between Bi-6s and O-2p bands in the valence band states, while between Ti-3d(e_g) and O-2p bands and Bi-6p and O-3s bands in the conduction band states. All of the XAS show interesting dependency on the concentration of the substituted La ions in BLT. The results suggest that, in BLT, a reducing spontaneous polarization induced by the La-substitution results from the deformation of the local structures around Ti and Bi ions and from modulation of the hybridized band states near E_F .

INTRODUCTION

$\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (PZT) and other lead-oxide compounds have been used for the micro-electromechanical systems. However, for a social problem of environmental pollution, it is desired that the materials used in the electromechanical systems are lead-free ones. Recently, Bismuth layer-structured ferroelectrics, called BLSF, have been attractively investigated for advanced applications of functional electric properties arisen from the dielectric materials of thin films, for examples, in nonvolatile memory and micro-electromechanical systems. $\text{SrBi}_2\text{Ta}_2\text{O}_9$, called SBT, had a layer structure mainly composed of $(\text{Bi}_2\text{O}_2)^{2+}$ sheets and pseudo-perovskite blocks $(\text{SrTa}_2\text{O}_7)^{2-}$ alternately stacked along the c-axis [1-4]. The $(\text{Bi}_2\text{O}_2)^{2+}$ sheets act as insulating paraelectric layers and control the electronic properties [5,6], while the ferroelectricity arises from the $(\text{SrTa}_2\text{O}_7)^{2-}$ blocks having a two-dimensional double network of TaO_6 octahedra, which are inserted between the next neighbor $(\text{Bi}_2\text{O}_2)^{2+}$ sheets. The SBT was found to overcome a fatigue, which reduces a remnant polarization (Pr) after repetitive read/write cycles. However, the SBT film shows a small value of (Psw–Pns) to be about 4 to 16 μCcm^{-2} , where Pns

and Psw are a linear non-switching response and a switching response respectively, and a high processing temperature of about 750°C to 850°C [7-10]. Bismuth titanate $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, called BIT, had been investigated as a new ferroelectric thin film to produce a ferroelectric random access memory, called FRAM. The structure of BIT is mainly characterized by perovskite-blocks $(\text{Bi}_2\text{Ti}_3\text{O}_{10})^{2-}$ having triple layers of TiO_6 octahedra. The perovskite-blocks are inserted between the next-neighbor $(\text{Bi}_2\text{O}_2)^{2+}$ sheets along the c-axis, as shown in Figure 1. The BIT film showed the fatigue and the low value of (Psw–Pns) to be about 4 to 6 μCcm^{-2} [11-13]. This suggested that the $(\text{Bi}_2\text{O}_2)^{2+}$ sheets do not make the fatigue free as insulating paraelectric layers. $\text{Bi}_3\text{TiTaO}_9$ substituting Sr and Ti ions with Bi and Ta ions in SBT, respectively, showed the fatigue failures, and it was found that Bi ions do affect the fatigue property [14]. $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ showed the large Pr of 12 μCcm^{-2} and (Psw–Pns) of 16 to 20 μCcm^{-2} and the processing temperature of about 650-750°C [15]. Recently, to improve the electric properties of $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$, called BLT, thin crystals, the sample preparations have been developed by several engineering methods [16-20]. On the other hand, the substituting effect of Bi ions with Nd^{3+} , Pr^{3+} , Sm^{3+} , and Ti^{4+} ions

with V^{5+} , W^{6+} , Mo^{6+} ions in BIT has been studied [21–28]. Similar Bismuth layer-structures of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$, called BBT, and (BIT-BBT) crystals have been reported [29–31]. Shimakawa et al [31] reported that the crystal structures of BIT and $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ are characterized by large distortions of Bi_2O_2 sheets and TiO_6 in perovskite-blocks of $(\text{Bi}_2\text{Ti}_3\text{O}_{10})^{2-}$, and that the constituent ions are mostly displaced along the *a*-axis. The spontaneous polarization appears to be parallel to the *a*-axis. In $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$, La ions can be substituted with only Bi ions, Bi(1), in the $(\text{Bi}_{2-x}\text{La}_x\text{Ti}_3\text{O}_{10})^{2-}$ blocks. From the structural refinement, they also calculated the electronic structure of BIT and $\text{Bi}_2\text{La}_2\text{Ti}_3\text{O}_{12}$. The total density of states suggested that there is a covalent interaction between Ti and oxygen ions originated from the strong hybridization between Ti-3d and O-2p orbitals. The substitution of Bi ions with La ions induces the less structural distortion and wider band gaps.

More recently, Mochado' group [32–34] reported the total and partial density of states (DOS) in BIT and BLT, calculated with the first principles using the full-potential linearized augmented plane-wave method. The results showed that there is a quite strong

hybridization between oxygen ions and cations. In BIT, the Bi contribution has s-like (mainly in the upper region of valence band) and p-like (mainly in the lower part of conduction band) character. The contribution arises from the strong hybridization between O-2p valence bands with Bi-6s (fully occupied) and Bi-6p (conduction) bands. Kim et al [35] reported the total and partial DOS in BLT, the net charge, and the overlap population for Ti, O, Bi, and La, which depend on the concentration of the substituted La ions. And also, Higuchi et al [36] reported the partial bands of O-2p and Ti-3d in BIT and $\text{Bi}_{4-x}\text{Nd}_x\text{Ti}_3\text{O}_{12}$, calculated with the high-resolution soft X-ray emission spectroscopy of O-1s and Ti-2p. They suggested that there is the hybridization effect between Ti-3d and O-2p bands depending on the substituted Nd^{3+} concentration in $\text{Bi}_{4-x}\text{Nd}_x\text{Ti}_3\text{O}_{12}$. Hidaka et al [37] developed a XAS method using a sensitive X-ray fluorescence detector, called XF-XAS method, which can accurately measure X-ray photons emitted from a front surface of the specimen (crystal, powders, thin film, pellet, or liquid) to the incident X-ray beam. The XF-XAS method is useful and convenient to obtain the XAS including XANES and EXAFS spectra even in compounds having large X-ray absorbing elements, as Sr, Bi, Pd, Ba et al. In the present paper, we report the correlation between the local structures around Ti and Bi ions, and the partial electronic band states near E_F in BLT with $0.00 \leq x \leq 1.46$, by means of the XF-XAS method using synchrotron radiation, as comparing with the total and partial DOS of BIT and BLT reported until now [31–36].

