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Growth of Bismuth layer-structured ferroelectrics $BaBi_4Ti_4O_{15}$ single crystals and their piezoelectric properties

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Barium bismuth titanate (BBT) single crystal is one of bismuth layer structured ferroelectrics (BLSFs). In this study, BBT single crystals were successfully grown by the slow cooling method. The size of BBT single crystal was about 1x1x3-4mm^3. At first, crystallographic direction was investigated using a pole figure measurement system, and c-axis was determined. As a result, it was found that the crystals grown in this study had a pillar shape with thick thickness along the c-axis direction. The piezoelectric k_t vibrator was prepared by cutting and polishing, and Au electrodes were sputtered on the surface of this vibrator. This vibrator was poled at 200°C under a high electric field of 2-4kV/mm. Their piezoelectric property was measured using a conventional resonance-antiresonance method.

Key words: barium bismuth titanate, single crystal, bismuth layer structured ferroelectrics, slow cooling method, poling treatment

1. INTRODUCTION

In the future, the spread spectrum communication will be the main current in mobile communication. Therefore, it is necessary to invent high frequency broadband piezoelectric filter. For this purpose, the piezoelectric materials with the higher electromechanical coupling coefficient (k) and the higher mechanical quality factor (Qm) are required. At present, PZT ceramics with high piezoelectric performance was used as filters and resonators, but because of environment problem, piezoelectric materials without lead will be desirable.

Then, bismuth layer structured ferroelectrics (BLSFs) materials are one of the candidates of non-lead piezoelectric materials. Since BLSFs were firstly discovered by Aurivillius[1], their characterization and properties have been reported by many researches.[2-6] BLSFs are known to have a crystal structure in which bismuth oxides layers are interleaved with pseudo-perovskite blocks along the crystallographic c-axis. Bismuth oxides layers don't contribute to the ferroelectrics. On the other hand, pseudo-perovskite blocks contribute to the ferroelectrics. $(Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-}$ is the general formula of BLSFs. A is a mono-, di-, or tri-valent cation, B is a tetra-, penta-, hexa-valent small cation and m is the number of octahedral in pseudo-perovskite blocks. [7]

However, there is a problem. Because of strong crystal anisotropy, the electromecanical coupling coefficients determining a bandwidth of piezoelectric filter is not enough in ceramics without preferred orientation. The piezoelectric filter can be fabricated by using single crystals indicating enough electromecanical coupling coefficient.

Barium bismuth titanate (BBT) is one of a family of BLSFs materials with even m number, and there is no spontaneous polarization along the c-axis, i.e., strong anisotropy. Moreover, its melting point is 1150°C, and is the lower value for BLSFs with even m number. Therefore, this lower melting point is very effective for the growth of BBT single crystal.

In this paper, BBT was chosen on the viewpoint of the above reason, and BBT single crystals were grown by the slow cooling method. Moreover, their piezoelectric properties were investigated.

2. EXPERIMENT

The starting materials for BBT single crystal growth were $BaCO_3$, TiO_2 and Bi_2O_3. They were weighted at Ba:Bi:Ti ratio of 1:4:4 and mixed. The mixtures were close-packed into a double crucible. It was necessary to prevent from volatilizing Bi_2O_3 components. The single crystal growth was performed by the slow cooling method. The mixtures were heated up to 1250°C at a heating rate of 300°C/h and kept at this temperature for 4 hours. Next the temperature was decreased to 950°C at the cooling rate of 4°C/h. Finally, the temperature was cooled to room temperature naturally.

The structure of the BBT single crystals was confirmed by the XRD method. The domain wall structure was observed by using a polarizing microscope. The compositional analysis of the single crystals was performed by using wavelength dispersive X-ray spectroscopy (WDS). The X-ray pole figure measurements for the miller index (109) was carried out. To prepare samples for investigating electric property and piezoelectric property, the obtained single crystal was cut, polished, and Au electrodes were sputtered. However, when the sample along the a-b in-plane direction was prepared, the sample was cleaved. This is because that layers are piled in the c-axis direction. The cleave was prevented by covering the sample with crystal wax and using the modified abrasive holder. The temperature dependence of dielectric constant of BBT single crystal was measured up to 550°C at the frequency of 1 MHz by using an impedance analyzer (Hewlett Packard Ltd., HP4192A). The P-E hysterisis loop of BBT single crystal was measured by using a ferroelectric tester (Radiant Technologies., RT66A). The sample was poled by applied electric field of 2-4 kV/mm at 200°C. Then, piezoelectric property was investigated by a conventional resonance-antiresonance method with an impedance analyzer (Hewlett Packard Ltd., HP4294A). Finally, in order to enlarge BBT single crystal, some conditions of crystal growth were changed.

