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Crystal growth of bismuth tungstate Bi_2WO_6 by slow cooling method using borate fluxes

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Abstract

Ferroelectric Bi_2WO_6 (BWO) single crystals have been grown by a flux method below the phase transition (ferro- to paraelectric) temperature. Sodium chloride, $LiBO_2$, $Li_2B_4O_7$ (LBO), $Na_2B_4O_7$ (NBO) and $Na_2B_4O_7{\cdot}10H_2O$ were selected as the flux. We found that LBO and NBO are suitable flux materials for crystal growth. The phase diagram of the BWO–LBO(NBO) system was investigated by the combination of the differential thermal analysis and the quench method. In the BWO–LBO(NBO) binary system, the mixtures of the end members without intermediate compounds were observed. On the basis of the phase diagram, we have obtained plate-like crystals with sizes up to 0.7 mm thickness from the solidified melts with the mole ratio BWO:LBO of 7:3. The crystals are single domain, yellow in color, and have well developed smooth $\{0\,0\,1\}$ faces. The dielectric constant, $\varepsilon_{33}/\varepsilon_0$, of the crystals is 90 at room temperature and the ferroelectric behavior is available.

Keywords: Crystal growth; Dielectric properties; Ferroelectric properties

1. Introduction

Bismuth tungstate, Bi_2WO_6 (BWO), is one of the bismuth layered-structure ferroelectrics with the general formula $(Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-}$: $m = 1$–5, which consists of pseudo-perovskite $(A_{m-1}B_mO_{3m+1})^{2-}$ layers interleaved with $(Bi_2O_2)^{2+}$ layers along the *c*-axis. BWO single crystals shows a high Curie temperature, $T_c = 940\,°C$, and a high electromechanical coupling coefficient, $k_{33} = 0.4$.[1] Therefore, this compound is expected to be a lead-free material for use in piezoelectric devices suitable under high frequencies and high temperatures if large single crystals can be grown. BWO single crystals were grown by the Czochralski technique[2] because the BWO melts congruently at 1080 °C.[3] However, the crystals crack near the T_c during their cooling process. Therefore, researchers have grown crack- and strain-free BWO single crystals by the slow cooling method with fluxes. Muramatsu et al.,[4] L'eprevier and Payne[5] and Yanovskii and Voronkova[1] succeeded in growing BWO single-domain crystals using Na_2WO_4, $Na_2WO_4 + NaF$ and $NaVO_3$ as the flux materials, respectively. In their reports, the maximum size of 20 mm × 10 mm × 1 mm is reported.[1] Plate-like BWO single crystals normal to the *c*-axis are always obtained by the flux growth. In order to utilize the piezoelectric property for a device, it is necessary to grow crystals with a high thickness.

The aim of this study is to find a novel flux suitable for bulk crystal growth methods such as Bridgemann or top-seeded solution growth techniques. We describe the decision process of a flux by means of the phase diagram, which is determined by differential thermal analysis and the quenching method. Subsequently, growth of the BWO crystal by the selected flux and slow cooling method is reported. Moreover, we have characterized the essential physical properties such as dielectricity and ferroelectricity.

2. Experimental procedure

Powders of 99.99% pure Bi_2O_3 and WO_3 were used as the starting materials with a stoichiometric composition. The powders were mixed in acetone, dried, and then calcined at 800 °C for 2 h in air. The phase identification of the BWO powders was performed using powder X-ray diffraction

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(XRD) method. Sodium chloride, $LiBO_2$, $Li_2B_4O_7$ (LBO), $Na_2B_4O_7$ (NBO) and $Na_2B_4O_7{\cdot}10H_2O$ (borax) were chosen as the flux. For a pre-growth of the BWO crystal, the mixed powders with the mole ratio BWO:flux = 1:1 were charged into platinum crucibles. The powders were heated to 900 °C and kept at this temperature for 10 h. Then the temperature was decreased to 750 °C at the rate of 5 °C/h, and finally the melts were allowed to cool to room temperature naturally. The grown crystals was picked up from the solidified melts, and then the thickness was measured in order to judge which flux materials are suitable for crystal growth.