EXPERIMENTAL

In order to study the structural deformation localized around Ti and Bi ions and the partially electronic band states of Ti and Bi ions in ferroelectric layers of $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ (BLT), we carried out measurements of X-ray absorption spectra (XAS) at the K-edge of Ti and the L-edges (L_I , L_{II} , and L_{III}) of Bi for thin single crystals of BLT with $0.0 \leq x \leq 1.46$ and the powders of BIT. The sizes of the used crystals were about $5 \text{ mm} \times 5 \text{ mm}$ in flat surface and less than 0.1 mm in thickness. Powder samples of BLT were prepared by a solid-state reaction, and its single crystals were grown by a self-flux method using the BLT powder and Bi_2O_3 as a flux. The detail of the crystal growth was already described in the reference [38]. The XAS, including the XANES and EXAFS and spectra were measured by the XF-XAS method using the synchrotron radiation at the Pohang Light Source (2.5GeV). Although the XAS strongly depends on the crystallographic structure of the compound, it is generally considered that the XAS consists of XANES spectrum in the region of about -100 to +80 eV and EXAFS one in the region of about 50 to 700 eV around its X-ray

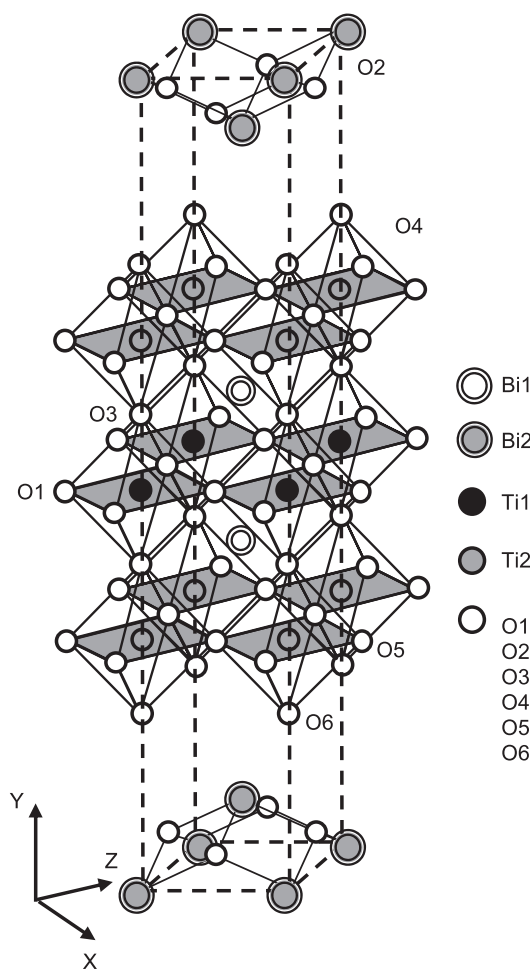


Figure 1. Ideal tetragonal structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$.

absorption thresholds (E_0). It is also considered that the XANES spectrum is approximately characterized by a pre-edge region of about -100 to E_0 , a main region of E_0 to about 30 eV, and an intermediate region of about 30 to 80 eV, where the spectral regions are called a pre-edge XANES, a main XANES, and an intermediate XANES, respectively. The pre-edge and main XANES gives information of electronic band states in a top region of valence band and in a bottom of conduction band, respectively.

At the present experiments, the used double crystal monochromators of Si (111) and Si (311) gave an energy resolution ΔE to be less than about 0.2 eV for the XAS near the X-ray absorption edge. The incident X-ray photons (I_0) were detected with an ionic chamber set in front of the thin crystal or the pellet, and the X-ray fluorescence photons (I_F) emitted from the specimen front-surface were simultaneously detected with an X-ray fluorescence detector (Canberra Planar Silicon detector; PD3000). The front-surface of the specimen was always set with about 80° to the incident X-ray beams, of which the size on the specimen surface was about 5 mm in horizontal and 1 mm in vertical to the electron orbital of the accelerator. The setting condition with a higher scattering angle gave no ordinary X-ray reflections, diffracted by the specimens, in the XAS. At that case, the detector was set at the edge of the specimen in a horizontal plane and could measure the X-ray fluorescence with a small glazing angle to the flat-surface of the specimen. In the present investigations, we used a soft program of *Artemis* and *Athena* to analysis the XAS data [39]. The XANES spectra were obtained by subtracting a smooth background from the XAS after selecting two energy points in the pre-edge region of the XAS, while the EXAFS spectra were automatically obtained by a spline treatment after selecting a high-energy region above the X-ray absorption threshold (E_0).

RESULTS AND DISCUSSION

The XAS in the region of 4950 to 5150 eV and 4980 to 5150 eV near the Ti-K edge are shown in Figure 2 (a) and (b) for BLT with $0.0 \leq x \leq 1.46$, respectively. In the figures, the ordinate refers a count ratio between the incident X-ray photons (I_0) and the fluorescence X-ray photons (I_F), emitted from the front-surface of the specimens, to the respective X-ray photon energy E (eV). The data were drawn with error bars compared with a size of each used symbolic character. In this paper, figures related to the XAS data were made by using only the data point at specific intervals, for instance the fourth point or eighth point, from a lot of observed data points for figure easiness to see. Although the XANES spectra show a slightly complicate patterns, we determined E_0 of Ti-K edge ($E_0(\text{Ti})$) of BIT and BLT by differentiation of XAS curve in a large jump-region of the XANES

spectra in Figure 2. The results showed $E_0(\text{Ti})$ of about 4981 eV. As described later in the analysis of the EXAFS spectra, the $E_0(\text{Ti})$ determination was clearly confirmed by a good refinement of an observed oscillating EXAFS spectrum, $X_{\text{obs}}(E)$.

