

# A Combined Rietveld Refinement on the Crystal Structure of a Magnetolectric Aurivillius Phase $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ Using Neutron and X-ray Powder Diffractions

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An ambiguity on the correct room temperature structure of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  was resolved using a combined Rietveld refinement of neutron and X-ray diffraction. The structure of this compound has been reported to have a space group of  $F2mm$  (adopting 2-fold rotation symmetry along the  $c$ -axis) or  $A2_1am$ . However, our diffraction study reveals that some reflections would violate  $F$ -centering and confirm that they belong to  $A2_1am$ . Our refinement with the space group of  $A2_1am$  converged at  $R_p=6.85\%$ ,  $R_{wp}=9.23\%$  and  $\chi^2=1.66$  for an isotropic temperature model with 85 variables. The lattice constants are  $a=5.4677(1)$  Å,  $b=5.4396(1)$  Å, and  $c=41.2475(8)$  Å. In structure, Ti/Fe atoms at the oxygen octahedral sites of the perovskite unit are completely disordered, resulting in that these atoms are transparent in neutron diffraction. The octahedra of the perovskite unit are relatively displaced along the  $a$ -axis against the Bi atoms, which contribute as a major component to the spontaneous polarization of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ .

**Key words:**  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ , Structure, Refinement, Atomic displacement, Spontaneous polarization

## I. Introduction

Among the Aurivillius phase, a series of  $\text{Bi}_{4+2n}\text{Ti}_3\text{Fe}_n\text{O}_{12+3n}$  (BITnBF) are compounds complexing perovskite layers of ferromagnetic  $\text{BiFeO}_3$  (BF) into a ferroelectric Aurivillius phase  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  (BIT). As a result, BITnBF has been known an unusual oxide showing magnetolectricity at ambient conditions.<sup>1-4)</sup> For this compound, electric field can be induced by applying magnetic field, and *vice versa*. This conversion could make a polarized state retained even after removal of magnetic field. At present, the origin of the magnetolectric effect in BITnBF is not clearly known yet. However, it appeared to be influenced by various structural distortions in the perovskite layers containing ferromagnetic  $\text{Fe}^{3+}$  and polarizable  $\text{Ti}^{4+}$  ions. In the reported BITnBF compounds, the number ( $n$ ) allowed for the perovskite layers has been reported to be five.<sup>5)</sup> Such an accommodation is expected to be associated with various commensurate displacive modulations of constituent atoms resulting in orthorhombic distortion in common. Wither *et al.*<sup>6)</sup> suggested that for the Aurivillius phase, three major displacive modes can be derived from the parent structure having the space group of  $Fm\bar{3}m$ :  $F2mm$  mode for atomic shifts along the  $a$ -axis,  $Bmab$  or  $Amam$  mode for octahedral rotation about the  $a$ -axis, and  $Bbab$  or  $Bbam$  mode for octahedral rotation about the  $c$ -axis. In particular, the  $F2mm$  mode is considered to be a major displacive mode inducing sponta-

neous polarization.

For BIT1BF, Kubel and Schmid<sup>7)</sup> reported from both single and powder X-ray diffractions that the structure of BIT1BF is orthorhombic, whose space group belongs to  $F2mm$  (assuming  $a$ -axis as a polar direction). Later, Ko *et al.*<sup>1)</sup> showed that from a synchrotron X-ray diffraction data, it could have the space group of  $A2_1am$  implying that the true space group needs to be resolved. On the other hand, Kubel and Schmid<sup>7)</sup> suggested that BIT1BF undergoes phase transitions from  $F2mm$ - $Fm\bar{3}m$  at  $560^\circ\text{C}$  and  $Fm\bar{3}m$ - $I4/mmm$  at  $750^\circ\text{C}$ . These phase transition points have been also recognized from dielectric measurements at high temperatures.<sup>3,4)</sup> Therefore, if BIT1BF has the space group of  $A2_1am$ , the phase of  $F2mm$  could be an intermediate temperature one. This means that the  $F2mm$  phase could be metastably quenched, which is process-dependent. Otherwise, their X-ray diffraction data might not show the correct room temperature structure, very likely due to dominant scattering of Bi atoms over oxygen atoms. In this study, we attempt to reveal the nature of this room temperature structure adopting a combined neutron and X-ray diffraction, which can provide higher transparency for heavy atoms such as Bi and higher scattering for light atom such as O, compared to X-ray diffraction only.

