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Cation disorder study of $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ by neutron powder diffraction and Raman spectroscopy

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Abstract

Structural refinement and Raman spectroscopy were used to obtain structural information for $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$, including site preference of La atoms, cation distribution, cation occupancy and lattice parameters. Structural refinement was carried out for three cation disorder models. The best structural refinement result was obtained assuming that, of the three possible substitutions, La atoms substitute Bi atoms only in the perovskite $\text{Bi}_2\text{Ti}_3\text{O}_{10}$ unit. The final weighted R -factor, R_{wp} , and the goodness-of-fit indicator, S ($=R_{\text{wp}}/R_e$), were 4.81% and 1.56%, respectively. The results of Raman spectroscopy provided evidence for the cation disorder model. The band originating from the Bi atoms in the Bi_2O_2 layer did not show significant changes while the vibrational modes assigned to the Bi atoms in the perovskite units moved to high frequencies due to the substitution of La atoms. The final lattice parameters obtained from the refinement were $a = 5.4238(1)$ Å, $b = 5.4169(2)$ Å and $c = 32.9002(2)$ Å. The β angle was 90.09° .

1. Introduction

Ferroelectric thin films have been widely studied for application in ferroelectric random access memories (FeRAMs) because they have the advantage of rapid polarization switching, low power consumption and long life [1]. Among the ferroelectric materials, $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ (PZT) thin films are most promising because of their large remnant polarization ($2P_r = 20\text{--}70 \mu\text{C cm}^{-2}$) and high Curie temperature. However, PZT films have the fatal disadvantage of fatigue behaviour when platinum electrodes are used [2].

Recently, it was shown that La-substituted $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BTO) and $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ (BLT), films prepared by pulsed laser deposition exhibited excellent ferroelectric properties and fatigue-free behaviour up to 3×10^{10} switching cycles [3].

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Although many reports have noted the possibility that La atoms play a key role in the fatigue-free characteristics of BLT, the location of the La atoms that affect the ferroelectric properties in BLT has not been quantitatively determined yet. The crystal structure of BLT is also essential to understand the degree of spontaneous polarization at room temperature. However, structural studies of BLT and reported results have been few compared to research on preparation methods and the characterization of electrical and physical properties of the BLT compound [4]. In addition, as far as we know, the detailed crystal structure parameters of polycrystalline BLT such as atomic coordinates, cation distribution and amount of La atoms substituting Bi ones in the crystal lattice have not been reported.

The purpose of this paper is the determination of cation disorder of BLT by means of a Rietveld refinement using

neutron powder diffraction data and Raman spectroscopy. The neutron powder diffraction experiment is useful to obtain information about oxygen atoms in oxide compounds, even though it may be very insensitive to small amounts of extraneous phases and weak lattice distortions compared to x-ray diffraction. Raman spectroscopy is sensitive to the coordination of local sites resulting from the atomic substitution and the distortion of the polyhedron, because its spectrum originates from the lattice vibration mode. These respective characteristics of the two different experiments are the main reason why we adopted them.

2. Experimental

The BTO and BLT samples were prepared by a solid-state reaction using Bi_2O_3 , La_2O_3 and TiO_2 as starting materials. Stoichiometric quantities of starting materials were mixed and then annealed between 1000°C and 1100°C for 1 day. A second annealing process was performed at between 1050°C and 1150°C for 2 days with intermediate grindings.

Pellets were prepared for the measurement of hysteresis loops and sintered at 1150°C for 4 h in air. Then, they were cut with a diamond saw and polished. Silver electrodes were coated on both the polished surfaces of the pellets. A modified Sawyer–Tower circuit and an oscilloscope (Hewlett-Packard 1222A) were used to measure the ferroelectric hysteresis loop.

Neutron powder diffraction data were collected over scattering angles ranging from 0 – 160° using 1.8348 \AA neutrons on a high resolution powder diffractometer (HRPD) at the Hanaro Center of the Korea Atomic Energy Research Institute (KAERI). The General Structure Analysis System (GSAS) programme was used to conduct the refinement. A pseudo-Voigt function was used as a profile function among the profile functions in GSAS [5, 6]. Raman spectroscopy was used with the 1064 nm line from an Nd-YAG laser as the exciting source.