In order to study the local structure around the X-ray absorbing Ti ions, we carried out a Fourier transformation $|F(R)|$ of the EXAFS spectra near the Ti-K edges for BLT with $x = 0.00, 0.46, 0.85, 1.20$, and 1.46 in Figure 2. We first exchanged the energy (E) of the incident X-ray photons with a wavenumber $k \{= 8\pi^2 m_e (E - E_0)/h^2\}$, where E_0 , m_e , and h are $E_0(\text{Ti})$ of about 4981 eV, an effective mass of electron, and Plank constant, respectively. Secondly, the observed oscillating EXAFS spectrum $X_{\text{obs}}(E)$ was represented with the k -unit to be the $X_{\text{obs}}(K)$, and an observed Fourier transformation spectrum $|F_{\text{obs}}(R)|$ was obtained from the $X_{\text{obs}}(K)$. Figure 3 shows the $|F_{\text{obs}}(R)|$ of BIT and BLT, taken from the $X_{\text{obs}}(K)$ in Figure 2. The abscissa refers a radial distance ($R(\text{\AA})$) from a X-ray absorbing

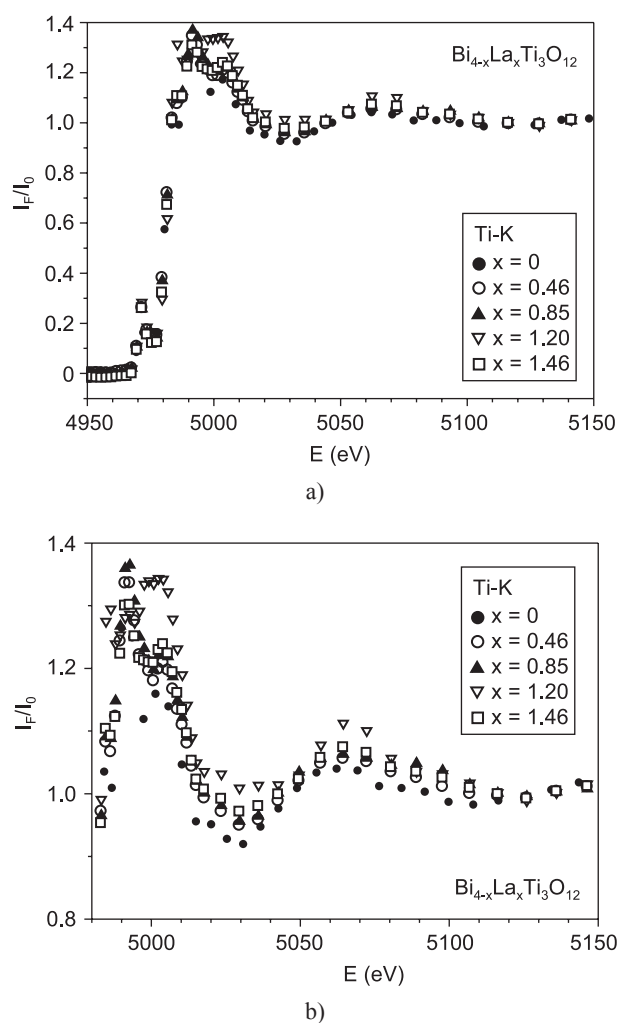


Figure 2. X-ray absorption spectra near the Ti-K edge for $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ in the region of a) 4950 to 5150 eV and b) 4980 to 5150 eV.

Ti ion to its surrounding shells including the cations or anions in the BIT structure. In Figure 3, the amplitudes of $|F_{\text{obs}}(R)|$ in the region of about 2.7 and 3.4 of $R(\text{\AA})$ indicate that there is a large modulation between $x = 0.85$ and 1.20. The results suggest that, as increasing the substituted La ions, the local structure around Ti ions is gradually deformed till $x = 0.85$, and that the structural phase transition occurs at about $x = 1.20$, as described in discussion later. However, It is not easy to index the amplitudes of the $|F_{\text{obs}}(R)|$ by the surrounding shells because of the complicate $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ structure. The main reason comes from two-type equivalent coordinates of Ti1 and Ti2 in the $(\text{Bi}_{2-x}\text{La}_x\text{Ti}_3\text{O}_{10})^{2-}$ perovskite-blocks of the BIT and BLT structures, as shown in Figure 1.

The BIT structure is an orthorhombic symmetry of space group Aba2 and lattice parameters of $a = 5.41029(3) \text{\AA}$, $b = 32.8372(3) \text{\AA}$, $C = 5.44794(4) \text{\AA}$, $\alpha = \beta = \gamma = 90.0^\circ$ at room temperature, taken from the neutron powder diffraction by using a Rietveld refinement [40]. Thus, the observed $|F(R)|$ near the Ti-K edge is summed with those for Ti1 and Ti2 in BLT, if the X-ray photoelectron waves emitted from the Ti ions of Ti1 and Ti2 are incoherent each other in the

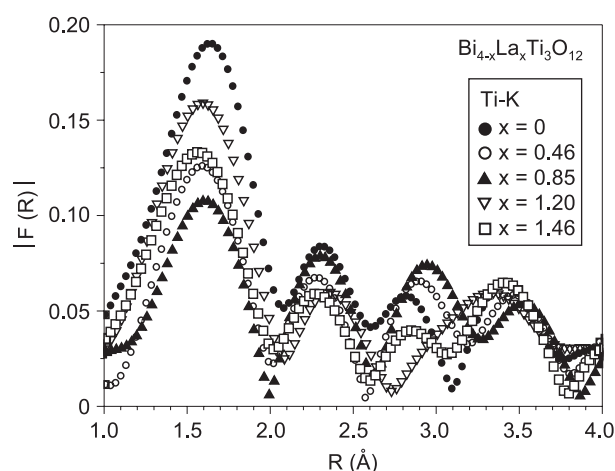


Figure 3. Observed $|F(R)|$ taken by the Fourier transformation of the EXAFS spectra near the Ti-K edges for $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ in Figure 2.

compound. We carried out refinement of the $X_{\text{obs}}(K)$ with a theoretical $X_{\text{cal}}(K)$, taken by the software programs of Artemis and Athena [39]. The curve fitting between the $X_{\text{obs}}(K)$ and the $X_{\text{cal}}(K)$ was done by a least squares method for several refined parameters, which consist of radial distance R_j , Debye-Waller factors (σ_j), a passive electron reduction factor (S_0^2), while the occupied number (N_j) sited on the shell having the same radial distance R_j is fixed in the theoretical value of the BIT structure. The refinements were always monitored by a following convergence factor RF ; $RF = \{\sum |S X_{\text{obs}}(K) - S X_{\text{cal}}(K)|^2\} / \sum |S X_{\text{obs}}(K)|^2$, where S is a scale factor.