As mentioned in the next section, we found that LBO and NBO are suitable flux materials for crystal growth. Subsequently, the binary phase diagram of the BWO–LBO(NBO) system was determined using thermogravity-differential thermal analysis (TG-DTA), quenching, and powder X-ray diffraction analysis. The TG-DTA was carried out up to 1100 °C at the heating rate of 10 °C/min in air with Al_2O_3 as the standard sample. For the quenching experiments, nine mixtures with compositions at 10 mol% interval of BWO in each system were prepared. Several small platinum boats (30 mm^3) containing a few milligrams of each mixture were placed in an electric furnace and heated stepwise in increments of several degrees at 15 min interval. After heating, the samples were quickly removed from the furnace and quenched in air. The melting point was visually determined.

On the basis of the determined phase diagrams, BWO single crystals were grown using LBO and NBO as fluxes. The mixture powders were heated up to 1000 °C and kept at this temperature for 5 h. The temperature was then decreased to 940 °C at the rate of 10 °C/h, and further decreased to 840 °C at the rate of 2 °C/h. Finally, the melts were allowed to naturally cool to room temperature. The size of the crystals was mainly dependent on the dimensions of the crucibles and the cooling rate. In this study, crystals of maximum size were obtained using 35 ml platinum crucibles at a cooling rate of 3 °C/h. The BWO crystals were separated from the obtained aggregates using concentrated nitric acid.

The growth facet of the BWO single crystals was analyzed by the back-scattering Laue X-ray diffraction method. The domain wall structure in the crystals was observed using a polarizing microscope. For determination of the electrical properties, the surfaces of the crystals were sputtered with gold as the electrodes. The dielectric constant of the BWO crystals was measured in the frequency range of 100 Hz–15 MHz and at a dc bias of 1 V using an impedance analyzer (Hewlett-Packard Ltd., HP4192A). The remanent polarization and coercive field of crystals were obtained from the *D*–*E* hysteresis loop using a ferroelectric tester (Radiant Technologies Ltd., RT-6000HV).

3. Results and discussion

The results of pre-growth of the BWO crystal using five flux materials are summarized as follows:

(i) A solidified melt of the BWO–$LiBO_2$ mixture was composed of almost the glass phase only.
(ii) In the case of NaCl, BWO did not dissolve in the NaCl melt. The solubility of BWO in NaCl was less than 0.1 mol%.
(iii) Plate-like BWO single crystals with approximately 0.3, 0.2 and 0.2 mm thicknesses were grown from BWO + LBO, BWO + NBO, and BWO + borax mixtures, respectively.

The same results were observed in the growth using the BWO + NBO and BWO + borax mixtures. This was because borax was transformed into NBO by dehydration during the heating process. Based on the above observations, we considered that LBO and NBO were flux materials suitable for crystal growth, and determined the phase diagrams useful for the growth below the T_c.

Fig. 1 shows the DTA curves of the BWO, BWO–LBO, BWO–NBO powders. For the BWO sample, there is one endothermic peak at 1080 °C, which corresponds to the melting point. In the DTA curves of the samples of BWO (90 mol%)–LBO (10 mol%) and BWO (50 mol%)–LBO (50 mol%), one clear endothermic peak at about 825 °C was observed. From the phase identification of these samples after the quenching experiment, it was found that the endothermic peaks were due to the eutectic point of the BWO and LBO mixture. Moreover, in the DTA curves of the samples of BWO (90 mol%)–LBO (10 mol%), we found a very small peak around 940 °C. This peak corresponds to the phase transformation (ferro- to paraelectric: T_c) point of BWO. For the sample of BWO (90 mol%)–NBO (10 mol%), the DTA curves showed three endothermic peaks at 675, 940 and 1000 °C. The endothermic peak at 940 °C originates from T_c of BWO. From the phase identification of the samples after the quenching experiment, it was found that the two endothermic peaks

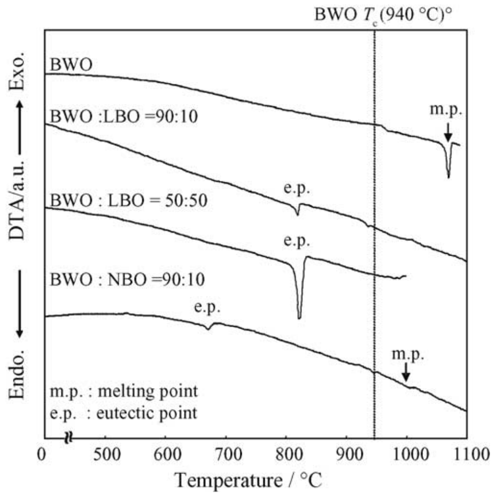

Fig. 1. Differential thermal analysis curves of BWO, BWO–LBO, and BWO–NBO powders. The BWO–borate ratios in the Figure are in mol%. The eutectic and melting temperatures were determined using the quenching technique.