3. RESULT & DISCUSSION

3.1 Identification of single crystals

The grown crystals had a plate-like shape and they were almost translucent as shown in Fig. 1. The maximum size of these single crystals was about 2x1x0.5mm^3. Figure 2 shows the X-ray diffraction pattern of the grown single crystal. This single crystal was assigned to BBT single phase by using an XRD identification software (Rigaku, Jade ver. 5.0) as shown in Fig. 2. The miller indexes were also defined. Table 1 shows the result of compositional analysis of the BBT single crystal, which is normalized using the Bi mol ratio of 4.00. The molar ratio of Bi with Ti was almost the same as a stoichiometric composition of BBT crystal while Ba was rich by 0.48 as compared to a stoichiometric composition of BBT crystal. At present, we cannot explain about this deviation, but this deviation may be to explained on the basis of the correction of calibration curve or cleaning of the crystal. Figure 3 shows the result of the domain observation of one BBT single crystal by using a polarizing microscope. When the sample was rotated by 45°, the existence of domain wall was observed between diagonal position and extinction position. The miller index (109) indicated the most intense peak in the X-ray diffraction pattern of the BBT as shown Fig. 1. The X-ray pole figure measurement was carried out using this peak. Figure 4 shows the result of the X-ray pole figure for the miller index (109), when X-ray is perpendicularly incident to the crystal surface. BBT exhibited orthorhombic phase in the crystallography. However, the lengths of the a-axis and the b-axis were almost equal. Therefore, BBT could be regarded as pseudo-tetragonal phase. In Fig.4, 4 X-ray diffraction spots of 109, -109, 10-9, and -10-9 were appeared. From this result, the crystal surface of BBT single crystal was defined as the C-face.

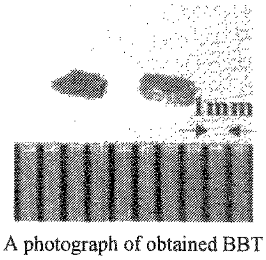


Figure 1 A photograph of obtained BBT single crystal

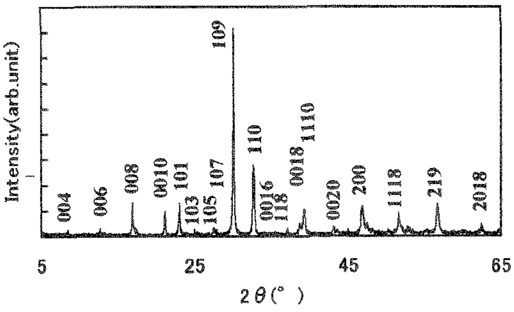
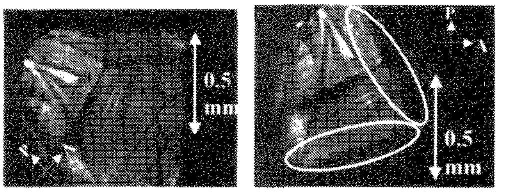


Figure 2 The XRD pattern of BBT single crystal.

Table 1 The result of compositional analysis of the BBT single crystal which is normalized using the Bi mol ratio of 4.00.

element	mol ratio
Ba	1.48
Bi	4.00
Ti	4.01



(a) the standard position. (b) the position rotated by 45°

Figure 3 The result of the domain observation of BBT single crystal

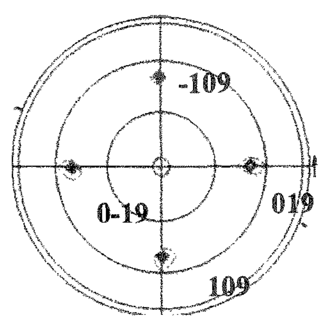


Figure 4 The result of the X-ray pole figure for the miller index (109), when X-ray perpendicularly is incident to the crystal surface.