In the present investigations, we analysed the EXAFS data only with a single scattering process, but not with a multi-scattering process of the backscattering wave induced by the surrounding ions, because the later process was small or negligible in the present refinement. Figure 4 shows the final refined results of the curve fittings for the EXAFS spectra, where the observed $|F_{\text{obs}}(R)|$ and the theoretical $|F_{\text{cal}}(R)|$ were represented by the open circles and the solid lines, respectively. In Figure 4a, the $|F_{\text{cal}}(R)|$ denoted by the solid line was obtained only from the $X_{\text{cal}}(K)$ of Ti1 ions in Figure 1. Thus, the slight inconsistency of the curve fitting results from the influence of the X-ray photoelectron waves (XPW) emitted by Ti^{2+} ions. The final refinement of $RF = 0.07$ was adequately satisfied. The refined parameters are listed in Table 1, where the ideal radial distances (R_{cal}) were calculated by the structural parameters taken by the neutron powder diffraction of BIT [40] and $dR = R - R_{\text{cal}}$. The values in brackets of R are a standard deviation. In the table, OM, BiM, and TiM; M = integer represents the oxygen, Bi, and Ti ions successfully ordered along the radial direction from the origin of the X-ray absorbing Ti ions (Ti1), while the notation of the oxygen, Bi, and Ti ions in the bracket represents the cations and the anions in Figure 1. It is usually known that there is slightly a difference between R_j and $R_{\text{cal}j}$. From Table 1, we knew that the amplitude occurring at 1.9 to 2.0 Å is produced mainly by the TiO_6 octahedra having Ti ions of Ti1-style in the $(\text{Bi}_{2-x}\text{La}_x\text{Ti}_3\text{O}_{10})^{2-}$ blocks. However, the R value of the amplitude in Figure 4a is slightly different to that in Figure 3. The difference is due to the phase shift of the wave-scattering process.

Table 1. Refined parameters of the EXAFS spectrum of the X-ray absorber Ti ion (Ti1) for BIT in Figure 4a.

	O1 (O1)	O2 (O3)	O3 (O1)	Bi1 (Bi1)	Bi2 (Bi1)	Bi3 (Bi1)	Bi4 (Bi1)	Ti1 (Ti1)	O4 (O3)
$R_F = 0.007, S_0^2 = 0.576$									
R	1.923 (.001)	1.991 (.001)	1.992 (.001)	3.208 (.001)	3.635 (.001)	3.664 (.014)	3.852 (.017)	4.010 (.001)	4.117 (.003)
dR	0.082	0.003	-0.053	-0.112	0.155	0.156	0.164	0.171	0.176
N	2	2	2	2	2	2	2	4	2
σ^2	0.020	0.003	0.003	0.002	0.002	0.030	0.030	0.003	0.003
R_{cal}	1.841	1.989	2.045	3.320	3.480	3.508	3.687	3.839	3.941

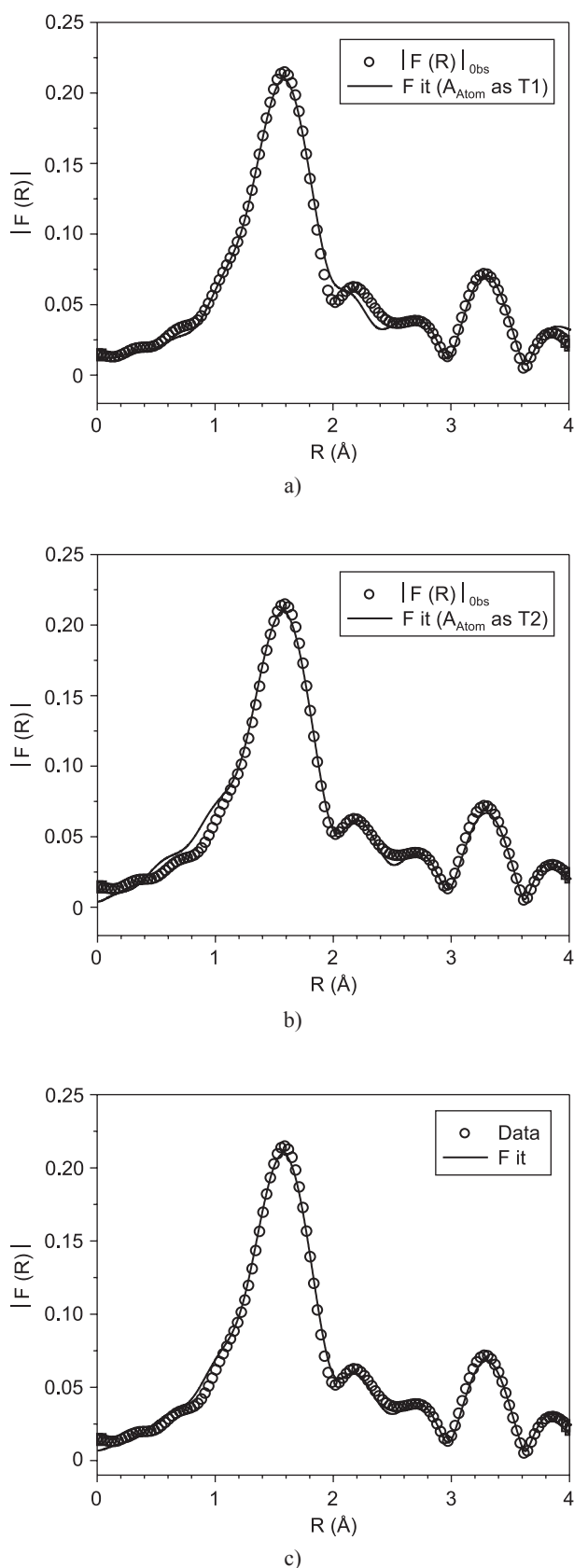


Figure 4. Observed $|F(R)|$ (solid circles) and theoretical $|F(R)|$ (solid line) of the EXAFS spectrum of Ti ions in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. The theoretical one is taken for Ti ions of a) Ti1, b) Ti2, and c) Ti1+Ti2, as shown in Figure 1.