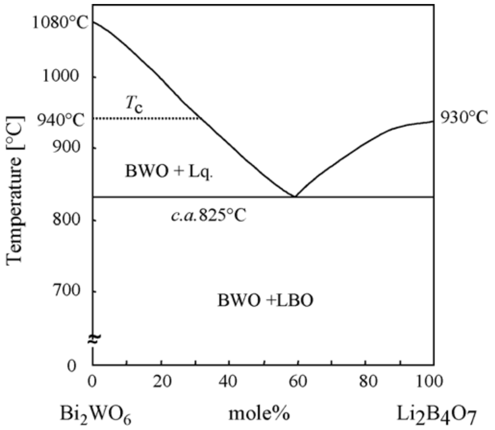

Fig. 2. Phase diagram of the BWO–LBO binary system in air.

at 675 and 1000 °C were due to the eutectic and melting points of the BWO and NBO mixtures, respectively.

Fig. 2 shows the phase diagram of the BWO–LBO system determined by DTA and a quenching experiment. The diagram shows that this system has one eutectic point at approximately 825 °C, and that a liquidus line is in the composition range up to about 60 mol% LBO. The phase diagram of the BWO–NBO system is similar to that of the BWO–LBO system. There is one eutectic point at approximately 675 °C and at about 70 mol% NBO in the diagram. The temperature width (275 °C) of the liquidus line containing the BWO solid phase under $T_c = 940$ °C in the BWO–NBO system is greater than that in the BWO–LBO system. Therefore, it was expected that thick BWO single crystals were grown from the BWO + NBO solution.

Referring to the determined phase diagrams, we attempted to grow BWO single crystals using LBO and NBO as fluxes. Fig. 3 shows the dependence of the thickness of the grown BWO crystals on the starting material compositions as a function of the BWO content in the LBO and NBO fluxes. The mean thickness of the crystals grown from both the BWO + LBO and BWO + NBO solutions increased with the increasing BWO content up to 70 mol% BWO. Over 80 mol% BWO, only aggregate consisting of multi-domain crystals was obtained. These results indicated that the crystal growth started above the T_c over 80 mol% BWO. This proved that the determined phase diagrams are reliable. The maximum thickness of 0.5 mm was obtained for BWO (70 mol%)–LBO (30 mol%). The BWO crystals grown from the solution using LBO were thicker than those using NBO. This result was unexpected. We tried to decant the solution at 840 °C (the growth end). In this procedure, we could pour out the BWO + LBO solution but not the BWO + NBO one. This result indicates that the viscosity of the BWO + NBO solution was higher than the BWO + LBO one. Due to the relatively high viscosity, it would be hard for the BWO solute to move in the solution. From these observations, we regarded that LBO is a good flux material. Compared with $NaVO_3$ producing large BWO crystals,[1] we found that 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. Therefore, we expect that LBO is the superior flux material. We will attempt to grow larger crystals using LBO by the Bridgemann technique.

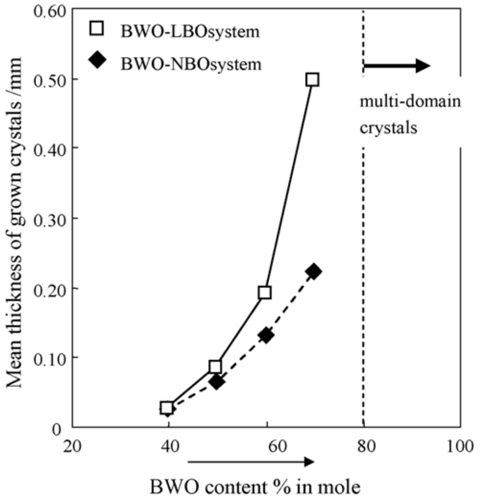

Fig. 3. Thickness of the grown crystals as a function of BWO content in LBO and NBO fluxes.