## II. Experimental Procedure

A stoichiometric amount of the oxides  $\text{Bi}_2\text{O}_3$  (99.99%, Ald-

rich), Fe<sub>2</sub>O<sub>3</sub> (99.98%, Aldrich), and TiO<sub>2</sub> (99.99%, Aldrich) was ball-milled over two days. The mixed powder was pressed to form into a pellet and then heated in a Pt crucible at 900°C for one hour. In the ascending heating stage, the sample was intermittently maintained at 650°C for one hour to avoid melting. After heating, the hardened sample was crushed, sieved to <150 mesh, and then ground using a motorized agate mortar and pestle. The powdered sample was pressed to form into a pellet and then heated at 1,050°C for 16 hours. Finally, the pellet was hand-crushed in an agate mortar, sieved to <400 mesh and annealed at 1,000°C for two hours followed by slow cooling. All the heating was performed in air with keeping the pellet sample contained inside the Pt crucible.

Neutron powder diffraction data were collected on HRPD at Hanaro (Korea) using a neutron wavelength of 1.8339 Å. About 10 g of BIT1BF was placed in a cylindrical vanadium can. The can was rotated during the data collection. Data collection was carried out with a 32 multi-detector system, which covered the 2θ range of 0°–160° with a step scan of 0.05°. Count time was given 70 seconds for each step. For analysis, the data below 10° and above 155° were excluded, which were interfered by beam line components.

X-ray powder diffraction data were collected on a Philips (X'pert) diffractometer (divergence slit=0.5°, receiving slit = 0.15°) with the Bragg-Brentano geometry at KBSI (Korea) using a monochromatic CuKα radiation operated at 40 kV and 40 mA. The step scan was adopted to cover the 2θ of 20°–140° with the step width of 0.02° in 2θ and the counting time of 7 seconds for each step.

A combined Rietveld refinement for the neutron and the X-ray data was performed using GSAS<sup>8)</sup> with the space group of A2<sub>1</sub>am. Starting structural parameters were estimated based on an assumed parent structure model with the space group of Fmmm. With a disordering of transition metal atoms, Ti and Fe in 3 : 1 atomic ratio, the neutron scattering length of Ti/Fe atom is virtually zero. Therefore, the initial refinement was carried out without these metal atoms for the neutron diffraction data, which gave the locations of the other atoms in structure. Our result confirmed that the sites of the Ti/Fe atoms were vacant. In other words, such a transparency for the Ti/Fe atoms in the neutron diffraction revealed that the Ti and Fe atoms are completely disordered. To locate the Ti/Fe atoms additionally, a combined refinement was performed including the X-ray diffraction data.

In the refinement, background was fitted by a cosine Fourier series with eight terms. Peak shape was modeled using the pseudo-Voigt profile function with coefficients parameterized by Thompson *et al.*<sup>9)</sup> for the parameters of profile width and the Lorentzian profile broadening. The neutron peaks showed a considerable degree of profile asymmetry for 2θ below 38°, while the X-ray ones did not show significant profile asymmetry. In the beginning, the neutron refinement was carried out for the whole range of the angle data. When an asymmetry correction was applied for the

lower angle data, a strong correlation occurred with the unit cell parameters. However, there was not a significant change in structural data. Therefore, the successive neutron refinement was performed for only the 38°–155° portion of the diffraction pattern in 2θ. This procedure could allow a stable convergence with a greater confidence on the refined structural data. In addition, the data showed a weak preferred orientation due to plate-shaped crystal forms, which was corrected to improve the peak fit. For X-ray diffraction data, an absorption correction for surface roughness gave an improvement on thermal parameters of the Ti/Fe atoms. Refinement of the bismuth occupancies gave no indication of any significant deviation from their stoichiometries. In the combined refinement, 85 refined parameters were globally varied including 36 positional parameters and 13 isotropic temperature parameters. The x parameter of Bi was fixed as an origin for a polar axis. A stable convergence for the final refinement was achieved to R<sub>p</sub>=6.85%, R<sub>wp</sub>= 9.23%, and χ<sup>2</sup>=1.66 with 8340 observations. The crystal data and standard R factors for the profile fits were given in Table 1, the refined structural parameters were presented in Table 2 and the fitted powder patterns for the neutron and X-ray diffractions were shown in Fig. 1.