In Figure 4b, the theoretical $|F(R)|$ was obtained only from the $X_{\text{cal}}(\text{K})$ of Ti2 ions in Figure 1. Thus, the slight inconsistency of the curve fitting results from the influence of the XPW emitted by Ti1 ions. The final refinement of $\text{RF} = 0.03$ was adequately satisfied, as that in Figure 4a. The refined parameters are listed in Table 2. We also knew that the amplitude occurring at about 1.7 to 1.9 Å is produced mainly by the TiO_6 octahedra having Ti ions of Ti2-style in the $(\text{Bi}_{2-x}\text{La}_x\text{Ti}_3\text{O}_{10})^{2-}$ blocks. To study whether the X-ray photoelectron waves emitted from the Ti ions of Ti1 and Ti2 are incoherent or not, we obtained a total theoretical $|F(R)|$ by summing the theoretical $|F(R)|$ for the X-ray absorbers of Ti1 and Ti2 in Figure 6a and b. The BIT structure of space group Aba2 in Figure 1 shows two kinds of equivalent positions of Ti ions as Ti1 and Ti2. The site occupancy of Ti1 and Ti2 is 4 and 8, respectively. Thus, we calculated a total theoretical $|F(R)|$ with a ratio of 1 : 2. The result shows in Figure 4c, where the total theoretical $|F(R)|$ is denoted by the solid line. Thus, we found that the refinement is adequately satisfied by a good fitting between the observed and theoretical $|F(R)|$. This also means that the X-ray photoelectron waves emitted from X-ray absorber ions having a different equivalent coordinate are incoherent in the compound each other, even if the same kinds of ions. Thus, in the present refinements, it is considered that the substitution of Bi^{3+} ions with La^{3+} ions affects the local deformation around Ti1 and Ti2 ions in the $(\text{Bi}_{2-x}\text{La}_x\text{Ti}_3\text{O}_{10})^{2-}$ blocks in BLT. The amplitude of the first peak in the $|F(R)|$ (Figure 3) suggests that, as increasing the substituted La ions, the TiO_6 octahedra gradually tilt till $x = 0.85$, and the structural phase transition occurs at about $x = 1.20$ [37]. The temperature dependence of the lattice constants (a, b) showed the structural transition at about $x = 1.20$, in addition to the decrease of the cation (Bi, La) displacements and the tilts of the TiO_6 octahedra in the $(\text{Bi}_{2-x}\text{La}_x\text{Ti}_3\text{O}_{10})^{2-}$ blocks, as increasing the substituted La ions [41]. The present results consist with those taken by the neutron diffraction. Furthermore, the good curve-fitting in Figure 4c suggests that it was correct to determine $E_0(\text{Ti})$ of about 4981 eV in Figure 2.

In Tables 1 and 2, we can approximately get information for the shape of the TiO_6 octahedra in the $(\text{Bi}_{2-x}\text{La}_x\text{Ti}_3\text{O}_{10})^{2-}$ perovskite-blocks of BIT. The octahedron centered at Ti ion, denoted by Ti1 and Ti2 in Figure 1, are called $\text{Ti}(1)\text{O}_6$ and $\text{Ti}(2)\text{O}_6$ respectively. The $\text{Ti}(1)\text{O}_6$ has a tetragonal symmetry of $a_p = 1.92$ Å, $b_p = 1.99$ Å, $c_p = 1.99$ Å, while $\text{Ti}(2)\text{O}_6$ has an orthogonal symmetry of $a_p = 1.71$ Å, $b_p = 1.81$ Å, $c_p = 1.91$ Å. The suffix “p” means a pseudo-perovskite cell. Thus, it is possible to consider that the substituted La ions reduces the symmetry of the $\text{Ti}(1)\text{O}_6$ octahedra and affect the cooperative displacements of the cations (Bi, La) surrounding around Ti ions of Ti1, in addition to the tilts and the distortion of the $\text{Ti}(1)\text{O}_6$ octahedra.

Figure 5 shows the XANES spectra in the pre-edge region of 4950 to 4980 eV for BLT expanded in Figure 2. The pre-edge XANES peaks at about 4972 and 4975 eV arise from the electronic transition between 1s and other bands of Ti ions. A Ti^{4+} ion has full occupied orbitals of Ti-3s, 3p and unoccupied ones of Ti-3d, 4s and 4p near E_F . It is well known that degenerated 3d bands split two band states of 3d(t_{2g}) valence bands and 3d(e_g) conduction ones in an octahedral crystal field [42-44]. Thus, it is considered that the pre-edge peaks in Figure 5 are induced by the transition between the 1s and 3d(t_{2g}) bands of Ti ion. However, the transition is usually forbidden as a quadruple transition. More recently, Machado's group [32-34] and Kim [35] reported the total and partial DOS in BIT and BLT. They cleared that there is a strong hybridization between O-2p

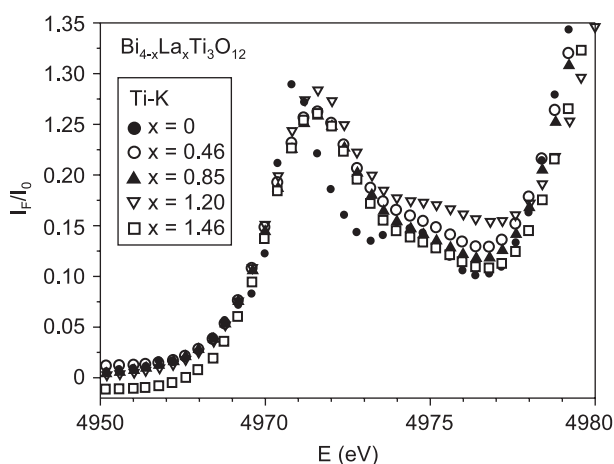


Figure 5. XANES spectra in the region of 4950 and 4980 eV near the Ti-K edge for $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$, expanded in Figure 2.

bands and the bands of the cations in the top region of valence band and in the bottom of conduction band, and that the hybridization induces s-like and p-like characters in the band states of the cations. Thus, the hybridizing effect produces the 3d(t_{2g}) valence bands having p-like character, called the hybridized 3d $^n(t_{2g})\bar{L}^m$ bands, by an electronic configuration interaction [45], where $\bar{L}$ means O-2p bands. It is possible to consider the pre-edge peaks are due to the transition between Ti-1s and Ti-3d $^n(t_{2g})\bar{L}^m$ bands. Figure 5 suggests that the La-substitution in BLT slightly affects the hybridization between O-2 and Ti^{4+} ions, and the covalence bonding of TiO_6 octahedra in the $(\text{Bi}_{2-x}\text{La}_x\text{Ti}_3\text{O}_{10})^{-2}$ perovskite-blocks of BLT.

