

Growth of Bismuth Tungstate Bi_2WO_6 Mono-Domain Crystals and Chemical Etching for Measuring Their Electrical Properties

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Bismuth tungstate, Bi_2WO_6 (BWO), mono-domain crystals were grown by a slow cooling method using $\text{L}_2\text{B}_4\text{O}_7$ as a flux below the Curie temperature of 940°C . The growth conditions, which produced the maximum thickness, were investigated by a solidification technique based on the changing volumes of the starting material solution. We obtained plate-like crystals with sizes up to 1.0 mm thick. The relationship between the crystallographic abc and rectangular XYZ axes in the BWO crystals was clarified using etch pit observations and static piezoelectric measurements. According to the relationship, when the $+Z$ axis was chosen such that the piezoelectric constant d_{33} is positive, it was found that both d_{31} and d_{32} are negative. The dielectric constant, ϵ_{ij}/ϵ_0 , of the BWO crystal was 70-100 at room temperature.

Key words: mono-domain, bismuth tungstate, flux growth, crystallographic axis, etching

1. INTRODUCTION

Recently, piezoelectric actuator materials for high temperature use are definitely required for gas injectors or combustion sensors directly placed in the cylinder part of engines. The lead zirconate titanate, $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT), ceramic is a well-known piezoelectric material. However, the PZT ceramics cannot be used in high temperature actuators, because their piezoelectricity disappears around 200°C due to their Curie temperature ($T_c \sim 400^\circ\text{C}$). Under this condition, we have focused on the bismuth layered-structure ferroelectric (BLSF) compounds with high T_c values. The general chemical formula of the BLSF compounds is represented as $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$: $m=1-5$ [1], which consists of pseudo-perovskite $(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$ layers interleaved with $(\text{Bi}_2\text{O}_2)^{2+}$ layers along the crystallographic c -axis. The titled compound, bismuth tungstate, Bi_2WO_6 (BWO), is one of the BLSF compounds having a high $T_c = 940^\circ\text{C}$ [2]. Recent progress in environmental safeguards requires environmentally friendly, that is, lead-free materials whose electric properties are comparable to those of the lead-containing ones. Therefore, BWO is expected to be a lead-free material for use in piezoelectric devices suitable for high temperatures as long as its piezoelectric properties are retained.

Generally, a poling treatment is necessary to provide the ferroelectric ceramics and crystals with piezoelectric properties. This process is difficult for ferroelectric materials with a high T_c . To the best of the author's knowledge, there is no report about the piezoelectric properties of the BWO ceramics. We have attempted to measure the piezoelectric properties using crack- and strain-free BWO mono-domain crystals. Such crystals can be obtained by synthesis below the T_c . The BWO crystals grown below their T_c using the flux method are composed of mono-domain crystals, and show a piezoelectricity without the poling treatment. Up to now,

various fluxes have been reported by researchers including us [3-6]. The thin crystals normal to the c -axis are always obtained by the flux growth. Among the all fluxes reported, we believe that $\text{L}_2\text{B}_4\text{O}_7$ (LBO) found by us [6] is a good flux material. Compared to NaVO_3 producing large BWO crystals [5], LBO has the following advantages for bulk single crystal growth: (1) low evaporation of the raw materials during the growth process, and (2) little contamination of the flux material. In ref.[6], the maximum thickness of the BWO single crystals was 0.7 mm. Since this size is still insufficient to investigate the electric properties, determining the growth condition which produces a higher thickness is required.

In this study, we describe the influence of the starting material volumes on thickness of the BWO crystals grown using the BWO-LBO solution by the slow cooling method. We demonstrate the relationship between the morphology of the crystal and the crystallographic abc - rectangular XYZ axes. This information provides very useful information to determine the orientation of the sample, which requires the cutting of the crystals during the sample preparation for the electric measurements. On the basis of the relationship, we characterized the dielectric and piezoelectric properties of the BWO mono-domain crystals.

2. EXPERIMENTAL PROCEDURE

Powders of 99.99% pure Bi_2O_3 and WO_3 were used as the starting materials in a stoichiometric composition. The powders were mixed in acetone, dried, and then calcined at 800°C for 5 h in air. LBO was chosen as the flux. Based on the phase diagram of the BWO-LBO binary system [6], the powder mixture with BWO (70 mol%)-LBO (30 mol%) was selected as the starting solution. The powder mixtures were heated to 1000°C and kept at this temperature for 5 h. The temperature

Table 1 The relation between the starting material solution volume and thickness of the BWO crystals

