# Preparation and magnetic properties of Bi<sub>m+1</sub>Fe<sub>m-3</sub>Ti<sub>3</sub>O<sub>3m+3</sub> thin films with magnetic order above room temperature

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Thin films of  $Bi_{m+1}Fe_{m-3}Ti_3O_{3m+3}$  (BFTO) with  $m \le 9$  have been successfully grown on (100) SrTiO<sub>3</sub> by chemical solution deposition. These films had the *c* axis normal to the film plane. The conversion electron Mössbauer spectoroscopy (CEMS) showed that the spectra of BFTO thin films exhibit an asymmetric quadrupole doublet for m=8 at 300 K, indicative of being paramagnetic, while, for m=9, clearly show six hyperfine lines indicating presence of magnetic order at 300 K. From the intensity ratio of asymmetric peaks, the polarization axis of BFTO films with  $m \ge 8$  was deduced to be likely along <101> of the perovskite-like unit. On the other hand, it was found from the spectral fitting that the BFTO thin film with m=9 has the Néel temperature around 310 K and the spin axis making an angle of about  $60^\circ$  to the *c*-axis. These indicate that the BFTO (m=9) thin film is a promising candidate for room-temperature multiferroics.

**Keywords**: Multiferroics, Ferroelectric antiferromagnet, Aurivillius family, Bi oxides, Chemical solution deposition, Epitaxy, Mössbauer spectoroscopy

## 1. Introduction

Multiferroic materials exhibiting simultaneously ferromagnetism and ferroelectricity have attracted much interest because of their potential for a large magnetoelectric effect due to order-coupling. One of the Aurivillius family of bismuth oxides,  $Bi_{m+1}Fe_m$ .  ${}_{3}Ti_{3}O_{3m+3}$  (BFTO) is a promising candidate. This oxide is characterized by a layered crystal structure in which a  $(Bi_{2}O_{2})^{2+}$  layer and *m* layers with a perovskite-like unit are periodically stacked [1, 2]. The unit cell has orthorhombic distortion (the ratio of lattice constant  $b/a \sim 1.002$ ). The well-known ferroelectric  $Bi_{4}Ti_{3}O_{12}$  with Curie temperature  $(T_{C})$  as high as 675 °C [3] is an end member of this compound. The typical ferroelectric

antiferromagnet BiFeO<sub>3</sub> (BFO) with  $T_{\rm C} \sim 1103$  K and Néel temperature ( $T_{\rm N}$ ) ~ 643 k [4,

5]) can be regarded as a limiting case of layered perovskite-like structures with  $m = \infty$ 

though the structure is not layered. As intermediates between them,  $BiFe_{1-x}Ti_xO_{3+\delta}$  (*x*  $\leq 0.2$ ) with chemical compositions close to BFO was also investigated [6-8]. However, the prepared oxides were not with layered structure characteristic of the Aurivillius family but with a simple perovskite structure as same as that of BFO.

Thus, the Aurivillius family oxide BFTO is unique as a multiferroic and of considerable interest: The perovskite-like packets allows ion replacement and thereby has flexibility in adjusting the order parameters as compared to BFO. In addition, the layered structure of BFTO is also interesting from the viewpoint of magnetoelectric effect of a natural magnetic superlattice. Sultanov et al. showed that exchange interaction between Fe atoms in BFTO occurs only within the confines of a single perovskite-like packet sandwiched between diamagnetic  $(Bi_2O_2)^{2+}$  layers [9, 10]. Magnetic anisotropy of Fe in

such a packet with a small volume should be susceptible to energetic change of spinorbit interaction via dielectric ion displacement as well as to thermal energy. Therefore, if BFTO has the magnetic order above room temperature, it is expected to show a magnetoelectric response of great interest.

It has been reported that the BFTO compounds exhibit ferroelectric Curie temperatures as high as nearly 650 K and antiferromagnetic order below room temperature for  $m \le 8$ 

[2, 9, 10]. The increase of *m* is expected to elevate the Néel temperature because Fe ions randomly occupying the octahedral sites of the perovskite-like layers increase and the magnetic long-range order is enhanced. However, BFTO synthesized so far was up to m=8 and, in addition, likely included other phases for  $m \ge 5$  because of volatility of Bi and/or structural instability increased with increasing *m* [1]. Thus, preparation of pure BFTO with larger *m* is requisite for achieving magnetic order above room temperature. To overcome this issue, we tried to epitaxially grow the thin films of BFTO with larger *m* using the chemical solution deposition (CSD). The epitaxy facilitates the film growth of BFTO phase on a substrate surface with a similar ionic arrangement because the lattice matching lowers interface energy between BFTO and the substrate. This leads to inhibiting the production of other phases. In addition, the CSD cause no compositional deviation.