3. Results and discussion

There are two crystal systems, orthorhombic and monoclinic, for BTO at room temperature. The orthorhombic system having a space group $B2cb$ was suggested by Dorrian [7] and Lightfoot and co-workers [8] through neutron diffraction experiments, while Rae *et al* [9] presented the monoclinic system with a space group $B1a1$ by means of a single crystal x-ray diffraction study at room temperature. It is difficult to distinguish a monoclinic from an orthorhombic system because the differences between two crystal systems depend on whether there is a b -glide or not. According to our previous result obtained from the Rietveld refinement of BTO, of the two crystal systems, the monoclinic system was more suitable than the orthorhombic one [10]. Consequently, in this study, the monoclinic system with the space group $B1a1$ was used as an initial structural model of BLT. The structural refinement of BLT was performed for the sample which shows a remnant polarization (P_r), $2P_r$, of $19.6 \mu\text{C cm}^{-2}$ (figure 1).

At first, initial structural refinement was carried out on the assumption that there was no substitution of La atoms for Bi atoms. Once convergence had been reached, three possibilities of La substitution were considered. La atoms may partially substitute for Bi atoms in either the Bi_2O_2

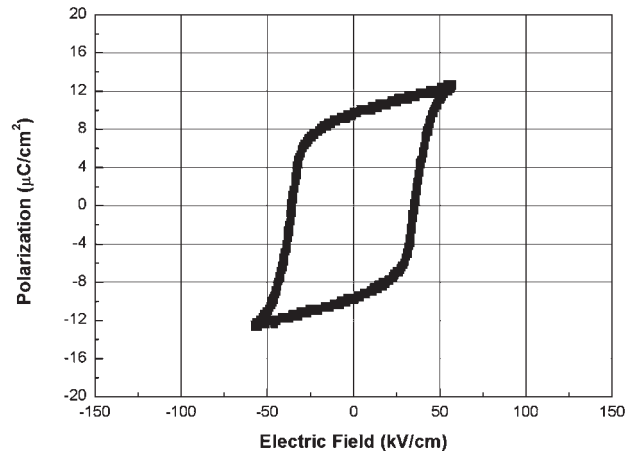


Figure 1. Hysteresis loop of $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$.

layer (L-model) only or in perovskite units, $\text{Bi}_2\text{Ti}_3\text{O}_{10}$ (P-model), only. It is also probable that Bi atoms are substituted into both the Bi_2O_2 layer and perovskite units (B-model). Based on the initial refinement results, structural refinements of the aforementioned three models were performed and the refinement patterns are shown in figure 2. The weighted R -factor, R_{wp} , for L-, P- and B-models was 5.30%, 4.81% and 5.30%, respectively. The goodness-of-fit, S ($=R_{wp}/R_e$), for L-, P- and B-models was 1.70, 1.56 and 1.68, respectively. Though it is difficult to detect the differences between the three models, from the R_{wp} and S values it can be concluded that the P-model is the most suitable of the three as the site preference model of BLT at room temperature.

In order to verify the site preference of La atoms, Raman spectroscopy was used as a complementary method. Figure 3 shows the Raman spectra of (a) BTO and (b) BLT at room temperature. The vibrational modes of BTO can be classified as lattice transitions involved in the displacement of cations and internal modes of the TiO_6 octahedron [11]. Considering the vibrational modes related to the atomic mass, the low-frequency modes below 200 cm^{-1} are attributed to the motion of heavy Bi atoms while internal vibrational modes of the TiO_6 octahedron having six kinds of modes are expected to appear above 200 cm^{-1} . As shown in figure 3(a), the bands at 228 , 269 , 334 , 541 , 616 and 850 cm^{-1} originate from the internal vibrational modes of TiO_6 . The bands below 200 cm^{-1} are ascribed to two different Bi sites, the Bi_2O_2 layer and perovskite units. The band at 65 cm^{-1} is assigned as a rigid-layer mode which originates from Bi displacement in the Bi_2O_2 layers. On the other hand, the triple bands at 90 , 119 and 148 cm^{-1} are related to the Bi atoms in the perovskite units [12].