Figures 6a and b show the main and intermediate XANES and the partial EXAFS spectra expanded above E_0 in Figure 2. Although there are unoccupied Ti-3d(e_g) bands in the bottom of conduction band, the electronic transition between 1s and 3d(e_g) bands of Ti ions is forbidden. However, as described before, the strong hybridization between Ti-3d(e_g) conduction bands and the O-2p bands induces p-like character in the Ti-3d(e_g) bands [32-34]. This suggests the appearance of the transition between Ti-1s and the hybridized bands, called Ti-3d $^n(e_g)\bar{L}^m$. Kim et al [35] cleared theoretically that there are partial empty O-2p bands near E_F even in the bottom of conduction band in BLT. This also gives a possibility of the hybridized bands of Ti-3d($e_g)\bar{L}^m$. Thus, we consider that the XANES peaks at about 4985 and 4992 eV in Figure 6a indicate the existence of the Ti-3d $^n(e_g)\bar{L}^m$ bands, having p-like character, near E_F . The energy site and profile of the peaks suggest that the hybridized band states of Ti-3d($e_g)\bar{L}^m$ are gradually modulated at $x \leq 0.85$ and largely changed by the structural phase transition occurring between $x = 0.85$ and 1.25, as described above.

Table 2. Refined parameters of the EXAFS spectrum of the X-ray absorber Ti ion (Ti2) for BIT in Figure 4b.

	O1 (O5)	O2 (O6)	O3 (O5)	O4 (O6)	O5 (O5)	O6 (O3)	Bi1 (Bi1)	Bi2 (Bi1)	Bi3 (Bi1)
$R_F = 0.003, S_0^2 = 0.926$									
R	1.708 (.005)	1.810 (.001)	1.906 (.002)	1.943 (.003)	2.041 (.001)	2.359 (.001)	3.088 (.005)	3.230 (.002)	3.337 (.016)
dR	-0.053	-0.055	-0.059	-0.061	-0.064	0.058	-0.096	-0.100	-0.104
N	1	1	1	1	1	1	1	1	1
σ^2	0.010	0.002	0.002	0.002	0.002	0.002	0.004	0.004	0.025
R_{cal}	1.762	1.865	1.965	2.004	2.104	2.301	3.184	3.331	3.441
	Bi4 (Bi1)	Bi5 (Bi2)	Ti1 (Ti2)	Bi6 (Bi2)	Bi7 (Bi2)	O7 (O6)	Ti2 (Ti2)	O8 (O6)	
R	3.496 (.001)	3.563 (.002)	3.654 (.008)	3.707 (.167)	3.761 (.220)	3.776 (.007)	3.794 (.034)	3.872 (.001)	
dR	-0.109	-0.111	-0.114	-0.115	-0.117	-0.118	-0.118	-0.121	
N	1	1	2	1	1	1	2	1	
σ^2	0.004	0.004	0.015	0.182	0.182	0.002	0.051	0.002	
R_{cal}	3.605	3.674	3.768	3.823	3.879	3.893	3.912	3.993	

As described before, the intermediate XANES in the region of about 30 to 80 eV gives information of a stereo chemical geometry of bounding distances and angles of the surrounding atoms to the X-ray absorbing atom, though there is a partially overlap with the lower energy region of EXAFS spectrum. The EXAFS spectrum in the region of about 50 to 700 eV gives local structural information of only the radial distance from the X-ray absorbing atom to its surrounding shells including the cations or anions. Thus, Figure 6b also shows that the local structure around Ti ions is gradually deformed till $x = 0.85$ and is changed at about $x = 1.25$ by the structural transition. Therefore, we suspect that the TiO_6 octahedra are tilted and/or distorted in the perovskite-blocks of $(\text{Bi}_{2-x}\text{La}_x\text{Ti}_3\text{O}_{10})^{2-}$ by the La-substitution.

Figures 7a and b show the XAS near the Bi-L_{III} edge in the region of 13360 to 13600 eV and 13420 to 13600 eV in BLT with $0.0 \leq x \leq 1.20$, respectively. E_0 of the Bi-L_{III} edge ($E_0(\text{Bi})$) was determined to be 13418 eV

by differentiation of the XAS curve in the large jump region of the XANES spectra, while $E_0(\text{Bi})$ is about 13424 eV for a free Bi element. We consider that the XANES spectra in BLT depend on the concentration of the substituted La ions. In order to estimate the dependency, we expanded the XAS near the X-ray absorption edge of Bi ions in Figure 7. Figure 8a shows the pre-edge XANES spectra, while Figure 8b shows the main XANES and the partial EXAFS ones. It is found that the XANES spectra in BLT show the weakly broader peaks at about 13400 eV just below E_F and at 13426 and 13435 eV just above E_F . A Bi^{3+} has fully occupied orbitals of $\text{Bi-5p}^6\text{5d}^{10}\text{6s}^2$ and unoccupied ones of Bi-6p . It is noted that the broadly pre-edge peaks of the XANES spectra is only in BIT, but not the La-substituted specimens of BLT. It is known that the pre-edge peaks of the XANES spectrum are induced by the electronic transition between Bi-2p and the other bands of Bi ions in the valence band. As described before, the strong