In this paper, we describe the thin film growth of BFTO with  $m \ge 8$  and discuss the structural and magnetic properties of them.

# 2. Experimental

The nitrates of Bi and Fe and a water-soluble Ti complex compound  $((NH_4)_4[Ti_2 (C_6H_4O_7)_2(O_2)_2] \cdot 4H_2O)$  were used as sources for the precursor solution. These were dissolved into the mixture of 2-methoxyethanol and nitric acid at the metal ion concentration of 0.68 mol /l. The thin films were prepared on (100) SrTiO<sub>3</sub> (STO) single crystal substrates by repeating the following process 5 times; spin-coating of the precursor solutions, drying at 200 °C, decomposition at 400 °C and rapid thermal annealing for 10 min at 900 °C. The structural and magnetic properties of the obtained thin films were evaluated by X-ray diffraction (XRD), reflection high energy electron diffraction (RHEED), vibrating sample magnetometer (VSM) and the conversion electron Mössbauer spectoroscopy (CEMS). The CEMS spectra were measured in the temperature range of 80 K to 300 K. To obtain clear CEMS spectra, a sample of BFTO (m=9) was prepared with Fe all replaced by the isotope <sup>57</sup>Fe. Another merit of using the CSD for fabrication is the easy preparation of these samples.

## 3. Results and discussion

#### 3.1 Epitaxial growth of BFTO thin films

Figure 1 shows the XRD  $\theta$ -2 $\theta$  scans of the films with *m* of 4 to 11. Only the peaks assigned to (002l) reflections of BFTO are clearly observed for all *m*. The position and linewidth of the (002l) (*l*=*m*+1, 2*m*+2) reflections are nearly independent of *m*. This is because they are fundamental reflections originated from the periodicity in units of *m*+1 layer and the lattice constant of *c*-axis increases roughly in proportion to the layer number *m*+1 of crystal unit. On the other hand, the (002l) satellite peaks around the fundamental reflections shift to higher angle for l < m+1 or 2m+2 and to lower angle for l > m+1 or 2m+2, along with broadening. The increased broadness is presumably

associated with structural disorder of each perovskite-like layer due to defects of oxygen and/or Bi ions.

Figure 2 shows typical RHEED images of a BFTO (m=5) thin film taken along (a) <100> and (b) <110> azimuths of STO substrate. The wider spacing between the streak lines observed in (b) than (a) means that the film has in-plane epitaxial relationship of film <100> or <010> // STO <110>. This epitaxy is inferred from that the in-plane lattice matching between STO <110> and BFTO <100> or <010> is roughly within 0.5 % (e.g. for m=5, the unit cell parameters: a=0.5490 nm, b=0.5500 nm, c=5.0185 nm) [2]. These suggest that the BFTO film with m=5 was epitaxially grown along the *c*-axis on (100) STO. While, we could not observe clear RHEED images of streak lines evidencing epitaxy for the BFTO film of m=9. This is likely due to the increased broadness of XRD peaks.

In order to examine whether the BFTO crystals with a large *m* were grown, the practical *m* values of thin films were estimated from the observed ratio  $d_{002m+2}/d_{002m}$  using the relationship of  $c = 2md_{002m} = 2(m+1) d_{002m+2}$ , where *c* denotes the lattice constant of *c*-axis,  $d_{002m}$  and  $d_{002m+2}$  the spacing of (002m) and (002m+2) planes, respectively. Figure 2 shows the results. The *m* values of the thin films equal to the nominal values within experimental error up to *m*=9, while become much smaller than them for  $m \ge 10$ . This

indicates a limit for the number of stacking layers of crystalline BFTO film grown under thermal equilibrium. The lattice constants of *c*-axis obtained assuming in-plane stress-free were 7.32 nm for m=8 and 8.14 nm for m=9.

#### **3.2 Magnetic properties**

Magnetization measurements for the BFTO film of m=8 and 9 showed that the films exhibit small magnetization proportional to applied magnetic field at room temperature,

being paramagnetic or antiferromagnetic. However, presence of magnetic order in the films could not be confirmed from the temperature dependences of magnetic susceptibility within experimental errors because of smallness of the induced magnetization.