Compared with the Raman spectrum of BTO, the band appearing at 65 cm^{-1} corresponding to the Bi atoms in the Bi_2O_2 layers moved to a lower frequency of 64 cm^{-1} in BLT because of structural hardening. However, the triple bands at 90 , 119 and 148 cm^{-1} , assigned to the modes of Bi atoms in the perovskite units, became diffusive and moved to higher frequencies. Of the triple bands, the first peak at 90 cm^{-1} became too diffusive to be distinguished from a broad peak near 105 cm^{-1} of BLT which originated from the shoulder near 101 cm^{-1} in BTO. The peak broadening was caused by the

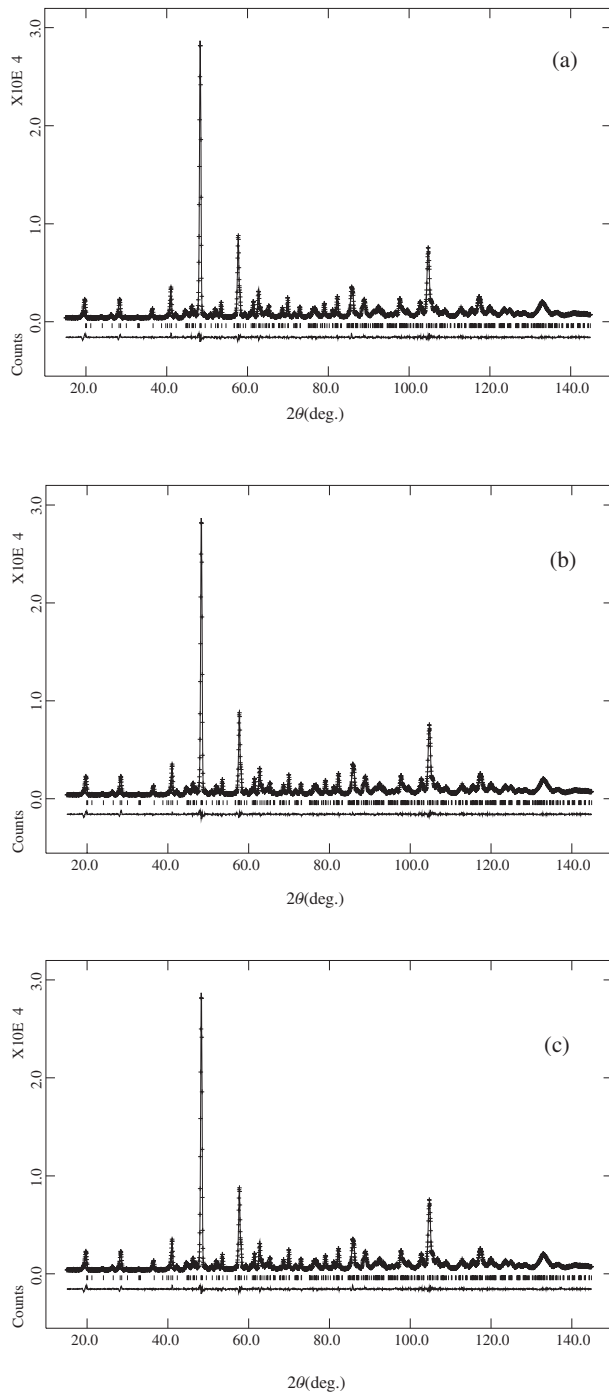


Figure 2. The structural refinement pattern of $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ using neutron diffraction data. (a) Substitution of La ions for Bi ones of Bi_2O_2 units (L-model), (b) Substitution of La ions for Bi ones of $\text{Bi}_2\text{Ti}_3\text{O}_{10}$ units (P-model) and (c) Substitution of La ions for Bi ones of both Bi_2O_2 and $\text{Bi}_2\text{Ti}_3\text{O}_{10}$ units partially (B-model). Plus (+) marks represent the observed intensities, and the solid line represents the calculated ones. A difference (observed–calculated) plot is shown beneath. Tick marks above the difference data indicate the reflection position.

compositional inhomogeneity of the Bi atoms in the perovskite units. However, the peaks at 119 and 148 cm^{-1} of BTO moved to higher frequencies of 125 and 156 cm^{-1} in BLT. The shift of Raman peaks towards higher frequencies indicates that an atom

