Giant polarization properties of Ba-based bismuth layer-structured ferroelectrics with superlattice-structure

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ABSTRACT

Bismuth layer-structured ferroelectric single crystals with the superlattice structure composed of $Bi_4Ti_3O_{12}$ and $BaBi_4Ti_4O_{15}$ (BiT-BBTi) were grown by a self-flux method. Dielectric measurements showed that Curie temperature (T_C) of the BiT-BBTi crystals was 540°C, which was 40°C higher than that of the BiT-BBTi ceramics with the stoichiometric composition. Polarization measurements using single crystals demonstrated that the P_s along the *a* axis of the BiT-BBTi crystals is over 52 $\mu C/cm^2$, which was larger than those of the constituent BiT and BBTi crystals. The giant P_s for the BiT-BBTi crystals is suggested to originate from the ferroelectric displacements of the Bi of the Bi_2O_2 layers as well as in the Bi substitution for Ba induced by compositional deviation from the stoichiometry.

Key words: bismuth layer structured ferroelectrics, single crystals, remanent polarization, spontaneous polarization

1. INTRODUCTION

Bismuth layer-structured ferroelectrics (BLSFs) have attracted much attention because of their applications to nonvolatile memories with high durability to polarization degradation and lead-free piezoelectric devices.[1-3] Since the layered structure of BLSFs plays an important role in the dielectric and ferroelectric properties, the relation of the crystal structure and materials properties has been widely investigated for the past several decades.[4] In the crystal structure, perovskite blocks ($A_{m-1}B_mO_{3m+1}$) are sandwiched with Bi_2O_2 layers, and the perovskite blocks are composed of *m* layers of BO_6 octahedra with *A*-site cations. The Bi_2O_2 layers play a role not only in the polarization properties but also in the high durability of ferroelectric capacitor.[1, 5] Furthermore, spontaneous polarization (P_s) and insulating properties markedly depend on *m* of the perovskite blocks.[6] Bismuth titanate $Bi_4Ti_3O_{12}$ (BiT; *m*=3) has a large P_s of about 50 $\mu C/cm^2$,[7] but suffer from poor insulating properties.[8] Noguchi *et al.* have shown that the suppression of oxygen vacancies by doping of higher-valent cations (V^{5+} and W^{6+} than Ti^{4+}) is effective for reducing leakage current of BiT ceramics.[8,9] In contrast, $BaBi_4Ti_4O_{15}$ (BBTi; *m*=4) has shown sufficiently high insulating property. However, the P_s of BBTi is as small as 15 $\mu C/cm^2$.[10]

Recently, superlattice-structured BLSFs, discovered by Kikuchi *et al.* [11, 12], have received a renewed interest as a promising candidate for ferroelectric materials with a relatively large remanent polarization (P_r).[13] For a superlattice-structured BiT-SBTi, two kinds of perovskite blocks of BiT(*m*=3) and $SrBi_4Ti_4O_{15}$(SBTi:*m*=4) are in turn sandwiched between Bi_2O_2 layers. A lattice mismatch between the two perovskite blocks and their different chemical character induce the large lattice distortion in the Bi_2O_2 layers, leading to a quite distinct type of the ferroelectric displacement of the Bi in the Bi_2O_2 layers along the *a* axis. [13] This Bi displacement is suggested to contribute partly to a larger P_r observed for the BiT-SBTi ceramics than the constituent BiT and SBTi. [13] Shibuya *et al.* [14] have established a large P_r for the thin films of the BiT-SBTi. While most investigations on the superlattice-structured BLSFs to data have been performed on bulk ceramics, their dielectric and ferroelectric tensor are not understood, mainly because of the lack of the single crystals[15, 16].

In this study, the single crystals of superlattice-structured BiT-BBTi(*m*=3-4) were grown and the crystal structure, dielectric and ferroelectric properties were compared with those of BiT-BBTi ceramics. The measurements of the single crystals have demonstrated that the superlattice-structured BiT-BBTi exhibited a P_s of 52 $\mu C/cm^2$, which was larger that that of BiT and BBTi.