Experiment No.	Starting material solution volume			Charge of starting materials in crucible / %	Average thickness of grown crystals / mm
	Volume / cm^3	Area / cm^2	Depth / cm		
1	7	44	0.16	5	0.5
2	14	44	0.32	10	0.7
3	28	44	0.63	20	0.5
4	70	44	1.58	50	0.4

was then decreased to 940°C at the rate of $10^\circ\text{C}/\text{h}$, then further decreased to 840°C at the rate of $2^\circ\text{C}/\text{h}$. Finally, the melts were allowed to naturally cool to room temperature. The size of the crystals was mainly rate dependent. In this study, the crystal growth was performed using 140 mm^3 platinum crucibles at the cooling rate of $2^\circ\text{C}/\text{h}$. The growth condition, which produced the maximum thickness, was investigated by measuring the thickness of the crystals solidified from various volumes of the starting material solutions. The BWO crystals were separated from the obtained aggregates using concentrated nitric acid. The growth facet of the BWO single crystals was analyzed using the back-scattering Laue X-ray diffraction method. The domain wall structures in the crystals were judged from polarizing microscopic and etch pit observations.

The cut and polished samples were subjected to a chemical etching study. The chemical etching was carried out at 80°C for 0.5-2 h. As an etchant, a 5 N nitric acid (for convenience, expressed as HNO_3 solution) was used. To etch all the faces under identical conditions, the samples were completely immersed in the stirred etching solutions. The etched samples were washed in distilled water and ethanol, and then dried in air. The etch figures of the etched samples were analyzed using a polarized microscope in the reflection mode.

BWO belongs to orthorhombic point group $mm2$. There are three dielectric, five piezoelectric, and ten elastic compliance constants (ϵ_{ij} , d_{ij} , and s_{ij}). The total number of constants to be determined should be 17. According to the *IEEE standard on piezoelectricity* [7], in point group $mm2$, $+Z$ is chosen so that the corresponding piezoelectric constants d_{33} is positive. Although the other axes are trivial, in this study, $+X$ and $+Y$ were set to form a right-handed system. The relationship between the morphology of the crystal and the crystallographic abc – rectangular XYZ axes was clarified by a back-scattering Laue X-ray technique, etch pit observation and the use of static piezoelectric measurement described in detail in ref.[7]. Using the plate form substrate, the dielectric constants of the BWO mono-domain crystals were determined using a YHP 4194A Impedance/Gain Phase Analyzer.

3. RESULTS AND DISCUSSION

Table 1 shows the relation between the starting material solution volume and thickness of the BWO crystals. Since there is a considerable difference in the density between the BWO ($9.50 \text{ g}/\text{cm}^3$) and LBO ($2.44 \text{ g}/\text{cm}^3$), we have assumed that the mixing of these oxides in the melted state was not going well due to gravity.

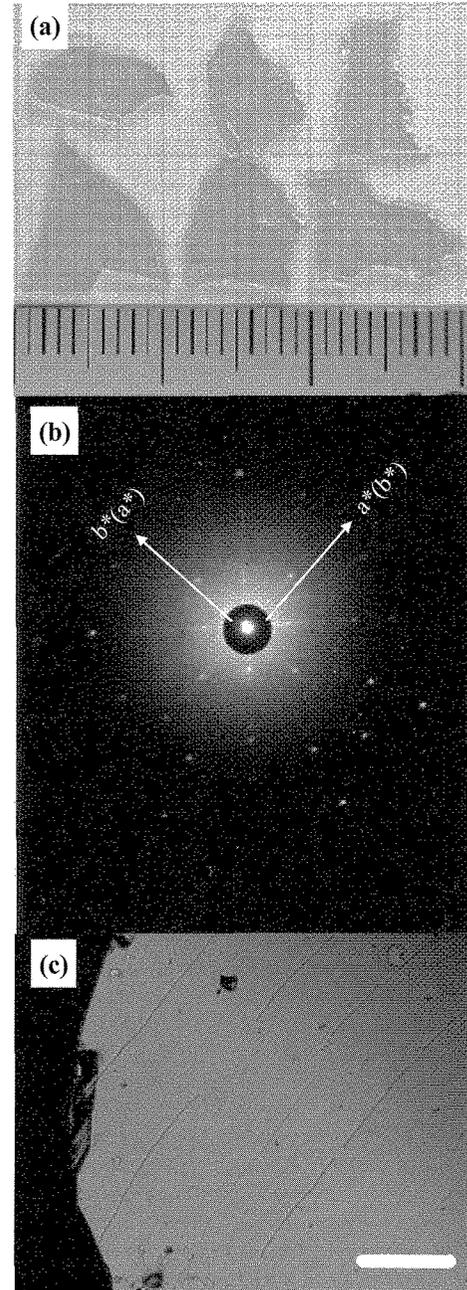


Fig.1 (a) Photograph, (b) back-scattering Laue X-ray diffraction photograph, and (c) (001) surface of as-grown Bi_2WO_6 crystals. Photograph (c) was obtained using a polarized microscope in the transmission mode. The markers represent $300 \mu\text{m}$.