Fig. 4(a) shows BWO plate-like crystals picked up from the solidified melt with BWO (70 mol%)–LBO (30 mol%). The crystals are transparent, yellowish in color, and have

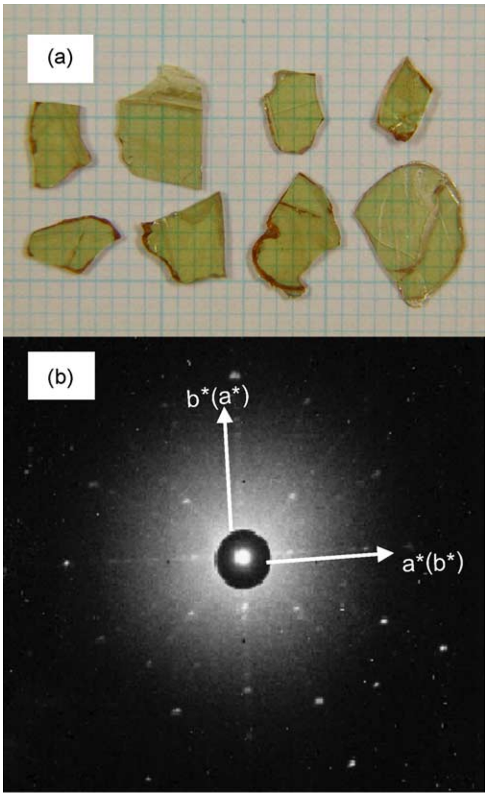

Fig. 4. Photograph (a) and back-scattering Laue X-ray diffraction photograph (b) of Bi_2WO_6 single crystals.

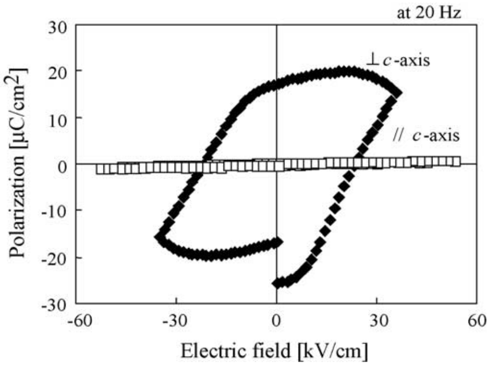

Fig. 5. *P–E* hysteresis loops measured at 160 °C for BWO single crystals.

smooth surfaces. The maximum size of the crystals was 10 mm × 10 mm × ~0.7 mm. Fig. 4(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, the crystal surface was defined as the ⟨0 0 1⟩ plane. Using this single crystal, the cell dimensions were determined to be $a = 5.456(1)$, $b = 5.424(1)$ and $c = 16.449(4)$ Å and the Laue group is *mmm*. However, it was very difficult to determine the space group which is *B*2*cb*[6] or *Pca*2_1.[7] The *h k l* reflections observed in the single crystal X-ray diffraction did not match either structure models. This phenomenon is now under consideration.

The dielectric constants, $\varepsilon_{33}/\varepsilon_0$ and $\varepsilon_{\perp c}/\varepsilon_0$, of the BWO crystal along and perpendicular to the *c*-axis are about 90 and 110 at room temperature, respectively. The corresponding loss factors, $\tan\delta$, were 0.005 and 0.003, respectively. These data are comparable to those reported by Yanovskii and Voronkova.[1] Wolfe et al.[6] reported that the BWO belongs to the point group *mm*2 and that the polar axis is a crystallographic *a*-axis. However, the ferroelectric properties have not yet been confirmed. We have measured the *P–E* hysteresis loop in order to confirm the ferroelectrisity along and perpendicular to the *c*-axis of the BWO crystals. Both hysteresis loops were not developed at room temperature. Fig. 5 shows the *P–E* hysteresis loops along and normal to the *c*-axis at 160 °C. The *P–E* hysteresis loop along the *c*-axis indicated the dielectric property only. Although we increased the driving electric field up to 200 kV/cm, the ferroelectricity along the *c*-axis was not confirmed. On the other hand, a developed *P–E* hysteresis loop normal to the *c* axis was obtained. This developed hysteresis loop of the BWO crystal has not been previously reported. The remanent polarization $2P_r$ and coercive field $2E_c$ were 34 μC/cm² and 44 kV/cm, respectively. These results revealed that the polar axis lie in the *c*-plane, and therefore BWO belongs to the point group *mm*2.

4. Conclusions

We tried to grow BWO single crystals using NaCl, $LiBO_2$, LBO, NBO and borax as fluxes below the phase transition temperature. LBO and NBO were found to be suitable fluxes for the bulk single crystal growth. The phase diagram of the BWO–LBO(NBO) binary system was determined. On the basis of this phase diagram, BWO single crystals with a maximum thickness of 0.7 mm were grown from the melt with the composition of BWO:LBO = 70:30 in mol%. The dielectric and ferroelectric properties of the BWO crystals revealed that spontaneous polarization occurred in the crystallographic *a*–*b* plane.

Acknowledgement

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