2. EXPERIMENTS

BiT-BBTi ceramics were prepared by a conventional solid-state reaction. The crystal structure of the powders was investigated by X-ray diffraction (XRD) and time-of-flight neutron diffraction measured using the Vega diffractometer at KENS.[17] Structural parameters were refined using the program RIETAN-TN.[18]

The single crystals of BiT-BBTi were grown by a self-flux method. After heat treatment at 950°C for 24 h in air, these crystals were annealed under high-pressure oxygen at 35 MPa at 750°C for 12 h to reduce oxygen vacancies in the crystals. The domain structure of a BiT-BBTi crystal is shown in Fig. 1. The fine domain structure composed of 90° domain walls was observed, and the width of 90° domain was lower than 2 μm. This value was much smaller than that of BiT single crystals (approximately 8 μm).[19] The composition of the BiT-BBTi crystals determined by inductively coupled plasma spectroscopy (ICP) was $Ba_{0.75}Bi_{8.32}Ti_7O_{27}$, which was a Ba-deficient and Bi-excess composition as compared to the ideal one ($BaBi_8Ti_7O_{27}$).

3. RESULTS AND DISCUSSION

Figure 2 shows the powder XRD data of BiT, BBTi and BiT-BBTi. The XRD patterns in the 2θ region of 5-15° are depicted in Fig. 2 (b) including the theoretical peak positions of the BiT-BBTi. The distinctive peaks associated with their layered structure with the different lattice parameter c appeared, and each pattern has its own typical peaks for m=3, m=4, and m=3-4 structures. The peak position observed for the BiT-BBTi powder was in good agreement with the theoretical one. Furthermore, the Rietveld analysis of the XRD data of the BiT-BBTi based on $P2_1am$ orthorhombic symmetry gave a sufficient fitting. [13]

Figure 3 shows the transmission electron microscope (TEM) image of a BiT-BBTi single crystal in the $a(b)$-c plane. The alternative superlattice stacking of m=3 and m=4 layer like m=3-4-3-4- was clearly found.

Figure 4(a) indicates the temperature dependence of dielectric permittivity of BiT, BBTi, and BiT-BBTi ceramics at a frequency of 1 MHz. It is interesting to note that the dielectric permittivity at 25°C of the BiT-BBTi ceramics was approximately 425, which was larger than those of BiT (71) and BBTi (247) ceramics. From the permittivity peaks, the Curie temperature (T_C) of BiT and BBTi ceramics were estimated to be 675°C and 410°C, respectively, and these T_C values agreed well with the previous reports [7,9,10,20]. The T_C of the BiT-BBTi
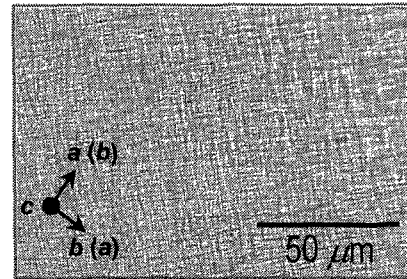

Fig.1. Domain structure of a BiT-BBTi single crystal in the a-b plane.
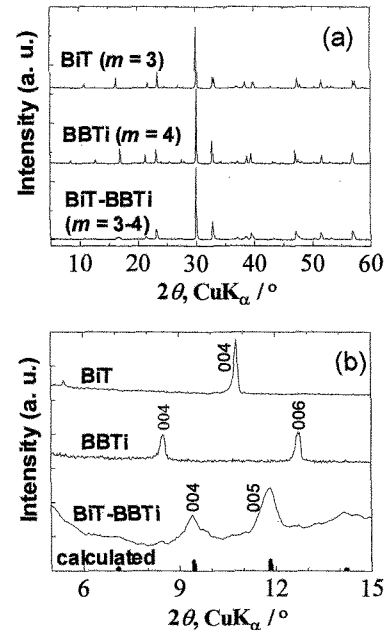

Fig. 2. XRD patterns of BiT, BBTi and BiT-BBTi powder. Figure (b) is the expansion of the low 2θ part.
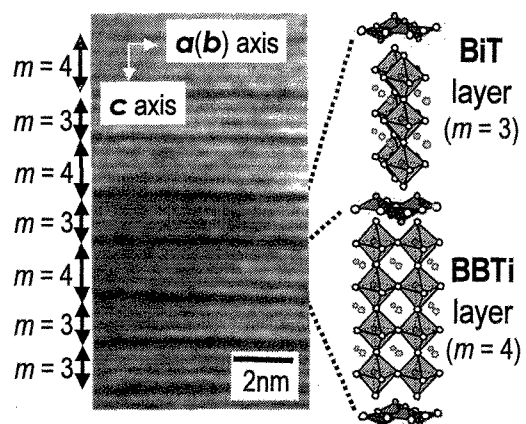