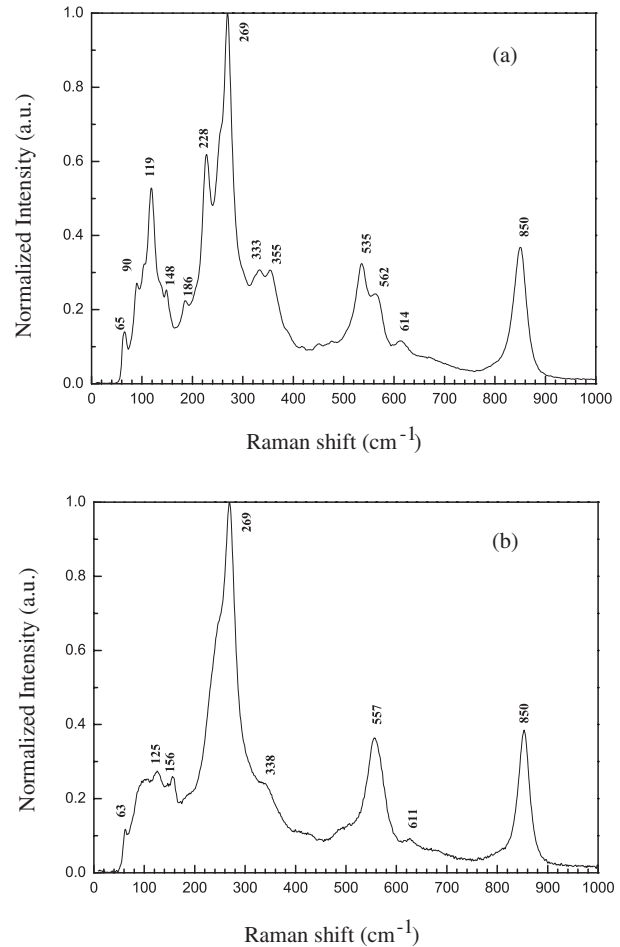


Figure 3. Raman spectra of (a) $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and (b) $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ at room temperature.

having a smaller atomic weight than a mother atom partially substitutes for the original atom. Consequently, the up-shift of Raman peaks in this study suggests that the substitution sites of La atoms were only the Bi atomic sites in the perovskite units. Also, this result confirms the P-model proposed by the structural refinement result, in which La atoms were only substituted for Bi atoms of the perovskite units, $\text{Bi}_2\text{Ti}_3\text{O}_{10}$.

The slight changes for modes at high frequencies above 200 cm^{-1} in BLT means the decrease of TiO_6 octahedron tilting and relaxation of structural distortion, which leads to the phase transition to a tetragonal structure, as shown in the previous study on $\text{Bi}_2\text{La}_2\text{Ti}_3\text{O}_{12}$ [13]. The relaxation of structural distortion can be seen from the smaller orthorhombicity, defined as $2(a-b)/(a+b)$, of 1.27×10^{-3} in BLT compared to 7.24×10^{-3} in BTO [10],

Through the structural refinement of BLT on the basis of the structural model (P-model) and the Raman study about the site preference of La atoms, the structural information for BLT such as cation distribution and lattice parameters, was successfully determined. Table 1 shows the refined structural parameters and table 2 lists the atomic distances and angles for BLT. Occupancies of La atoms for each Bi site in the perovskite unit were 0.13 and 0.62, respectively. The refined lattice parameters were $a = 5.4238(1)$ Å, $b = 5.4169(2)$ Å and $c = 32.9002(2)$ Å. The β angle was 90.09° .