### III. Results and Discussion

#### 1. Structure Refinement

Kubel and Schmid<sup>7)</sup> from a single crystal and a powder X-ray diffraction study showed that the space group for BIT1BF is F2mm. However, our neutron data was unable to

**Table 1.** Crystal Data and Details of the Combined Neutron and X-ray Refinements

Chemical formula	Bi <sub>3</sub> Ti <sub>1</sub> FeO <sub>15</sub>					
Z	4					
Calculated density (g/cm <sup>3</sup> )	8.037					
Space group	A2 <sub>1</sub> am					
a(Å)	5.4677(1)					
b(Å)	5.4396(1)					
c(Å)	41.2475(8)					
Number of Observations	2341	neutron	5999	x-ray		
Number of Reflections	454	neutron	1376	x-ray		
Number of Variables		85	total			
R <sub>wp</sub> <sup>+</sup>	0.0686	neutron	0.1097	x-ray	0.0923	total
R <sub>p</sub> <sup>++</sup>	0.0534	neutron	0.0824	x-ray	0.0685	total
χ <sup>2</sup> <sup>1:++</sup>			1.655	total		

Numbers in parentheses are esd's in the last significant digit.

$$*R_{wp} = \sqrt{\frac{\sum w(I_o - I_c)^2}{\sum w I_o^2}} \quad **R_p = \frac{\sum |I_o - I_c|}{\sum I_o}$$

$$***\chi^2 = \frac{\sum w(I_o - I_c)^2}{N_{obs} - N_{var}}$$

be fitted with the space group  $F2mm$  showing that some weak reflections violated  $F$ -centering. It is possible that the structure with  $F2mm$  could be a metastably quenched high temperature polymorph considering that  $F2mm$  is higher

**Table 2.** Refined Positional and Thermal Parameters for  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$

Atom	Site	x	y	z	$U(\times 10^3 \text{\AA}^2)$
O(1)	4a	.3310(26)	.3252(28)	0	.87(34)
O(2)	8b	.0082(18)	-.0075(17)	.25050(25)	.67(18)
O(3)	8b	.3271(20)	.1882(19)	.09477(21)	1.38(22)
O(4)	8b	.2918(22)	.3026(16)	.19455(15)	1.13(23)
O(5)	8b	.0419(23)	.0310(18)	.03988(20)	1.39(22)
O(6)	8b	.6088(19)	.4554(18)	.05110(20)	1.19(23)
O(7)	8b	.0843(18)	-.0311(21)	.14698(21)	1.32(27)
O(8)	8b	.5346(20)	.5144(21)	.13864(21)	0.96(23)
Ti/Fe(1)	8b	.2951(19)	.2514(38)	.04871(15)	.37(26)
Ti/Fe(2)	8b	.2916(20)	.2582(32)	.15292(16)	.28(25)
Bi(1)	4a	.250000 <sup>†</sup>	-.2441(10)	0	1.63(9)
Bi(2)	8b	.2322(12)	-.2696(6)	.21925(4)	0.95(6)
Bi(3)	8b	.2470(14)	-.2452(8)	.104682(34)	1.09(6)

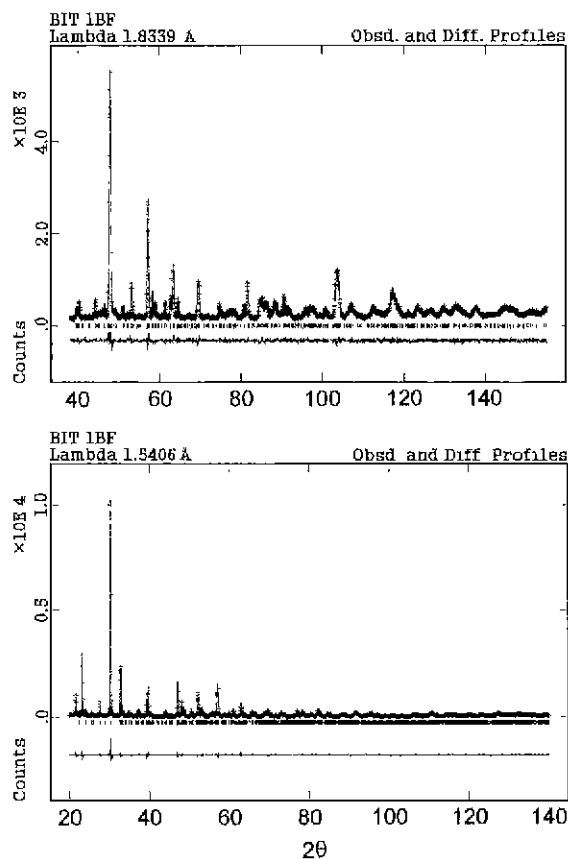
Numbers in parentheses are esd's in the last significant digits.