3.2 Electrical properties

Figure 5 shows the temperature dependence of dielectric constant along the a-b in-plane direction and the c-axis direction. The dielectric constant along the a-b in-plane direction and the c-axis direction at room temperature was 655 and 138, respectively. Although the Curie temperature of BBT crystal was reported as 395°C[8], in this case, the Curie temperature of BBT crystals along the a-b in-plane direction and the c-axis direction was 410°C and 393°C, respectively. This means that there was

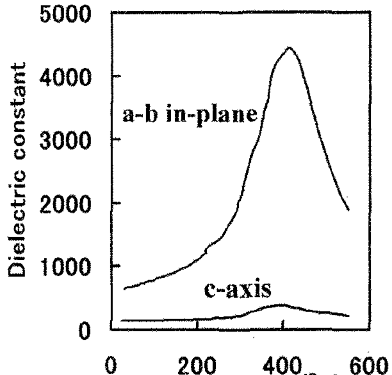


Figure 5 The temperature dependence of dielectric constant along the a-b in plane direction and the c-axis direction.

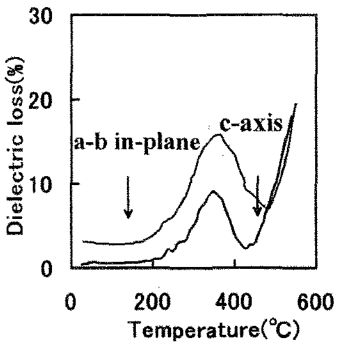


Figure 6 The temperature dependence of dielectric loss along a-b in plane direction and the c-axis direction.

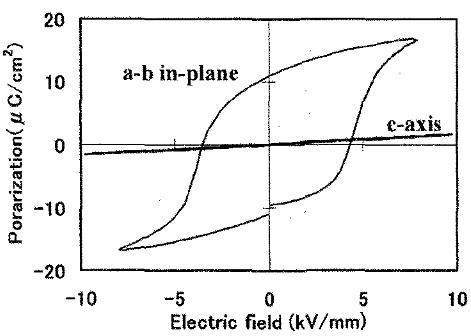


Figure 7 The P-E hysterisis loop of BBT single crystal measured along a-b in plane direction and the c-axis direction.

a compositional fluctuation between the as-grown crystals.

Figure 6 shows the temperature dependence of dielectric loss along the a-b in-plane direction and the c-axis direction. The dielectric loss of the sample along the a-b in-plane direction was less than 4% at room temperature. Hence, it suggested that even if the DC voltage was applied to the sample for poling, leakage current did not flow too much.

Figure 7 shows the P-E hysterisis loop of BBT single crystal along the a-b in-plane direction and the c-axis direction. The remnant polarization Pr and coercive field Ec was 11μC/cm^2 and 4.41kV/mm, respectively. The ferroelectricity of BBT single crystal was confirmed along the a-b in-plane direction. On the other hand, no remnant polarization was revealed along the c-axis direction. These results means that BLSFs which have even numbers of BO_6 octahedra indicates no remnant polarization along the c-axis direction.[9]

3.3 Piezoelectric property

The result of the measurement for the P-E hysterisis loop of BBT single crystal along the a-b in-plane direction revealed that BBT was a hard material. For obtaining full-poled sample, it was necessary to apply high DC bias field at high temperature. Therefore, the poling conditions were determined as follows; temperature of 200-230°C, DC bias field of 2-4 kV/mm. Figure 8 shows the frequency dependence of |Z| and θ of BBT single crystal poled along the a-b in-plane direction. The phase angle (θ) was limited to around 1.73° , because the poling treatment wasn't enough. If the ideal poling state is obtained for BBT single crystal with high Qm, the phase angle (θ) approaches to 90° in the frequency range between resonance frequency (fs) and antiresonance frequency (fp). This means that DC bias field of 2-4 kV/mm wasn't enough to reach the full poling state. When DC bias field above 4 kV/mm was applied for a sample, electrical breakdown occurred. However, from frequency dependence of |Z| and θ of BBT single crystal as shown in Fig.8, the resonance frequency fs and antiresonance frequency fp was 2.06 MHz and 2.10 MHz, respectively. Therefore, calculated electromecanical coupling coefficient kt (thickness mode) of BBT single crystal was 21%, by means of a conventional resonance-antiresonance method. This is higher than reported electromecanical coupling coefficient k_{33} of 18.5%[10] for BBT based ceramics with additives. The difficulty to obtain full-poled sample were caused by (1) complicated domain structures of BLSFs and (2) high Curie temperature. If the ideal poling condition is established, it is possible to improve the electromecanical coupling coefficient.