Figure 3 shows the CEMS spectra measured for the BFTO ((a) m=8, (b) m = 9) films. The BFTO (m=8) thin film exhibits a quadrupole doublet, indicative of being paramagnetic at 300 K. The doublet is asymmetric, having a quadrupole splitting (QS) of 0.55 mm/s. From the intensity ratio of two peaks, the angle between the principal axis of electric field gradient at the iron nuclei and the incident direction of  $\gamma$ -ray (parallel to the *c*-axis of film) was determined to be 51°. This value nearly equals the

angle 53° of [101] axis to the *c*-axis of a perovskite-like unit which was roughly calculated using the above lattice constant. This indicates that the polarization axis of BFTO films with  $m \ge 8$  is possibly along <101> of the perovskite-like unit. It is consistent with the fact that the polarization axis of BFO is <111> of pseudocubic structure which corresponds to <101> of the perovskite-like unit in BFTO.

On the other hand, the BFTO (m=9) thin film clearly shows six hyperfine lines indicative of presence of magnetic order at 300 K. With increasing temperature from 80 K, the hyperfine lines broaden and the quadrupole doublet appears at 300 K. These reflect a random distribution of the Ti and Fe ions and the resultant dispersion of magnetic-order range. The spectral parameters obtained from the curve fitting are summarized in Table 1. The isomer shift (IS) is 0.37 mm/s at 300 K, slightly smaller than the typical value of Fe<sup>3+</sup> reported for the magnetic oxide Y<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> [11]. Temperature that the internal magnetic field disappears was determined to be 310 K from Brillouin function fitted to the temperature dependence of average internal magnetic field. Taking into account that the prepared BFTO films show non-ferromagnetic magnetization curves at room temperature and the previously reported BFTO and BFO ( $m=\infty$ ) were antiferromagnetic, we speculated that this is Néel temperature. This speculation is also supported from the fact that this temperature is consistent with that extrapolated from the relationship between m and the Néel temperatures reported for BFTO with m less than 6 [12].

Since the thin film is *c*-axis-oriented, the spin order direction to the incident direction of  $\gamma$ -ray can be identified from the intensity ratio of six hyperfine lines. The ratio obtained by the curve fitting for the spectrum at 80 K is 3:2.4:1:1:2.4:3, from which the spin order axis was found to make an angle of about 30° normal to the *a-b* plane (about 60°

to the incident direction of  $\gamma$ -ray). However, in order to discuss the relationship between this value and the antiferromagnetic plane parallel to the pseudocubic (111) plane in BFO, the spin direction needs to be determined accurately by CEMS measurement for a film with another growth plane (e.g. (100)). This will be a subject in future.

#### 4. Conclusion

We have successfully grown the (001) thin films of BFTO with  $m \le 9$  on (100) STO by the CSD. The CEMS spectra of the BFTO thin films exhibited an asymmetric quadrupole doublet for m=8 at 300 K, indicative of being paramagnetic, while, for m=9, clearly showed six hyperfine lines indicating presence of magnetic order at 300 K. From the intensity ratio of asymmetric peaks, the polarization axis of BFTO films with  $m \ge 8$  was deduced to be possibly along <101> of the perovskite-like unit. On the other hand, it was found from the spectral fitting that the BFTO thin film with m=9 has the Néel temperature around 310 K and the spin axis making an angle of about 60° to the *c* axis. These indicate that the BFTO (m=9) thin film is a promising candidate for roomtemperature multiferroics.

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#### **Figure Captions**

Fig. 1. XRD  $\theta$ -2 $\theta$  scans of the films with *m* of 4 to 11.

**Fig. 2.** RHEED images of a BFTO (*m*=5) thin film taken along (a) <100> and (b) <110> azimuths of STO substrate.

**Fig. 3.** Measured *m* values of thin films estimated from the observed ratio  $d_{002m+2}/d_{002m}$  using the relationship of  $c = 2md_{002m} = 2(m+1)d_{002m+2}$ , where *c* denotes the lattice constant of *c* axis,  $d_{002m}$  and  $d_{002(m+1)}$  the spacing of (002m) and (002m+2) planes, respectively. The solid line shows a reference when the films have the same *m* as the nominal ones. **Fig. 4.** CEMS spectra measured for the BFTO ((a) m=8, (b) m = 9) thin films.

# Table 1

Parameters obtained from the curve fitting for the CEMS spectra of BFTO (m=9) thin film, where IS denotes the isomer shift, QS the quadrupole splitting and HF average means the average internal magnetic field.

Temp.	IS (mm/s)	QS (mm/s)	HF average (T)
300 K	0.37	- 0.03	23.2
260 K	0.42	- 0.03	30.4
220 K	0.44	- 0.05	35.9
150 K	0.47	- 0.07	43.1
80 K	0.50	- 0.07	47.9

Fig. 1.



Fig. 2.



Fig. 3.



Fig.4.