Fig. 3. Transmission electron microscope image of a BiT-BBTi single crystal in the $a(b)$-c plane.

ceramics was 500°C and lay between those of the BiT and BBTi ceramics. For superlattice-structured BLSFs with m=1-2 or 2-3, they have two T_C's originating from their components of two kinds of perovskite blocks, and are suggested to undergo two phase transitions.[12, 21] However, both the ceramics and the single crystals of BiT-BBTi underwent only one phase transition above room temperature in spite of having two kinds of constituent layers (BiT and BBTi). This result indicates that two kinds of perovskite blocks in the BiT-BBTi are transformed simultaneously at the transition temperature, due to the strong ferroelectric interaction between them, as observed for BiT-SBTi polycrystals.[13] Figure 4(b) shows the temperature dependence of dielectric permittivity of the BiT-BBTi crystals, and the data of the ceramics are redrawn for comparison. The dielectric permittivity at 25°C was 1000 along the a axis and 195 along the c axis. These values were relatively larger compared with the other BLSFs crystals.[10, 16, 22] The dielectric permittivity along the a axis was about 5 times as high as that along the c axis. The T_C of the BiT-BBTi crystals (540°C) was 40°C higher than that of the BiT-BBTi ceramics (500°C). The higher T_C observed for the crystals is attributed to a compositional deviation from the stoichiometry during crystal growth.[23] The Ba-deficient and Bi-excess composition of the crystals analyzed by ICP indicates that the excess Bi is substituted for Ba at the perovskite A site and that the crystals have a lager amount of Bi at the A site than the ceramics. The substitution of Bi for Ba has been observed also for BBTi ceramics, and led to a 25°C higher T_C than the stoichiometric BBTi ceramics.[23]

Figure 5(a) shows the ferroelectric hysteresis loops of BiT, BBTi and BiT-BBTi ceramics. The BiT-BBTi ceramics exhibited a remanent polarization (P_r) of 12 μC/cm^2 and coercive field (E_c) of 22 kV/cm. The P_r of BiT-BBTi ceramics was larger than those of BiT (7 μC/cm^2) and BBTi (8 μC/cm^2). The ferroelectric hysteretic loops of the crystals are shown in Fig. 5(b). The spontaneous polarization (P_s) of the BiT-BBTi crystals was estimated at 52 μC/cm^2. This value was much larger than that of BBTi crystals (16 μC/cm^2) and also larger than that of BiT (46 μC/cm^2) that is known as having the largest P_s of BLSFs.

The lattice parameters refined by the Rietveld analysis of neutron powder diffraction are as follows: a=0.544 668(4), b=0.540 865(4), c=3.283 48(4) for BiT, a=0.546 981(5), b=0.545 657(5), c=4.186 49(4) for BBTi, and a=0.545 56(3), b=0.543 251(3), c=3.740 0(6) for BiT-BBTi. The parameters a and b of the BBTi are much larger than those of the BiT, because the Ba ions with
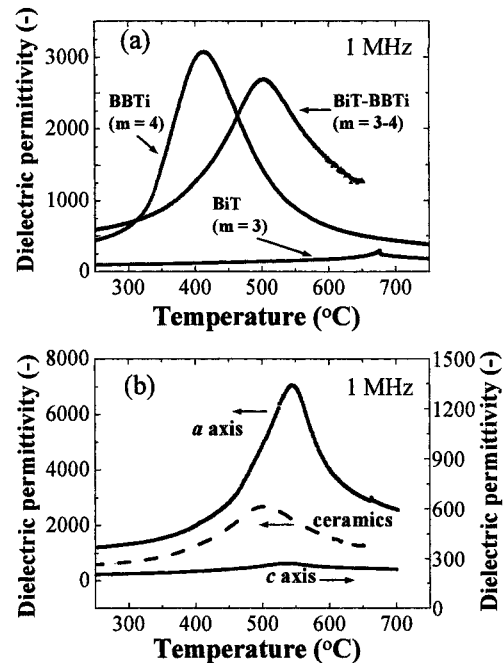

