

# Studies on the La substitution site in $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ by polarization-dependent x-ray absorption spectroscopy

D. W. Lee, J. W. Seo, S. Cho, S. R. Park, and C. Kim<sup>a)</sup>  
*Institute of Physics and Applied Physics, Yonsei University, Seoul 120-749, Korea*

B. J. Kim and S.-J. Oh  
*Department of Physics and Center for Strongly Correlated Material Research, Seoul National University, Seoul 151-742, Korea*

B. S. Kang and T. W. Noh  
*Department of Physics and Research Center for Oxide Electronics, Seoul National University, Seoul 151-742, Korea*

B. H. Park  
*Department of Physics, Konkuk University, Seoul 143-701, Korea*

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We performed polarization-dependent x-ray absorption spectroscopy studies on epitaxially grown  $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$  thin films at the  $3p \rightarrow 6s$  edges to find the La substitution site. Our results show a clear difference between the absorption spectra taken with parallel and perpendicular polarizations, which is consistent with the view that La replaces Bi in the layer rather than at the perovskite site. Calculated absorption spectra also support the interpretation. We therefore conclude that some, if not all, La atoms replace the Bi atoms in the layer. © 2006 American Institute of Physics.

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## I. INTRODUCTION

Dynamic random access memories (DRAMs) lose their stored information when power is turned off. This volatility is not desirable for certain applications such as memory cards for digital cameras. Therefore, steady efforts have been focused to develop nonvolatile memories. Among different types of nonvolatile memories, ferroelectric random access memories (FRAMs) have attracted much attention because of their structural similarity to DRAMs and low operating voltage. The key issue in FRAM research is finding suitable ferroelectric materials. Among many ferroelectric materials,  $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$  (PZT) has been considered as one of the most promising candidate materials due to its large remnant polarization value, small coercive field, and low deposition temperature. However, PZT suffers from fatigue problems which shorten the FRAM lifetime. A short lifetime poses a serious problem for its applicability to FRAMs.

Another ferroelectric material that has been considered is  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  (BTO), whose structure is shown in Fig. 1. This material also suffers from fatigue problems but it was recently found that partial replacement of Bi in BTO by La considerably reduces the fatigue problem.<sup>1</sup> Since then  $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$  (BLT) has been rigorously reinvestigated as a potential material for FRAMs. A natural question then is what the mechanism behind the fatigue-reduction in this material is. The answer to the question should be very important for further search for better materials. Even though the fatigue reduction mechanism is not well understood and existing theories are somewhat controversial,<sup>2-5</sup> the current understanding is that Bi atoms in BTO tend to create fatigue by

causing oxygen vacancies.<sup>6,7</sup> In that case, replacement of Bi by La should reduce oxygen vacancies and thus fatigue problems as well.<sup>1</sup>

As shown in Fig. 1, BTO has two  $\text{Bi}_2\text{O}_2$  layers and a double-perovskite structure. Note that Bi exists both in the layer and at the perovskite site. If La substitution indeed reduces oxygen vacancies and thus the fatigue problem, it would be important to know which Bi atoms of those in the layer and/or those at perovskite sites are replaced. This is how we can then find out where oxygen vacancies are created in the crystal. This could further help us understand the mechanism behind the oxygen-vacancy migration in the system. Even though La was initially thought to replace the Bi at the perovskite site,<sup>1</sup> a different view (that is, Bi in the  $\text{Bi}_2\text{O}_2$  layer being replaced) has recently been proposed.<sup>8</sup> Therefore, the issue is worth resolving experimentally.

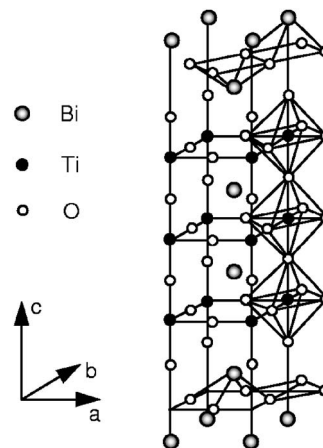


FIG. 1.  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  crystal structure. One may replace Bi atoms by La to make  $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ .

<sup>a)</sup>Electronic mail: cykim@phya.yonsei.ac.kr

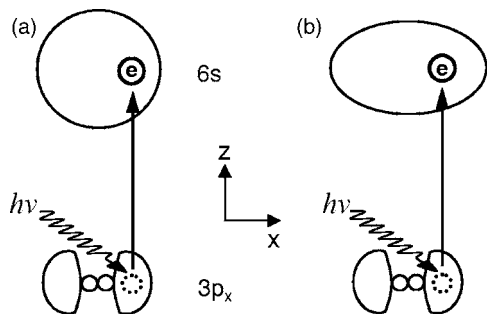


FIG. 2. (a) Photoexcitation of an electron from  $3p$  to  $6s$  orbitals in an isotropic environment (at the perovskite site). The  $6s$  orbital is symmetric due to the isotropic crystal field. (b) Excitation from  $3p$  to  $6s$  at the layer site. The  $6s$  orbital is deformed due to the anisotropic crystal field.