<sup>†</sup>Fixed parameter.

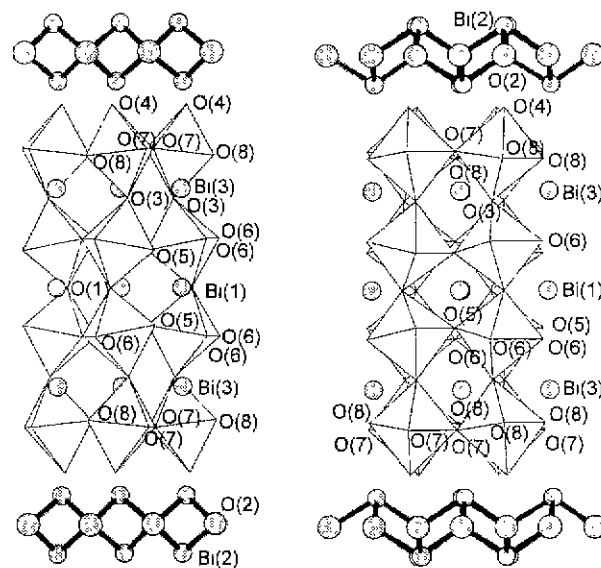
than  $A2_1am$  in symmetry. At high temperatures, BIT1BF has been suggested to undergo the phase transitions from  $F2mm$  to  $Fmmm$  at  $560^\circ\text{C}$  and from  $Fmmm$  to  $I4/mmm$  at  $750^\circ\text{C}$ .<sup>7)</sup> If the high temperature polymorph has the space group  $F2mm$ , a phase transition from  $A2_1am$  to  $F2mm$  may exist below  $600^\circ\text{C}$ . In BIT1BF, Ko *et al.*<sup>11)</sup> reported that an anomaly exists around  $400^\circ\text{C}$  in the variations of dielectric constant with temperature. However, this change has not been detected in birefringence<sup>7)</sup> with the increase of temperature. At present, it is not clear that the change of dielectric constant at  $400^\circ\text{C}$  is associated with a structural change. On the other hand, the refined structure based on  $A2_1am$  was very similar on average to that of  $F2mm$ . A major difference was in splitting of equatorial oxygen atoms of oxygen octahedra in structure. Therefore, if BIT1BF undergoes a symmetry change from  $A2_1am$  to  $F2mm$ , a very little change occurs in structure. We could consider that some weak scattering arising from  $A$ -centering such as  $0k1$  ( $k+1=2n$ ) might not be well resolved in X-ray diffraction, in which the splitting oxygen atoms largely causes such scattering. Furthermore, X-ray diffraction can be dominated by strong scattering from heavy atoms such as Bi. Hence, it might be not possible to derive a correct structural model from X-ray diffraction data.

## 2. Coordinations of Bi atoms

The crystal structure of BIT1BF is presented in Fig. 2. The perovskite unit of  $[\text{Bi}_3\text{Ti}_3\text{FeO}_{13}]^{2-}$  consists of four oxygen octahedra containing Ti/Fe atoms, which is interleaved with  $[\text{Bi}_2\text{O}_2]^{2+}$  layers. Table 3 presents the interatomic distances of metal-oxygen calculated from the refined positional parameters. The distributions of Bi-O distances indicate that all Bi environments appear to be highly asymmetric since each  $\text{Bi}^{3+}$  ion has a lone pair of electrons. The Bi atoms of the  $\text{Bi}_2\text{O}_2$  layers have apparently a tetragonal pyramidal



**Fig. 1.** Neutron(upper) and X-ray (lower) diffraction profiles for  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  from the combined neutron and X-ray Rietveld refinement: observed profile (cross) and calculated profile (solid). The difference curve appears at the bottom of the figure. The tick marks below the profile indicate the positions of the Bragg reflections.