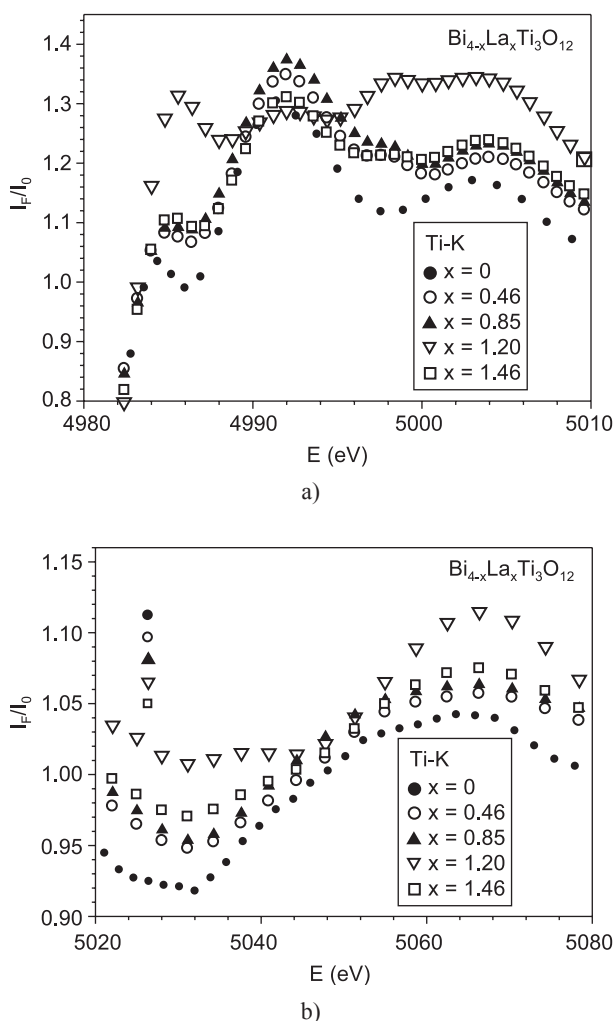


Figure 6. X-ray absorption spectra near the Ti-K edge for $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ in the region of a) 4980 to 5010 eV and b) 5020 to 5080 eV.

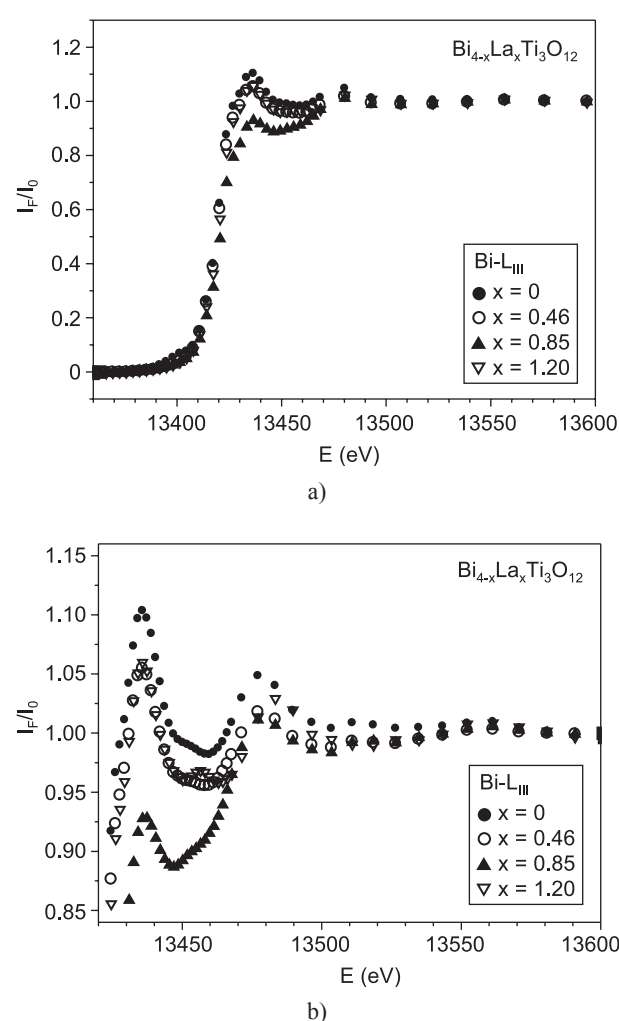


Figure 7. X-ray absorption spectra near the Bi-L_{III} edge of $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ in the region a) from 13360 to 13600 eV and b) 13420 to 13600 eV.

hybridization between O-2p valence bands with fully Bi-6s (valence) bands and Bi-6p (conduction) bands contributes the s-like and p-like characters in the top region of valence band [31-35]. This suggests the appearance of partially empty hybridized bands, called Bi-6s $^n\text{L}^m$ and Bi-6p $^n\text{L}^m$, just below E_F [45]. Thus, it is possible to consider the transition between Bi-2p and Bi-6s $^n\text{L}^m$ bands having the s-like character. However, in Figure 8a, the hybridized Bi-6s $^n\text{L}^m$ bands disappeared in BLT with $x \geq 0.45$. On the other hand, it was reported that La ions can be substituted with only Bi ions in the perovskite-blocks of $(\text{Bi}_{2-x}\text{La}_x\text{Ti}_3\text{O}_{10})^{-2}$, that is Bi(1) in Figure 1 [31]. Thus, the disappearance of the pre-edge XANES peaks in Figure 8(a) indicates that the La-substitution affects the hybridization between O-2p and Bi-6s valence bands. Of course, in the present measurements, the XANES spectra give no information of the hybridized Bi-6p $^n\text{L}^m$ bands in BLT, as a forbidden transitional rule, though the total and partial DOS suggest the quite strong hybridization between O-2p and Bi-6s(valence), 6p(conduction) in VB, as reported [31-35].