Table 1. Structural parameters for Bi_{3.25}La_{0.75}Ti₃O₁₂ obtained from the Rietveld refinement using neutron powder diffraction data at room temperature. The symbol, *g*, is the occupation factor. The numbers in parentheses are the estimated standard deviations of the last significant figure.

| Atom Site | | <i>x</i> | <i>y</i> | <i>z</i> | <i>g</i> | 100 × <i>U</i> _{iso} Å ⁻² |
|---------------------|----|------------------------|-------------------------|------------------------|----------------------|---|
| Bi ₁ (a) | 4a | 0.0559(2) ^a | 0.5030(13) ^a | 0.5667(3) ^a | 0.87(1) ^b | 0.78(2) ^c |
| La ₁ (a) | 4a | 0.0559(2) | 0.5030(13) | 0.5667(3) | 0.13(1) | 0.78(2) |
| Bi ₂ (a) | 4a | 0.0530(4) | 0.4863(1) | 0.7104(2) | 1.0 | 0.18(4) |
| Ti ₁ (a) | 4a | 0.0756(11) | 0.0073(4) | 0.5008(2) | 1.0 | 0.28(2) |
| Ti ₂ (a) | 4a | 0.0880(7) | 0.0048(12) | 0.6261(4) | 1.0 | 0.07(1) |
| O ₁ (a) | 4a | 0.3014(1) | 0.2908(4) | 0.5048(1) | 1.0 | 2.92(15) |
| O ₂ (a) | 4a | 0.3222(21) | 0.2519(5) | 0.2500(2) | 1.0 | 0.69(8) |
| O ₃ (a) | 4a | 0.1048(11) | -0.0623(20) | 0.5584(3) | 1.0 | 0.06(8) |
| O ₄ (a) | 4a | 0.0767(15) | 0.0586(2) | 0.6813(1) | 1.0 | 1.04(1) |
| O ₅ (a) | 4a | 0.3269(23) | 0.2630(14) | 0.6093(1) | 1.0 | 2.10(1) |
| O ₆ (a) | 4a | 0.3823(12) | -0.2146(27) | 0.6226(1) | 1.0 | 1.68(7) |
| Bi ₃ (b) | 4a | 0.0557(7) ^a | 0.4913(5) ^a | 0.4321(1) ^a | 0.37(4) ^b | 2.18(12) ^c |
| La ₂ (b) | 4a | 0.0557(7) | 0.4913(5) | 0.4321(1) | 0.62(4) | 2.18(12) |
| Bi ₄ (b) | 4a | 0.0445(2) | 0.5180(1) | 0.2879(1) | 1.0 | 2.16(5) |
| Ti ₃ (b) | 4a | 0.0793(29) | 0.0031(23) | 0.3691(1) | 1.0 | 2.11(18) |
| O ₇ (b) | 4a | 0.3732(6) | -0.2170(1) | 0.4924(1) | 1.0 | 1.10(5) |
| O ₈ (b) | 4a | 0.3199(8) | -0.2431(14) | 0.7503(3) | 1.0 | 0.76(4) |
| O ₉ (b) | 4a | 0.1189(3) | 0.0423(5) | 0.4401(1) | 1.0 | 1.39(5) |
| O ₁₀ (b) | 4a | 0.0822(1) | -0.0329(4) | 0.3171(4) | 1.0 | 2.56(5) |
| O ₁₁ (b) | 4a | 0.3282(14) | -0.2653(12) | 0.3839(1) | 1.0 | 0.61(2) |
| O ₁₂ (b) | 4a | 0.3650(10) | 0.2214(7) | 0.3768(1) | 1.0 | 0.99(1) |

^a Constraint on atomic coordinate: *x*(Bi) = *x*(La), *y*(Bi) = *y*(La) and *z*(Bi) = *z*(La).^b Constraint on occupancy: *g*(Bi) + *g*(La) = 1.0.^c Constraint on isotropic temperature factor: *U*_{iso}(Bi) = *U*_{iso}(La).**Table 2.** Selected interatomic distances and bond angles for Bi_{3.25}La_{0.75}Ti₃O₁₂ at room temperature.

