

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

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Bismuth tungsten oxide, Bi_2WO_6 (BWO), is one of bismuth layered-structure ferroelectrics (BLSFs) with general formula $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$: $m=1-5$, 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 c -axis. Since BWO single crystals shows a high Curie temperature $T_c=940^\circ\text{C}$ and a high electromechanical coupling coefficient $k_{33} = 0.4$, this material is expected to be lead-free materials for use in piezoelectric devices suitable under high frequencies and high temperatures. Although BWO single crystals have been grown by a flux method, the flux materials are toxic or easily incorporated into BWO phase. In this study, we searched for new flux materials suitable for crystal growth of BWO. We also grew the BWO single crystals and attempted the characterization of the essential physical properties such as dielectricity, piezoelectricity, and conductivity.

LiBO_2 , $\text{Li}_2\text{B}_4\text{O}_7$ and $\text{Na}_2\text{B}_4\text{O}_7$ were chosen as the flux. The mixed powders with the ratio BWO:flux=1:1 in mole were charged into platinum crucibles. The starting powders were heated up to 900°C and kept at is temperature for 10 h. Then the temperature was decreased to 750°C at the rate of $5^\circ\text{C}/\text{h}$, and finally the samples were allowed to cool to room temperature naturally. The solidified melts in the BWO- LiBO_2 binary system were composed of almost glass phase only. On the other hand, in BWO- $\text{Li}_2\text{B}_4\text{O}_7$ and BWO- $\text{Na}_2\text{B}_4\text{O}_7$ binary systems, the mixtures of the end members without intermediate compounds were observed. The phase diagram of the BWO- $\text{Li}(\text{Na})_2\text{B}_4\text{O}_7$ system was investigated by the combination of the differential thermal analysis and the quench method. The results showed that the solid BWO exists in equilibrium with the liquid consisting up to approximately 60 mol% BWO BWO- $\text{Li}_2\text{B}_4\text{O}_7$ system and 70 mol% BWO for BWO- $\text{Na}_2\text{B}_4\text{O}_7$ one. On the basis of the phase diagram, BWO single crystals were grown by the traveling solvent floating zone method. We have obtained plate-like single crystals with sizes up to 0.5 mm thickness from the solidified melts with the ratio BWO: $\text{Li}_2\text{B}_4\text{O}_7=1:1$ in mole. The crystals were single domain, yellow in color, and have well developed smooth $\{010\}$ faces.