**Fig. 2.** The crystal structures of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  viewed down the  $[100]$ (left) and  $[110]$ (right).

**Table 3.** The Interatomic Distances (Å) of Metal-Oxygen

[Bi <sub>2</sub> O <sub>2</sub> ] <sup>2-</sup> layer	Bi(2)-O(2)	2.176(10)	2.279(9)	2.303(10)	2.492(10)
	Bi(2)-O(4)	2.561(8)	2.621(10)	3.230(10)	3.291(8)
	Bi(2)-O(7)	3.350(9)			
	Bi(1)-O(1)	2.333(13)	2.384(15)	3.128(14)	3.207(12)
[B <sub>13</sub> Ti <sub>3</sub> FeO <sub>13</sub> ] <sup>2-</sup> perovskite layer	Bi(1)-O(5)	2×2.495(10)	2×2.571(11)		
	Bi(1)-O(6)	2×2.522(8)	2×3.311(9)		
	Bi(3)-O(3)	2.352(10)	2.432(11)	3.140(11)	3.213(10)
	Bi(3)-O(5)	3.262(9)	3.334(8)		
	Bi(3)-O(6)	2.600(9)	3.382(9)		
	Bi(3)-O(7)	2.279(9)	2.950(9)		
	Bi(3)-O(8)	2.335(11)	2.479(11)		
	Ti/Fe(1)-O(1)	2.058(7)			
	Ti/Fe(1)-O(3)	1.939(10)			
	Ti/Fe(1)-O(5)	1.870(17)	2.073(20)		
	Ti/Fe(1)-O(6)	1.895(21)	2.045(16)		
	Ti/Fe(2)-O(3)	2.436(11)			
Ti/Fe(2)-O(4)	1.734(9)				
Ti/Fe(2)-O(7)	1.955(18)	2.037(16)			
Ti/Fe(2)-O(8)	1.963(16)	2.013(17)			

Numbers in parentheses are esd's in the last significant digit.

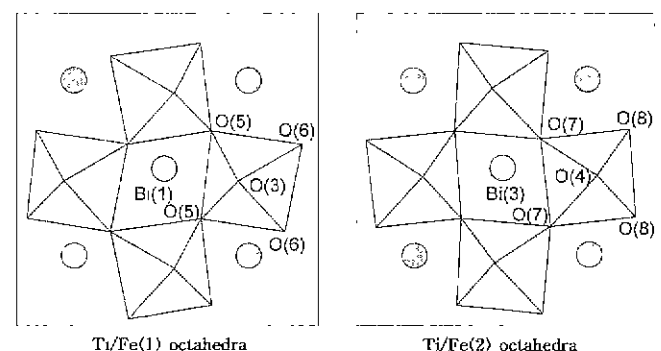
coordination showing a typical presence of lone-paired electrons of Bi<sup>3+</sup> rather than 12-coordination observed in the perovskite unit. However, in these layers, a Bi atom make the distances of 2.18 Å-2.49 Å with four oxygens of O(2), while the distances to the nearest oxygen atoms O(4), which are the apex oxygens of the perovskite unit, are 2.56 Å-3.29 Å. The two oxygens of O(4) are close enough to be the nearest neighbors of the Bi atom. The other two oxygens of O(4) are located to be at the distances 3.23 Å and 3.29 Å. The distribution of the Bi-O(4) distances is very anisotropic, which is associated with the rotation of the octahedra about the a-axis. Furthermore, the Bi atom is at the distance of 3.35 Å with one of O(7) oxygen atoms. A wide spread in the atomic distances of Bi-O indicates the presence of a lone pair of electrons. Within the Bi<sub>2</sub>O<sub>2</sub> layers, the Bi atom shows a rather regular bond distances of Bi-O forming a pyramidal coordination with the four oxygens of O(2). However, the Bi atom of the Bi<sub>2</sub>O<sub>2</sub> layer can be described nine-fold coordinated including all the oxygen atoms within the distance of 3.5 Å. In addition, the Bi<sub>2</sub>O<sub>2</sub> layers keep a certain distance, 1.02 Å, to the top of the perovskite unit by the presence of O(4), which is a bridging oxygen connected to Bi(2) of the Bi<sub>2</sub>O<sub>2</sub> layer and Ti/Fe(2) of the perovskite unit. The distance between the Bi(2) and the O(4) atoms along the c-axis almost exactly corresponds to the Bi<sup>3+</sup>-lone pair distance of 0.98 Å.<sup>10)</sup>