| Bond | Distance(Å) | Bond | Distance(Å) | Bond | Distance(Å) |
|--|-------------|---|-------------|---|-------------|
| M(1) ^a -O ₁ (a) | 2.690(9) | M(1)-O ₁ (a) | 2.927(9) | M(1)-O ₃ (a) | 3.082(11) |
| M(1)-O ₃ (a) | 2.389(8) | M(1)-O ₃ (a) | 2.475(8) | M(1)-O ₃ (a) | 3.009(10) |
| M(1)-O ₅ (a) | 2.407(8) | M(1)-O ₅ (a) | 2.386(7) | M(1)-O ₆ (a) | 2.972(10) |
| M(1)-O ₆ (a) | 2.366(7) | M(1)-O ₇ (b) | 3.347(11) | M(1)-O ₇ (b) | 2.869(8) |
| M(2) ^b -O ₁ (a) | 2.941(9) | M(2)-O ₁ (a) | 3.150(9) | M(2)-O ₇ (b) | 3.061(10) |
| M(2)-O ₇ (b) | 2.522(7) | M(2)-O ₉ (b) | 2.470(8) | M(2)-O ₉ (b) | 3.015(10) |
| M(2)-O ₉ (b) | 2.389(8) | M(2)-O ₉ (b) | 3.072(10) | M(2)-O ₁₁ (b) | 2.546(8) |
| M(2)-O ₁₁ (b) | 2.486(7) | M(2)-O ₁₂ (b) | 2.875(9) | M(2)-O ₁₂ (b) | 2.392(7) |
| Bi ₂ (a)-O ₂ (a) | 2.215(7) | Bi ₂ (a)-O ₂ (a) | 2.334(7) | Bi ₂ (a)-O ₄ (a) | 2.513(8) |
| Bi ₂ (a)-O ₄ (a) | 3.250(11) | Bi ₂ (a)-O ₄ (a) | 2.758(11) | Bi ₂ (a)-O ₄ (a) | 3.021(11) |
| Bi ₂ (a)-O ₆ (a) | 3.282(8) | Bi ₂ (a)-O ₈ (b) | 2.436(7) | Bi ₂ (a)-O ₈ (b) | 2.289(7) |
| Bi ₄ (b)-O ₂ (a) | 2.421(7) | Bi ₄ (b)-O ₂ (a) | 2.267(7) | Bi ₄ (b)-O ₈ (b) | 2.156(6) |
| Bi ₄ (b)-O ₈ (b) | 2.298(7) | Bi ₄ (b)-O ₁₀ (b) | 3.143(10) | Bi ₄ (b)-O ₁₀ (b) | 2.622(8) |
| Bi ₄ (b)-O ₁₀ (b) | 2.687(10) | Bi ₄ (b)-O ₁₀ (b) | 3.071(12) | Bi ₄ (b)-O ₁₂ (b) | 3.353(8) |
| Ti ₁ (a)-O ₁ (a) | 1.965(5) | Ti ₁ (a)-O ₁ (a) | 1.858(5) | Ti ₁ (a)-O ₃ (a) | 1.931(4) |
| Ti ₁ (a)-O ₇ (b) | 2.035(5) | Ti ₁ (a)-O ₇ (b) | 1.937(5) | Ti ₁ (a)-O ₁₀ (b) | 2.015(4) |
| Ti ₂ (a)-O ₃ (a) | 2.277(4) | Ti ₂ (a)-O ₄ (a) | 1.827(3) | Ti ₂ (a)-O ₅ (a) | 1.993(5) |
| Ti ₂ (a)-O ₅ (a) | 1.981(5) | Ti ₂ (a)-O ₆ (a) | 1.985(5) | Ti ₂ (a)-O ₆ (a) | 1.932(5) |
| Ti ₃ (b)-O ₉ (b) | 2.352(4) | Ti ₃ (b)-O ₁₀ (b) | 1.725(3) | Ti ₃ (b)-O ₁₁ (b) | 2.043(5) |
| Ti ₃ (b)-O ₁₁ (b) | 1.916(5) | Ti ₃ (b)-O ₁₂ (b) | 1.983(5) | Ti ₃ (b)-O ₁₂ (b) | 1.910(5) |
| Bond angle (°) | | | | | |
| O ₁ (a)-Ti ₁ (a)-O ₇ (b) | 174.6(1) | O ₁ (a)-Ti ₁ (a)-O ₇ (b) | 176.3(1) | O ₃ (a)-Ti ₁ (a)-O ₁₀ (b) | 167.6(5) |
| O ₃ (a)-Ti ₂ (a)-O ₄ (a) | 178.8(2) | O ₅ (a)-Ti ₂ (a)-O ₆ (a) | 158.5(1) | O ₅ (a)-Ti ₂ (a)-O ₆ (a) | 159.0(1) |
| O ₉ (b)-Ti ₃ (b)-O ₁₀ (b) | 173.3(8) | O ₁₁ (b)-Ti ₃ (b)-O ₁₂ (b) | 157.7(2) | O ₁₁ (b)-Ti ₃ (b)-O ₁₂ (b) | 157.1(1) |

^a M(1): Bi₁(a) or La₁(a).^b M(2): Bi₃(b) or La₂(b).