## II. EXPERIMENT

A simple way to identify the substitution site is to check the anisotropy of the local environment with x-ray absorption near-edge structure (XANES) measurements. We note that the local environments for the two sites are different. While the crystal field at the perovskite site is isotropic, that of the layer site is very anisotropic. In general, such difference in the local environment should be manifested in polarization-dependent XANES data.

Even though the basic idea is simple, application of the idea to the BLT case turned out to be difficult. The accessible edges with our experimental setup were La  $3p \rightarrow 6s$  and  $3d \rightarrow 4f$  edges. Of the two, the  $3d \rightarrow 4f$  edge is strong and appears to be the proper absorption edge to be studied. XANES spectra normally reflect the anisotropic local environment through occupations in the outermost orbitals. However, La  $4f$  orbitals are empty and thus polarization-dependent XANES at the  $3d \rightarrow 4f$  edges may not reflect the anisotropic local environment. In addition, the large ratio between the peak and step heights makes the normalization of the spectra with different polarizations difficult, which in turn makes testing the anisotropy unreliable.<sup>9</sup> Therefore, we had to resort to the  $3p \rightarrow 6s$  edge. This edge has its own difficulties though: there is only one orbital involved in the final state ( $6s$ ) and, as a result, we do not expect polarization dependence in the first order. However, as depicted in Fig. 2, the  $6s$  orbital at a site with an anisotropic local environment should be deformed. In that case, we expect some degree of polarization dependence in the XANES spectra. Polarization along the  $x$  direction, for example, probes the transitions from  $3p_x$  to  $6s$ , while polarization along the  $z$  direction probes  $3p_z$  to  $6s$  transitions. If the  $6s$  orbital is deformed as depicted in panel (b), the overlap between  $3p_x$  and  $6s$  would be different from that between  $3p_z$  and  $6s$ , resulting in a polarization-dependent XANES structure.

For the experiments, epitaxially grown BLT thin-film samples were used. Thin films were epitaxially grown on a  $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  (LSCO) layer on MgO substrates [see Fig. 3(c)] with the  $c$  axis of BLT perpendicular to the substrate surface. The LSCO layer not only acts as a buffer layer but also serves as the conducting path for the photocurrent in the experiment. Experiments were performed at Beamline 10-1 of the Stanford Synchrotron Radiation Laboratory (SSRL).

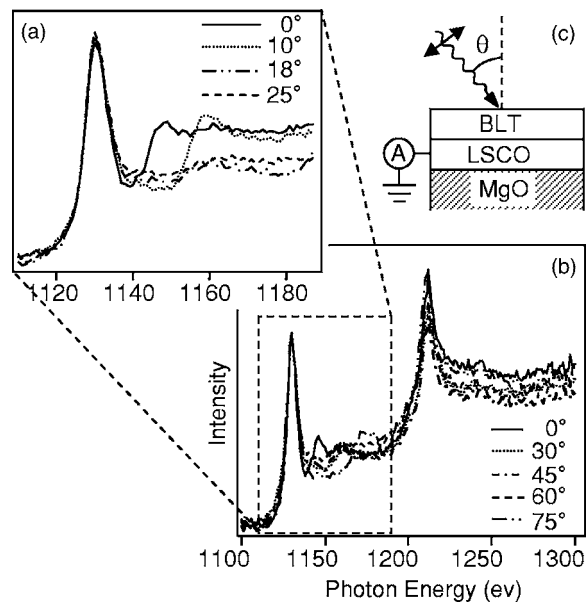


FIG. 3. The La  $3p \rightarrow 6s$  XANES spectra for (a) small and (b) wide energy ranges. Corresponding energy window for the data in panel (a) is shown in panel (b) as a dotted rectangle. (c) Experimental configurations. The TEY was measured by taking the sample current through the LSCO layer. Definition of the polarization angle is also shown.  $\theta=0^\circ$  (normal incidence) corresponds to the polarization in the  $ab$  plane.

Polarization-dependent XANES spectra were taken at the La  $3p$  edges in the total electron yield mode (TEY). The incident photons were  $p$  polarized and the polarization direction relative to the  $ab$  plane could be varied by rotating the sample. Data were taken at room temperature.