On the other hand, Bi atoms in the perovskite unit are approximately 12-coordinated to neighboring oxygens of octahedra. The Bi-O distances are in the range of 2.33 Å-3.31 Å for Bi(1) and 2.28 Å-3.35 Å for Bi(3). The parent structure of the space group Fmmm is very close to be tetragonal, in which octahedra containing Ti and Fe ions would not tilt. As a result, the Bi atoms are regularly coordinated with 12 oxygen atoms. However, with the space group A2<sub>1</sub>am, the octahedra of the transition metal atoms become

rotated along the a- and c-axes, resulting in highly anisotropic distributions of the Bi-O distances for either Bi(1) or Bi(3). The coordinations of Bi(1) and Bi(3) can be better assumed seven-fold, if the Bi-O distances are limited within 3 Å. In general, it has been suggested that the Bi atoms of the perovskite unit may not show a steric effect like the Bi atoms of the Bi<sub>2</sub>O<sub>2</sub> layer, since the Bi atoms are in high coordination<sup>9)</sup>. As shown in Fig. 2 and Fig. 3, the Bi atoms of BIT1BF are asymmetrically displaced off the assumed center of the 12-coordinated polyhedra. It can be considered that the presence of the lone paired electrons affects the displacement of the Bi atoms even in the perovskite unit.

## 2. Ti/Fe-environments

From the metal-oxygen distances in Table 3, the Ti/Fe(1)-O distances are 0.20 Å in the difference between the minimum and maximum distances in the horizontal plane of the oxygen octahedra, while the corresponding difference between Ti/Fe(2)-O distances is 0.08 Å. This implies that the oxygens surrounding Ti/Fe(1) are more displaced than the



**Fig. 3.** The rotations of the Ti/Fe octahedra about the c-axis in Bi<sub>5</sub>Ti<sub>3</sub>FeO<sub>15</sub>. The +a direction is down and the +b direction is right.

ones for Ti/Fe(2). In addition, the distances between Ti/Fe atoms and apical oxygens such as O(1), O(3), and O(4) indicate that the Ti/Fe atoms are displaced along the c-axis. The component of the displacement along the c-axis is 0.13 Å for the Ti/Fe(1), while it is 0.42 Å for the Ti/Fe(2). The Ti/Fe(2) atoms in the outer oxygen octahedra of the perovskite unit appear to be substantially displaced along the c-axis. However, unlike the perovskite compounds, this displacement along the c-direction will not contribute to the spontaneous polarization, since their polarization vectors are opposite in direction due to the mirror plane at  $z=0$ .

### 3. Rotations of Ti/Fe octahedra

In the structure of BIT1BF, Ti/Fe octahedra of the perovskite unit are rotated about the a-axis as well as the c-axis, which are presented in Fig. 2 and Fig. 3, respectively. The rotations of the Ti/Fe octahedra about the a-axis occur alternately in direction, which can be described as the Bbam mode assuming that the parent structure is based on Fmmm. When viewed down the a-axis, the inner octahedra rotate counterclockwise, while the outer octahedra rotate clockwise. The average rotation angles are  $-9.80^\circ$  and  $+7.42^\circ$  for the inner octahedra and the outer octahedra, respectively. As a related phase,  $\text{Bi}_3\text{Ti}_2\text{NbO}_9$ <sup>11)</sup>, the similar behaviors of the atoms are observed to follow the Bbam mode, in which the octahedra rotate about the polar a-axis with alternating signs for the rotation as  $z$  increases. In addition, as shown in Fig. 2 and 3, the rotation of the Ti/Fe octahedra about the a-axis appears to be associated with an asymmetric displacement of the nearest neighboring Bi atom. About the c-axis, the inner Ti/Fe(1) octahedra surrounding Bi(1) atoms rotate counterclockwise, while the outer Ti/Fe(2) octahedra close to Bi(3) atoms rotate in opposite way. These rotations with respect to the c-axis can be described in the Amam mode.<sup>6)</sup> The degree of the rotation angle is  $-7.77^\circ$  for the inner octahedra, while  $+5.87^\circ$  for the Ti/Fe(2) octahedra. In the structure of BIT1BF, the octahedral rotations become higher in the inner perovskite unit, about either the a- or c-axis. In the outer octahedra, the Ti/Fe atom is much displaced toward the apical oxygen O(4). This indicates that the rotations of the outer octahedra are rather constrained by bonding between O(4) of the apical oxygen and Bi(2) of the  $\text{Bi}_2\text{O}_2$  layer, which Newnham *et al.*<sup>12)</sup> noted for resulting in octahedral tilt or atomic shifts.