Figure 4 illustrates the crystal structure of Bi_{3.25}La_{0.75}Ti₃O₁₂ on the basis of the refined structural parameters. Compared with the idealized parent structure of all the Aurivillius phases, i.e. a tetragonal system, constituent atoms mostly deviated along the three axes from corresponding

positions of the tetragonal structure. The Bi₂O₂ layers and TiO₆ octahedron in the perovskite units were distorted and the TiO₆ octahedron along the *c*-axis was buckled. These displacements are the main cause of the remnant polarization of BLT at room temperature as shown in figure 1.

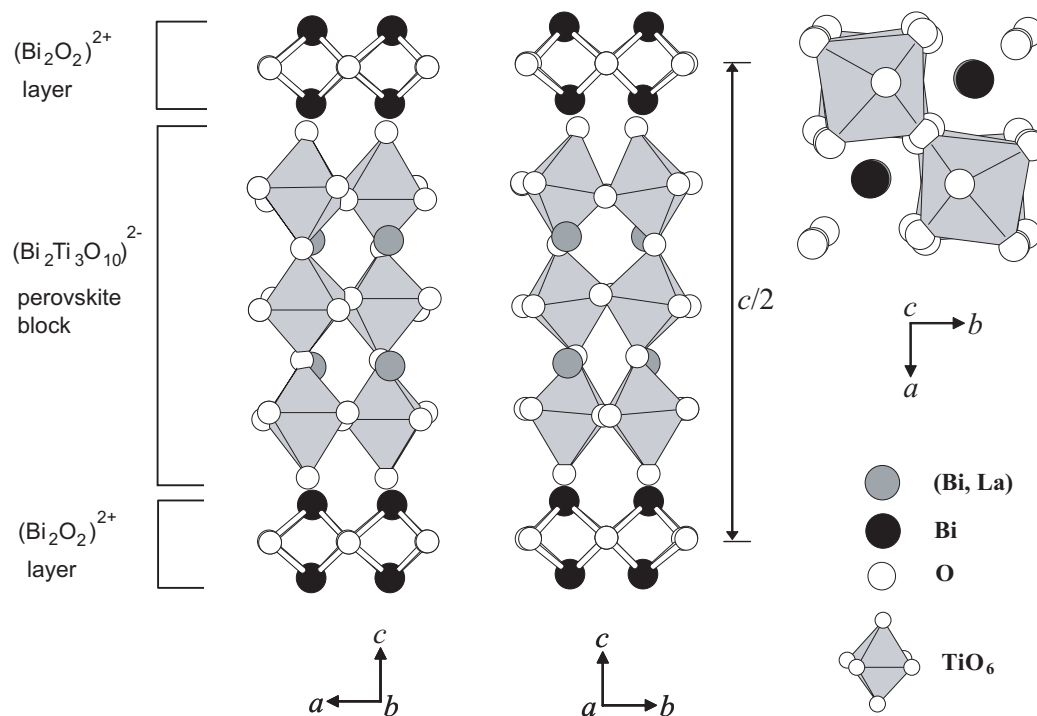


Figure 4. The crystal structure of $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ based on the parameters obtained from the structural refinement.

4. Conclusion

The substitution site and distribution of La atoms in BLT were studied using neutron powder diffraction and Raman spectroscopy. Three possibilities of La substitution were considered in neutron powder diffraction. The lowest R_{wp} factor of 4.81% and goodness-of-fit, S , value of 1.56 were obtained on the assumption that only the Bi atoms in the perovskite units were replaced by La atoms. The up-shift of the triple band in the Raman spectrum, originating from the Bi atoms in the perovskite units, verified the substitution. Structural refinement and Raman spectroscopy may quantitatively be complementary methods to each other, in particular, for determination of the site preference and the occupancies.

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