Fig.4. Temperature dependence of dielectric permittivity of (a) BiT, BBTi and BiT-BBTi ceramics and (b) BiT-BBTi ceramics and single crystals.
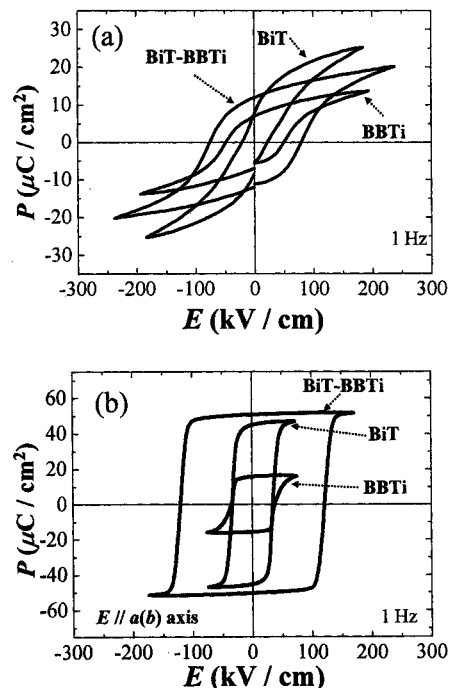

Fig. 5. Polarization hysteresis loops of (a) BiT, BBTi and BiT-BBTi ceramics and (b) single crystals (25°C).

large ionic radius are present in the BBTi. The lattice mismatch between the BiT and BBTi is estimated at 0.42% along the a axis and 0.88% along the b axis. The lattice parameters a and b of the BiT-BBTi are the average of those of the BiT and BBTi. Thus, the lattice

mismatch, *i.e.*, the lattice distortion caused by the alternate stacking of BiT ($m=3$) and BBTi ($m=4$) layers, plays an important role in the ferroelectric distortion of the BiT-BBTi ($m=3$-4). The structural analysis indicates that tensile and compressive stresses built up in the $m=3$ and the $m=4$ layers of the superlattice structure, respectively. These stresses are suggested to concentrate in the Bi_2O_2 layers that interleave two kinds of perovskite blocks. This crystallographic environment induces a local symmetry breaking of the Bi_2O_2 layers. Two Bi ions of the Bi_2O_2 layers in BiT and BBTi *etc.* are identical from the crystallographic point of view, while the Bi ions of the Bi_2O_2 layers in the BiT-BBTi are regarded as crystallographically different cations; one is connected to the perovskite blocks of the $m=3$ layer, and the other is adjacent to that of the $m=4$ layer. The symmetry breaking results in a peculiar ferroelectric displacement of the Bi ions of the Bi_2O_2 layers in the BiT-BBTi. Noguchi *et al.* have reported that the Bi ions of the Bi_2O_2 layers in BiT-SBTi are displaced along the *a* axis (the polar direction) by 2 % of the parameter *a* from the corresponding positions of the high-temperature tetragonal structure.[13] The similar displacements of the Bi ions are expected to the BiT-BBTi ceramics and single crystals, and enhance P_s and also P_r.

4. SUMMARY

The single crystals of BiT, BBTi and their superlattice-structured BiT-BBTi were grown, and the structural, dielectric and polarization properties were compared. The Rietveld analysis of powder X-ray and neutron diffractions and transmission electron microscope observations confirmed the superlattice structure of the BiT-BBTi. The T_C of BiT-BBTi crystals was 540°C, which was 40°C higher than that of the stoichiometric BiT-BBTi ceramics. The P_s of the BiT-BBTi crystals was found to be over 52 $\mu C/cm^2$ along the *a* axis, which was larger than those of BiT (46 $\mu C/cm^2$), BBTi (16 $\mu C/cm^2$) crystals and the BiT-BBTi ceramics (12 $\mu C/cm^2$). It is suggested that the local symmetry breaking of the Bi_2O_2 layers (ferroelectric displacements of Bi) as well as the Bi substitution for Ba induced by compositional deviation are responsible for the larger P_s observed for the BiT-BBTi crystals.

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