### 4. Disorder of transition metal atoms

Our neutron refinement shows that transition metal sites appear to be vacant. When Ti and Fe atoms are disordered, the scattering length of Ti/Fe in the atomic ratio of 3 : 1 would be virtually close to zero. Thus the disappearance of the transition metal atoms implies the disordering of Ti and Fe atoms at their sites. The average value of Ti/Fe-O distance is 1.98 Å for the Ti/Fe(1) octahedra, while that of the Ti/Fe(2) octahedra is 2.02 Å. The small difference between the Ti/Fe(1) and Ti/Fe(2) octahedra could reflect some degree of difference in deformation, which are related to the

rotations of the octahedra. The  $\text{Bi}_3\text{Ti}_3\text{FeO}_{15}$  has four Ti/Fe octahedral layers in the perovskite unit, which forms a long chain of the octahedra sandwiched between the  $\text{Bi}_2\text{O}_2$  layers. Therefore, the inner Ti/Fe(1) octahedra are a little more compressed in the perovskite unit, compared to the outer Ti/Fe(2) ones. This is consistently associated with the greater rotations of the inner octahedra.

### 6. Bond valences

Using the bond valence parameters<sup>13)</sup> and the interatomic distances given in Table 3, the calculated bond valence sums of Bi atoms in the perovskite unit are 2.76 for the inner layer and 2.69 for the outer layer. Similarly, the Bi atoms of the  $\text{Bi}_2\text{O}_2$  layer have the valence of 2.68. All of the Bi atoms are underbonded showing almost the same degree of deviation from the formal valence 3+ of the Bi cation. On the other hand, the Ti/Fe atoms of the octahedra appear to be saturated. The bond valence sums of Ti/Fe are 3.79 and 3.76 for the inner and outer octahedra, respectively. These values are very close to the formal valence of 3.75 for  $\text{Ti}_3^{4+}\text{Fe}^{2+}$ . Withers *et al.*<sup>6)</sup> suggested that in the parent structure of Fmmm, Bi atoms in the perovskite unit are strongly underbonded, while the transition metal atoms are strongly overbonded for the Aurivillius phases. Such deviations from the formal valence in metal atoms tend to be reduced by the various modes of orthorhombic structural distortions: in particular, the displacements of the constituent atoms along the a-direction can remedy the underbonding of the Bi atoms in the perovskite unit, while the octahedral rotation about the a-axis can reduce the overbonding of the metal atoms of octahedra.

For the parent structure of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  (BIT), the calculated bond valence sum of Bi atom has been known to be 2.35<sup>6)</sup> for the perovskite unit. When compared to this value, the valence of the Bi atoms in the perovskite unit of BIT1BF shows a significant improvement from the underbonding of the Bi atoms. For BIT1BF, the little higher bond valence sum of the Bi atom in the inner layer may indicate the slightly more distorted environment of the Bi atom, compared to that of the outer layer. Furthermore, the Bi atoms in the  $\text{Bi}_2\text{O}_2$  layers are in a low coordination, which can be typically ascribed to an asymmetric bonding environment due to lone-paired electrons. These Bi atoms also show a slightly incomplete underbonding in their valence sums.

In BIT1BF, the underbonding of the Bi atoms either in the perovskite unit or the  $\text{Bi}_2\text{O}_2$  layer appears to be not fully corrected by displacive modes of the constituent atoms responsible for spontaneous polarization only. This may indicate that in the structure of BIT1BF, the distortion of the Bi-coordination seems to be optimized for an additional structural distortion such as magnetolectric coupling, which needs a further study. In contrast, the saturation of the bond valence sums for the Ti/Fe atoms indicates that the rotations of the octahedra fully complete the orthorhombic distortion. Any further rotation of the octahedra might result in the underbonding for the metal atoms in the octahedra, which could destabilize the structure.