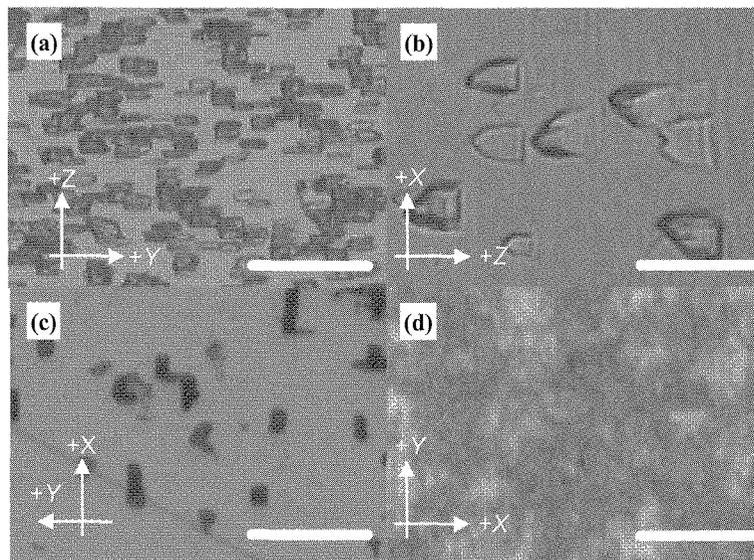


Fig.2 Surface morphology on (a) +X-, (b) +Y-, (c) +Z and (d) -Z-cut surfaces of Bi_2WO_6 mono-domain crystal after immersion in 5 N HNO_3 solution at 80°C for 0.5 h. These photographs were obtained using a polarized microscope in the reflection mode. The markers represent 5 μm .

Hence, we have tested the growth of the BWO crystal using four kinds of melt depths, that is, the solution volume. The maximum mean thickness of 0.7 mm was obtained in experiment No.2. In this experiment, the maximum size of the crystals was $15 \times 10 \times \sim 1.0 \text{ mm}^3$. As seen in Table 1, the mean thickness of the crystals decreased with the increasing solution volume of the starting materials over a 10% charge of the starting materials into the crucible. This proved that our assumption is correct. It was postulated that the melt composition was not uniform and a concentration gradient of BWO existed along the depth of the solution. Transparent and large BWO crystals were always taken from around the melt surface. During the crystallization process, it was suggested that supersaturation was achieved by the evaporation of raw materials as well as supercooling.

Fig.1(a) shows the BWO plate-like crystals obtained from the solidified solution of experimental No.2. The crystals are transparent, light yellow in color, and have smooth surfaces. All peaks in the X-ray diffraction patterns of the crystals were identified to be those of the BWO structure. Fig.1(b) shows the back-scattering Laue X-ray diffraction pattern of the reflected radiation incident to the perpendicular of the BWO crystal surface. Since the a - b plane reflection was only obtained, it was determined that the crystal had a well-developed smooth $\{001\}$ surface. Fig.1(c) shows a typical $\{001\}$ surface of the BWO crystals under a polarized microscope in the reflection mode. Although growth striations are observed, no domain structure and few inclusions were found inside the grown crystals. Therefore, it was found that all the grown BWO crystals consisted of a mono-domain fabric.

Fig.2 shows the etch patterns of the +X-, +Y-, +Z and -Z-cut surfaces of the BWO mono-domain crystal after immersion in a 5 N HNO_3 solution at 80°C for 0.5 h. The plus or minus signs were determined using the static piezoelectric measurement described in a later section. In this study, we adopted the HNO_3 solution as the

etchant, because we already know that BWO crystals were easily dissolved in other acids such as the hydrochloric and sulfuric acids. The shapes of the pits on the +X-cut surface (Fig.2(a)) are like a round rectangle or parallelogram. The same figures were observed on the -X-cut surface. In Fig.2(b), the etch patterns of the +Y-cut surface are shown. These patterns are the same as those on the -Y-cut surface. The shape of the pits is like a pentagon piece used in a Japanese chess game. The shapes also confirmed that there is a 2-fold rotation axis and mirror plane along the Z axis. Based on these observations, it was found that the HNO_3 solution was a selective etchant for observing dislocations on the X- and Y-cut surfaces. Moreover, these patterns indicated that an anisotropic physical property exists along the Z axis. The etch pit figures observed on the X-

