

Direct Observation of Oxygen Stabilization in Layered Ferroelectric $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$

Ferroelectric crystals have several polarization states under zero electric field, which can be switched by applying an electric field. Recently, this has been utilized in ferroelectric random access memory (FRAM), which is one type of nonvolatile memory. Bismuth titanate, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BiT), has been regarded as a promising material for FRAM because BiT shows a high Curie temperature T_C of 675 °C and a large spontaneous polarization [1]. However, BiT has a small remanent polarization P_r , and exhibits “polarization fatigue”, with P_r decreasing with the polarization switching [2]. It has been reported that La-substituted BiT, $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ (BLT), shows a relatively large P_r and a high endurance to polarization fatigue [3].

It is widely recognized that the small P_r and polarization fatigue are attributed to domain clamping, i.e., a decrease in the number of domains that can be switched by applying an electric field. The domain clamping is caused by the strong interaction between domain walls and defects such as oxygen vacancies [4]. Since the stability of oxygen ions strongly depends on the local crystallographic environment, it is essential to investigate the chemical bonding in BiT

and BLT to elucidate the role of La and to develop designs for high-performance BiT-based-devices.

The aim of the present study is to clarify the role of La in BLT on the stability of oxygen ions in terms of the chemical bonding obtained by electron charge density analysis. Analyzing X-ray diffraction data using the maximum entropy method (MEM)/Rietveld method allows us to get information about the nature of chemical bonding directly from the electron density map. We performed high-energy synchrotron radiation (SR) powder diffraction measurements on BiT and BLT. The electron density distributions show clear evidence of the stabilization of oxygen ions in the perovskite layer in BLT [5]. Powder samples of BiT and BLT were prepared by a solid-state reaction. The SR diffraction experiments were performed at 300 K in the ferroelectric phase of BiT and BLT using a large Debye-Scherrer camera with an imaging plate installed at beamline **BL02B2**. We used high-energy SR with a wavelength of $\lambda = 0.35639(2)$ Å ($E = 35$ keV) to reduce absorption by the samples because BiT and BLT contain heavy atoms such as Bi and La.

Figure 1 shows the crystal structure and the equidensity map of the electron density distribution of

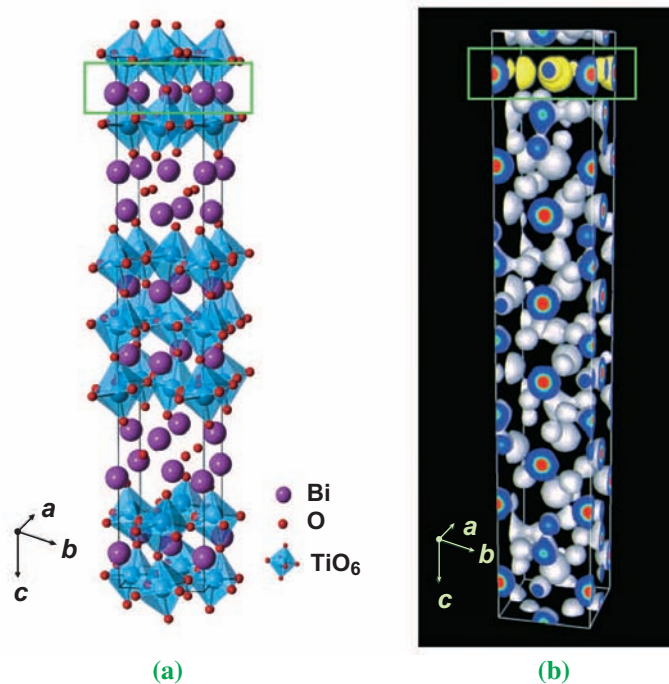


Fig. 1. Structure of ferroelectric BiT at 300 K. **(a)** Crystal structure determined by Rietveld analysis. **(b)** Equidensity map of electron charge density distribution derived by MEM/Rietveld analysis. The surface level is $1.0 e\text{\AA}^{-3}$. The perovskite layer shown in Fig. 2 is indicated by the green rectangle in the figure.

BiT. The structure has alternate stacking of Bi_2O_2 layers and perovskite $\text{Bi}_2\text{Ti}_3\text{O}_{10}$ layers along the c axis. In BLT, it is found that most La occupies the Bi sites in the perovskite layers, one of which is indicated by the green rectangle in Fig. 1. As a result, the substitution of La leads to a significant change in the chemical bonding of Bi–O in the perovskite layer. Figures 2(a) and 2(b) exhibit the Bi–O and Bi/La–O planes in the perovskite layer viewed along the c axis in BiT and BLT, respectively. It is clear that, in BiT, the chemical bonding of Bi–O along the a axis (polarization direction) is stronger than that of Bi–O

along the b axis. Note that the chemical bonding around Bi/La in BLT is quite different from that around Bi in BiT. The La substitution provides an additional chemical bond of Bi/La–O along the b axis in addition to that along the a axis. It is natural to think that fewer oxygen vacancies occur in BLT than in BiT because the oxygen ions are stabilized by the newly formed Bi/La–O bonds in BLT. Thus, the high endurance to polarization fatigue achieved for BLT can be ascribed to the stabilization of oxygen ions by La substitution in the perovskite layer due to the isotropic chemical bonding of Bi/La–O.

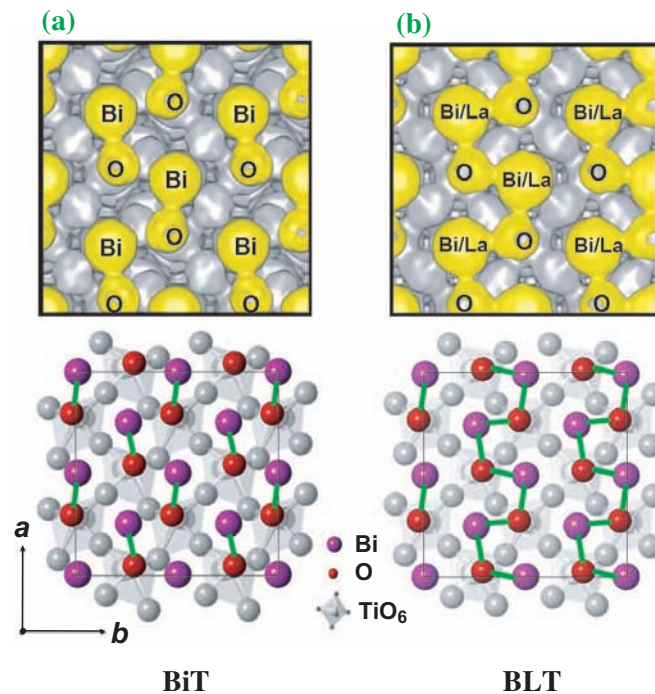


Fig. 2. Ferroelectric structures of BiT and BLT in the perovskite layer at the c axis coordinate $\sim 0.07c$. In each figure, the lower section is the crystal structure and the upper section is the equidensity map of the electron density distribution (surface level $0.55 \text{ e}\text{\AA}^{-3}$) derived by the MEM/Rietveld analysis. The depicted cell size is $2a \times 2b$. The oxygen ions in BLT are connected by Bi/La–O chemical bonding along the a and b axes.

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