### 7. Spontaneous polarization

With the space group of  $A2_1am$ , the mirror plane perpendicular to the  $c$ -axis may not allow a component of the spontaneous polarization along the  $c$ -axis. The permissible direction of the polarization would be along the  $a$ -axis. For the Aurivillius phases, Newnham *et al.*<sup>14)</sup> suggested that octahedral cations such as W, Ti, or Nb are displaced about 0.4 Å toward an octahedral edge, resulting in spontaneous polarization. For BIT1BF, the displacements of the atoms along the  $a$ -axis can be described with the modulation of the  $F2mm$  mode. In this description, the relative displacement between Bi atoms and adjacent octahedra are mainly responsible for spontaneous polarization. Spontaneous polarization observed along the  $a$ -direction can be largely attributed to the gross underbonding of  $Bi^{3-}$  in the perovskite unit and to a lesser extent in the  $Bi_2O_2$  layer originated from the parent structure. The atom displacement of the  $F2mm$  mode may correct these underbonding.

For BIT1BF, the Bi and Ti atoms are virtually stationary in the perovskite unit when viewed along the  $c$ -axis. The shifts of the all the constituent atoms along the  $a$ -axis relative to the [001] chain of the Bi atoms are shifted in the same direction. On average, the octahedral chain containing the transition metal atoms is displaced about 0.24 Å along the  $a$ -axis with respect to the Bi atoms, which contributes a substantial amount in the total spontaneous polarization. Based on the point charge model given in  $P_s = \sum_i (\Delta x_i q_i) / V$ , where  $P_s$  is spontaneous polarization,  $\Delta x_i$  is the displacement of the  $i$ th ion along the  $a$  axis,  $q_i$  is the ionic charge of the  $i$ th ion, and  $V$  is the volume of the unit cell. The calculated spontaneous polarization of  $Bi_5Ti_3FeO_{15}$  is 17.3  $\mu C/cm^2$ . This value is approximately the half of that of  $Bi_4Ti_3O_{12}$ , 36.3  $\mu C/cm^2$ , which has the octahedral atomic displacement of 0.41 Å along the  $a$ -axis. The contribution of each unit to the total spontaneous polarization is listed in Table 4. The Bi and O atoms of the  $Bi_2O_2$  layer are the minor components in the spontaneous polarization.

## IV. Conclusions

Our combined neutron and X-ray diffraction study can reveal the correct room temperature structure for  $Bi_5Ti_3FeO_{15}$ , which belongs to the space group of  $A2_1am$ . Ti and Fe atoms are disordered, which can not be located in the neu-

tron refinement only. In the refined structure of BIT1BF, the rotation of the inner octahedra about the  $a$ - or  $c$ -axis is higher than that of the outer ones. Particularly, the rotation of the octahedra along the  $c$ -axis appears to be related to the asymmetric environment of Bi atoms. The Bi atoms are relatively displaced off the center of both the perovskite and the  $Bi_2O_2$  layers. Such coordination environments of the Bi atoms indicate the effect of the lone-paired electrons. In bond valences, the transition metal atoms are fully saturated, while the Bi atoms are rather underbonded. The atomic shifts of the perovskite unit along the  $a$ -axis are responsible for the spontaneous polarization of BIT1BF, which appear to be associated with the underbonding of  $Bi^{3-}$  resulted from the parent structure.

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**Table 4.** The Atomic Shifts along the  $a$ -direction Relative to Virtually Stationary [001] Chains of the Bi Atoms in the Perovskite Unit and the Components of the Ferroelectric Spontaneous Polarization for  $Bi_5Ti_3FeO_{15}$

Components	Direction	Shift (Å)	Polarization ( $\mu C/cm^2$ )	
In the $[Ba_2O_2]^{2+}$ layer	Bi	-	0.089	-2.8
	O	+	0.053	-1.1
In the perovskite	Ti/Fe	+	0.245	19.2
	O	+	0.240	-32.6
Total				-17.3

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