## III. RESULTS AND DISCUSSION

The experimental results are shown in Fig. 3. In panel (b), we plot the polarization-dependent XANES results over a wide energy range. The two primary peaks at around 1130 and 1215 eV correspond to the  $3p_{3/2} \rightarrow 6s$  and  $3p_{1/2} \rightarrow 6s$  transitions. A quick look at the spectra does not reveal much polarization dependence, which would mean La substituting for the Bi atoms at the perovskite site. However, a close look at the data at around 1150 eV shows polarization dependence. We took finer scans in the region between 1110 and 1190 eV and plotted them in panel (a). Polarization dependence is apparent in the data. For the normal-incidence data ( $\theta=0$ ), an edge structure exists near 1150 eV. This edge quickly disperses to the higher-energy side and does not come back to the lower-energy side up to  $\theta=75^\circ$ .

As discussed above, polarization dependence in XANES reflects the local symmetry around the La atoms in BLT. Therefore, the polarization dependence shown in Fig. 3 appears to suggest an anisotropic local environment for La atoms. However, the interpretation of the data may not be straightforward. While the high-energy features show considerable polarization dependence, the main absorption peak at 1130 eV hardly shows any polarization dependence. Without detailed and accurate calculations on the absorption spectra, it is not possible to extract quantitative information from the data. Yet one can obtain qualitative information on the local symmetry. If La atoms were at the perovskite sites, the ex-

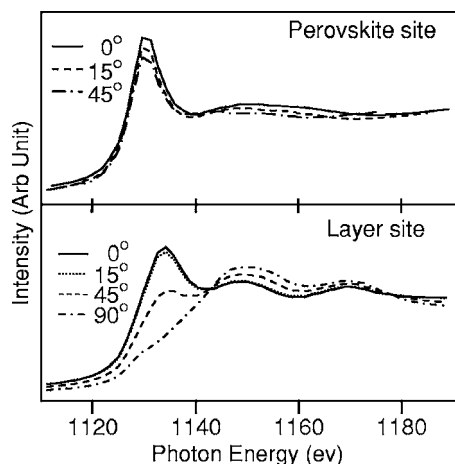


FIG. 4. La  $3p \rightarrow 6s$  XANES spectra calculated by FEFF 8.0 for (a) the perovskite and (b) the layer sites.

perimental conditions for polarizations parallel ( $\theta=0^\circ$ ) and perpendicular to ( $\theta=90^\circ$ ) the  $ab$  plane would be identical due to the cubic symmetry. In that case, the edge structure that disperses from 1150 eV at  $\theta=0^\circ$  to the higher-energy side should disperse back as  $\theta$  goes over  $45^\circ$  (this is the same as saying, for example, that the  $\theta=15^\circ$  spectrum should be the same as that with  $\theta=75^\circ$ ). It is not what is observed in the experimental data. Therefore, one can say that the experimental XANES spectra are consistent with the view that La atoms are located at the layer sites. We note that this does not rule out a possibility of some La atoms going into the perovskite sites. However, we may conclude that a major portion of the La atoms replace the Bi atoms at the layer site considering the anisotropy in the polarization-dependent XANES spectra.

Even though the conclusion we have drawn from the experimental data is quite robust, we also tried to calculate the polarization-dependent XANES spectra using the FEFF 8.0 package.<sup>10</sup> We note that currently available XANES programs do not provide reliable results for the  $3p \rightarrow 6s$  edge. Therefore, only limited discussions on the following results will be given. Figure 4 compares the calculated XANES results for the two cases: La at the perovskite site [panel (a)] and at the layer site [panel (b)]. As expected, the spectra in panel (a) show less polarization dependence than those in panel (b). More importantly, the  $\theta=90^\circ$  spectrum (not shown) is exactly the same as the  $\theta=0^\circ$  spectrum for the

perovskite-site case. Meanwhile, the spectra in panel (b) calculated for the layer site do not show such symmetry (note the difference between  $\theta=0^\circ$  and  $90^\circ$  data). Therefore, the anisotropic local environment around the La atom is indeed manifested in the absorption spectra. We point out that, in spite of the crudeness of the calculation, our discussion on the symmetry should be valid. The calculated results thus support our interpretation of the experimental data even though the calculation does not reproduce the detailed aspect of the experimental spectra.

In conclusion, we have performed polarization-dependent XANES experiments on epitaxially grown BLT thin films to resolve the issue on the preferential substitution site for La in  $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ . The results strongly suggest that some, if not all, La atoms replace the Bi atoms in the layer.

## ACKNOWLEDGMENTS

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<sup>9</sup>In general, an x-ray absorption spectrum shows remnant spectral weight in the flat region above the edge due to the transition from the core level to the continuum. The "height" refers to the height of the underlying step structure.

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