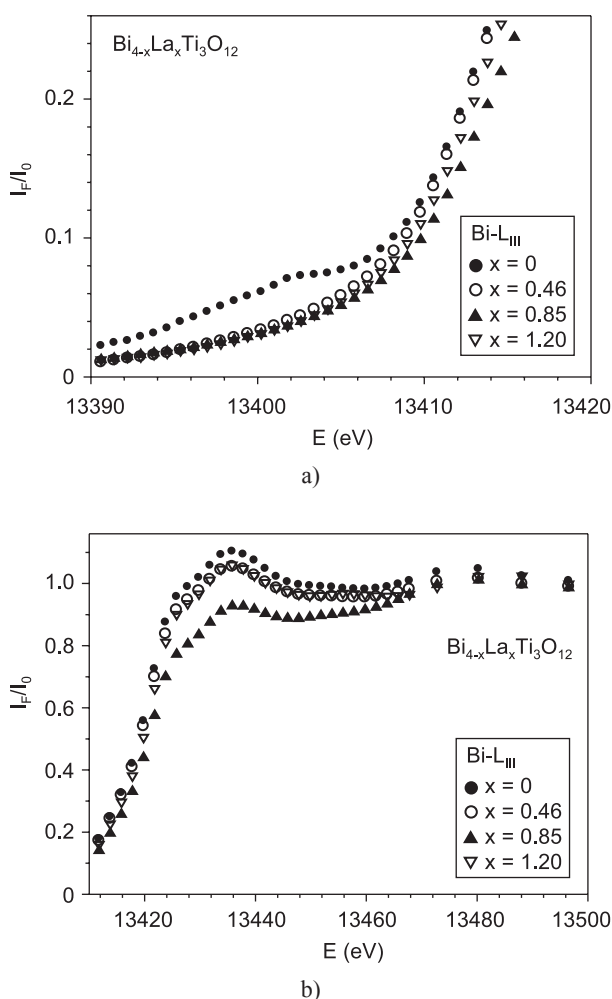


Figure 8. XANES spectra near the X-ray absorption edge of Bi-L_{III} edge for $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ in the region a) from 13390 to 13420 eV and b) 13410 to 13500 eV in Figure 7.

Figure 8b shows the main and intermediate XANES and the partial EXAFS spectra in BLT. The total and partial DOS reported by the references [31-35] indicated that there is a strong hybridization between O-2s,2p valence bands and Bi-6p conduction bands even in the conduction band. Kim et al [35] further reported that the partial empty O-2p bands are in the bottom region of conduction band. It is considered that the hybridization gives s-like and p-like characters in the unoccupied Bi-6p bands. That is, the electronic configuration interaction [45] produces the hybridized bands in the conduction band, called Bi-6p $^n\text{M}^m$, where M means O-3s conduction bands. Thus, the XANES peaks at 13426 and 13435 eV indicate the existence of the hybridized Bi-6p $^n\text{M}^m$ bands having the s-like character. In the present investigations, it is found that the Bi-6p $^n\text{M}^m$ bands are gradually modulated till $x = 0.85$ and are largely changed by the structural phase transition occurring between $x = 0.85$ and 1.25. The La-substitution in BLT strongly affects the Bi-6p band states. However, we cannot observe the Bi-6p $^n\text{M}^m$ bands having the p-like character as a forbidden transitional rule. In the contrast with the EXAFS spectra near Ti-K edge in Figures 2 and 4, we could not analyze the EXAFS ones near Bi-L_I, L_{II}, and L_{III} edges, because the EXAFS spectrum overlaps in lower and/or higher energy region each other. However, as the XANES spectra near Ti-K edge in the intermediate region near Ti-K edge in Figure 6b, it is found in Figure 8b that the La-substitution affects the local structure around Bi ions in the $(\text{Bi}_{2-x}\text{La}_x\text{Ti}_3\text{O}_{10})^{-2}$ perovskite-blocks. The results consist with the refined local structures around Ti ions.

CONCLUSIONS

In the present investigations, the X-ray absorption spectra (XAS) near Ti-K edge and Bi-L_{III} edges in BLT with $0.0 \leq x \leq 1.46$ gave the interesting information for the local structures around Ti and Bi ions and the partial electronic band states of Ti and Bi ions in the top region of valence band states and in the bottom region of the conduction band states. It is known that the La-substitution in BLT reduces the remnant polarization (Pr). We found that the local structures around Ti and Bi ions in the perovskite-blocks are gradually deformed till $x = 0.85$ and are largely changed by the structural phase transition occurring between $x = 0.85$ and 1.25. Recently, Soga et al [38] reported by means of the neutron powder diffraction that, as increasing the substituted La ions, the displacements of the cations (Ti, Bi, La) and the tilts of the TiO_6 octahedra in BLT are decreased, and the structural transition occurs at about $x = 1.20$. The present results consist with those taken by the neutron powder diffraction.

We also found that the hybridized Ti-3d $^n(t_g)\text{L}^m$ bands and Bi-6s $^n\text{L}^m$ bands are in the top region of valence band, while hybridized Ti-3d $^n(e_g)\text{L}^m$ and Bi-6p $^n\text{M}^m$

bands in the bottom region of conduction band. The hybridized band states considerably depend on the concentration of the substituted La ions in BLT. Thus, we think that the reducing spontaneous polarization produced by the La substitution is related to the correlation between the structural deformation around Ti and Bi ions in the $(\text{Bi}_{2-x}\text{La}_x\text{Ti}_3\text{O}_{10})^{-2}$ perovskite-blocks and the electronic modulation of the partial band states in the valence band and the conduction band near E_F . Especially, the disappearance of the Bi-6s n $\underline{L}^m$ bands in BLT, but not BIT, implies that the partial charge contributing the hybridization between Bi-6s and O-2p bands is transferred to the substituted La ions, to produce the hybridized bands between La-5d and O-2p bands, as like the Bi-6p conduction bands [32–35]. Thus, we deduce that the substituted La ions receive more electrons from the surrounding O ions in the perovskite-blocks, and the hybridized Bi-6s n $\underline{L}^m$ bands simultaneously disappear at $x \geq 0.45$ in BLT. However, the hybridized Ti-3d n (t_{2g}) $\underline{L}^m$ bands are not so largely affected by the La substitution in the region of $0.0 \leq x \leq 1.46$, as shown in Figure 5. Furthermore, it is found that the local structure around Bi ions (Bi1) is deformed in Figure 8b by the substituted La ions, as the refined results of the EXAFS spectra near the Ti-K edge. The refinements indicate the structural deformation around Bi ions (Bi1) in the perovskite-blocks. Thus, we consider that the functional electric properties of BLT are related to the strong correlation between the local structures around the cations (Ti, Bi) and the hybridized bond states of Ti and Bi ions near E_F .

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