Moreover, in this case, the size of the grown BBT single crystal was about 2x1x0.5mm^3. Therefore, obtained piezoelectric vibrator for kt mode was below 1x0.5x0.2mm^3. It was so small that handling sample and holding sample for the measurement of frequency dependence of |Z| and θ were very difficult. Thus, for the precise impedance measurement, BBT crystals with mach larger sizes are required.

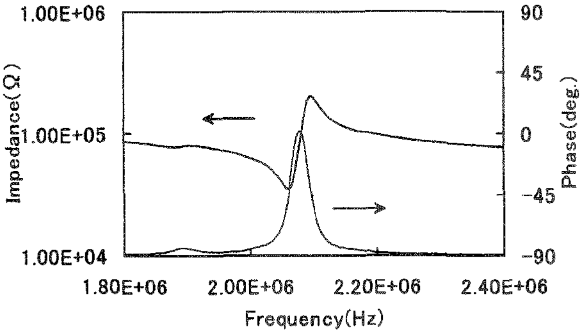


Figure 8 Frequency dependence of |Z| and θ of BBT single crystal poled along a-b in plane direction and the c-axis direction.

3.4 The growth of large BBT single crystals

The growth of larger BBT single crystal was attempted for preparation of the large piezoelectric vibrator for kt mode. The mixtures of the starting materials were fully loaded in a big crucible, and close-packed into double crucible. The single crystal growth was performed by the slow cooling method. The mixtures were heated up to 1250°C at a rate of 300°C/h and kept at this temperature for 4 hours. Next, the temperature was decreased to 950°C at the rate of 2°C/h. Finally, the temperature was cooled to room temperature naturally. The above method differed from the previous mentioned method on the viewpoint of the cooling rate. The grown crystals had a pillar shape and they were translucent as shown in Fig. 9. The grown

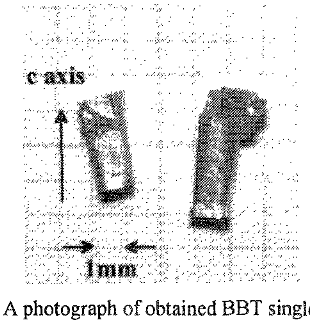


Figure 9 A photograph of obtained BBT single crystal

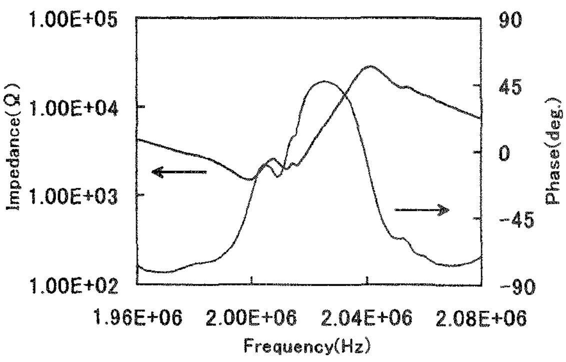


Figure 10 Frequency dependence of |Z| and θ of enlarged BBT single crystal poled along a-b in plane direction and the c-axis direction.

crystals were not a plate-like shape which was thin along the c-axis direction, but a pillar shape which was thick along the c-axis direction. Although only the examples of thin BLSFs crystals along the c axis direction have reported[11-12], the thick BLSFs crystals along the c-axis direction were successfully grown in this study. The size of enlarged BBT single crystal was about 1x1x3-4 mm^3. By using these crystals, the larger piezoelectric vibrator was fabricated. Figure 10 shows frequency dependence of |Z| and θ of enlarged BBT single crystal poled along the a(b) axis direction. The phase angle (θ) was limited to around 47.4° and there were some spurious peaks. Although the poling condition was not optimum, electromecanical coupling coefficients kt became to 23%. This value of 23% was larger than 21% when the small sized crystal was used. This enlargement may be originated from easy handling sample and easy holding sample for the measurement. Therefore, if the poling condition is optimized using this large crystal, it is possible to obtaion much larger electromecanical coupling coefficients kt. Much harder work will be required for this purpose.

4. SUMARRY

By the slow cooling method, the BBT single crystals were successfully grown. Changing some conditions of crystal growth, enlarged BBT single crystal along the c-axis direction were successfully grown so that the sample could be handled and measured easily. Dielectric properties and ferroelectric properties were characterized. Piezoelectric properties were investigated. Piezoelectric vibrators were fabricated by using small BBT single crystals and frequency dependence of |Z| and θ of BBT single crystal was observed. Although the poling condition was not optimum, electromecanical coupling coefficients kt was 23%.

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