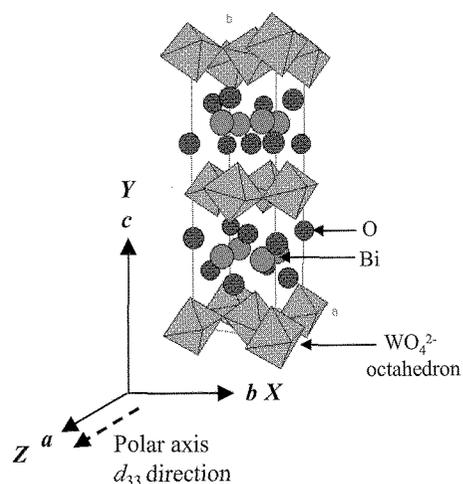


Fig.3 Schematic illustration of the Bi_2WO_6 crystal structure constructed using the data from ref.[2] and correspondence between the crystallographic and rectangular axes.

and Y -cut surfaces are all in the same direction inside the grown crystals. This clearly demonstrated that the grown crystals were mono-domain. The characteristic etch patterns of the $+Z$ - and $-Z$ -cut surfaces of the BWO crystal was observed (Fig. 2(c) and (d)). The etch pits formed on both surfaces had indefinite shapes. The $+Z$ -cut surface was smooth with etch pits, whereas the $-Z$ -cut one was too rough to identify any etch pits. The number of etch pits on the $+Z$ -cut surface was significantly lower than that on other surfaces. This observation showed that the etching rate in the $+Z$ -cut was lower than that on the other surfaces.

Fig.3 shows the correspondence between the crystallographic abc and rectangular XYZ axes when comparing the BWO crystal structure. The BWO has an orthorhombic symmetry (point group: $mm2$, the space group which is $B2cb$ [2] or $P2_1cb$ [8]), and has the cell dimensions of $a=5.456$, $b=5.424$ and $c=16.449$ Å [6]. In this structure, the a axis is not only the polar axis, but also the piezoelectric constant d_{33} direction. According to ref.[7], the Z axis is defined as d_{33} direction. Therefore, it follows that the crystallographic a , b and c axes are the rectangular Z , X and Y ones, respectively (cf. BaTiO_3 , PbTiO_3 , other perovskite-type ferroelectrics [9]).

We have always obtained plate-like BWO single crystals normal to the $c(Y)$ -axis when using the flux method. By using only the back-scattering Laue X-ray technique, the polar $a(Z)$ axis and non-polar $b(X)$ one are virtually indistinguishable because the lengths of the two axes are very similar as shown in Fig.1(b). However, the etch pit shapes on the Y -cut surface clearly show a difference. By using the static piezoelectric measurement, the $+Z$ axis was chosen such that the piezoelectric constant d_{33} is positive. Subsequently, the $+X$ and $+Y$ -axes were determined to form a right-handed system. The geometric relationship between the etch pit shape on the $+Y$ -cut surface and the crystallographic abc - rectangular XYZ axes summarized in Fig.4. This information has made the cutting process during the sample preparation for piezoelectric characterization very convenience.

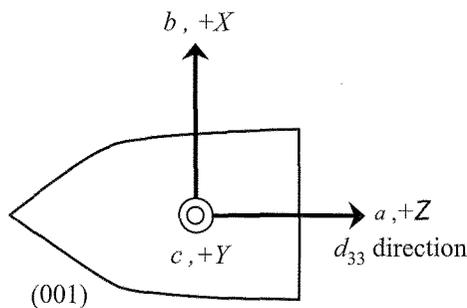


Fig.4 Relationship between the etch pit shape and the crystallographic abc - rectangular XYZ axes. The $+X$, $+Y$ and $+Z$ axes are defined according to ref.[7].

By employing the relationship, we could prepare the specimens for electrical measurements. By using the static piezoelectric measurement, it was found that both d_{31} and d_{32} are negative. The sign of d_{31} is the same as that for the BaTiO_3 and $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ piezoelectric

ceramics [9]. The dielectric constants, ϵ_{ij}/ϵ_0 , of the BWO crystal were about 100, 70, 70 for $ij=11, 22$ and 33 at room temperature, respectively.

4. CONCLUSION

BWO mono-domain crystals were grown by a slow cooling below the T_c . A $15 \times 10 \times \sim 1.0$ mm³ size crystal was obtained. By etch pit observations and static piezoelectric measurements, we attained a relationship between the etch pit shape and the crystallographic-rectangular axes, which provided useful information for the cutting process during the sample preparation for electrical measurements. By using this relationship, all the dielectric constants and the sign of three piezoelectric ones of the BWO crystal were evaluated.

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