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Bridgman growth of bismuth tellurite crystals

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Abstract. **The photorefractive crystal, Bi_2TeO_5, was grown by the modified Bridgman method for the first time. High purity Bi_2O_3 and TeO_2 were used as starting materials and were mixed thoroughly with molar ratio of $Bi_2O_3/TeO_2 = 1 : 1$. Platinum crucible was fabricated with a seed well of 10 mm in diameter and several folds were pressed so that the spontaneous nuclei could be eliminated through competition. The crucible was sealed during the growth so that the evaporation of TeO_2 was controlled effectively. By optimizing growth parameters, transparent and crack-free Bi_2TeO_5 crystal up to 25 mm in diameter and 40 mm in length was grown successfully.**

Keywords. **Bi_2TeO_5 crystal; Bridgman; photorefractive materials.**

1. Introduction

Volume holographic memories have been widely investigated during the last decade and have demonstrated their advantages in terms of storage capacity and fast read-out speed (Berger *et al* 2003). However, volume holographic storage system still suffers from the lack of an appropriate memory material. Such a material has to fulfill a series of properties, for example, high sensitivity, good optical quality, non-volatile, etc. These storage materials can be photorefractive inorganic crystals, polymers or doped glasses. So far, photorefractive $LiNbO_3$ crystal is still the most important crystal material for the volume holographic storage application. However, the vulnerability of the holograms is the major shortcoming of $LiNbO_3$ crystal. The more practical fixing approach was realized by using doubly, Fe and Mn doped photochromic $LiNbO_3$, which caused many difficulties in crystal growth. Recently, bismuth tellurite (Bi_2TeO_5) has attracted much attention as a new photorefractive material (Foldvari *et al* 1990; Berger *et al* 2003). Bi_2TeO_5 crystals demonstrate a long living (more than 6 years) photorefractive signal component that developed in the four-wave-mixing (FWM) write process without any specific fixing. In addition, its photorefractive sensitivity is about hundred times more than that of $LiNbO_3$ crystals (Foldvari *et al* 1992; Peter *et al* 1996). This suggests that Bi_2TeO_5 crystal might be an ideal material for holographic memory application.

So far, all of Bi_2TeO_5 crystals have been grown by Czochralski method (Foldvari *et al* 1999; Kumaragurubaran *et al* 2000). It is difficult to grow large size and high quality Bi_2TeO_5 crystals due to the cracking and evaporation of TeO_2 during the crystal growth process. Thus, Bi_2TeO_5 crystals had been grown by Czochralski methods through adjusting the Bi_2O_3/TeO_2 ratio in the starting composition. However, the chemical inhomogeneity of the crystal hindered its application (Foldvari *et al* 1999). To our knowledge, the vertical Bridgman method has obvious advantages such as (a) controlling crystal cracking due to its lower temperature gradient in solid–liquid interface and (b) suppressing component evaporation because the melt could be sealed in the small space of the crucible. In the present work, the vertical Bridgman method was employed to grow Bi_2TeO_5 crystals for the first time and the preliminary results are reported here.

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2. Experimental

Chemical reagents, TeO_2 (4N) and Bi_2O_3 (4N), were used as starting materials and were weighed with the molar ratio of Bi_2O_3: $TeO_2 = 1 : 1$. They were mixed thoroughly with an agate mortar and pestle, and then were loaded into a platinum crucible with a dimension of 25 mm in diameter and 250 mm in length. A seed well of Φ 10 × 60 mm was designed in the bottom of the crucible. After charging, the crucible was sealed to prevent component deviation from stoichiometric composition due to the evaporation of TeO_2 and sintered in a muffle furnace. Polycrystalline Bi_2TeO_5 raw materials were synthesized by a two-step solid-phase reaction. The first step was conducted at 650°C in a Pt crucible for 24 h. The melting temperature of TeO_2 being 733°C, higher reaction temperature may result in the evaporation of TeO_2 component and the formation of other phases (Szaller *et al* 1996). Then the reaction was completed by a subsequent heating treatment at 750°C for 24 h.

The crucible was put into the refractory tube, which was filled with Al_2O_3 powder to support the crucible as well as to isolate it from external temperature fluctuations. Two pairs of Pt–Pt/Rh thermocouples were installed in the tube to measure the temperature of the melt and the bottom of the seed well. Crystal growth was carried out in a home-made vertical Bridgman furnace. Powder X-ray diffraction (XRD, D/max 2250 V) was performed to examine the phase structure of as-grown crystals.

3. Results and discussion

3.1 *Control of Bi/Te ratio*

Bi_2TeO_5 single crystal was previously grown by the Czochralski method, and there was no report about other growth techniques so far. Due to the cracking and the high evaporation of TeO_2 component, it is difficult to obtain large size and high quality Bi_2TeO_5 crystals. In order to compensate the loss of TeO_2 component during the sintering and growth process, both Foldvari *et al* (1999) and Kumaragurubaran *et al* (2000) used the starting materials with the molar ratio of Bi_2O_3: TeO_2 = 0·925 : 1·05 to grow Bi_2TeO_5 single crystal. Furthermore, an excess of TeO_2 may minimize the risk of the harmful reaction of Bi_2O_3 with platinum crucible. However, the compositions of as-grown Bi_2TeO_5 crystal varied from 50·5 mol% TeO_2 at the top to 52·9 mol% TeO_2 at the bottom, and only 70% of the melt was crystallized (Foldvari *et al* 1999; Kumaragurubaran *et al* 2000).

According to our previous work on the crystal growth of $Pb_5Ge_3O_{11}$ and $Sr_3Ga_2Ge_4O_{14}$, the evaporation of the compositions can be controlled effectively by sealing the melt in small space of the crucible during the crystal growth (Ding *et al* 2004; Wu *et al* 2004). Therefore, the sealed crucible was employed to synthesize polycrystalline Bi_2TeO_5 and grow the crystal. The starting materials with the molar ratio of Bi_2O_3: TeO_2 = 1 : 1 was used and nearly all of the melt transformed into Bi_2TeO_5 crystals.

3.2 *Optimum of growth parameters*

The furnace temperature was set to about 80°C higher than that of its melting point (900 ± 5°C), so that the polycrystalline Bi_2TeO_5 melted thoroughly. Two pairs of Pt–Pt/Rh thermocouples were installed in the refractory tube. The upper one showed the temperature of Bi_2TeO_5 melt near the middle of the crucible and the lower one showed the temperature near the bottom of the seed well. The position of the crucible in the furnace was adjusted by a mechanism. When the lower thermocouple showed a temperature 15°C higher than the melting point of Bi_2TeO_5, the crucible began to descend at the rate of 0·2–0·6 mm/h. The growth cycle was calculated based on the growth rate and size of the crucible in advance. After all the melt solidified, the crucible lowering was stopped and the furnace was cooled down to room temperature at a rate of about 50°C/h.

In order to eliminate the spontaneous nuclei through competition, the seed well of the crucible was pressed with several folds, as schematically shown in figure 1. When the temperature value of the bottom thermocouples reached 915°C, the crucible was held for 5 h so that a homogeneous melt was accomplished. Then the crucible was pulled down 5 ~ 10 mm suddenly to form fast cooling nuclei. Single crystal seed was obtained through competition of these nuclei in the folded seed well. Figure 2 shows a typical as-grown Bi_2TeO_5 crystal. The crystal was slightly yellow and transparent, and the length of the cylindrical part was about 70 mm with a diameter of 25 mm. The top part of as-grown crystal was dark yellow and only small amount of residual melt was found. This demonstrated that nearly all of the melt crystallized during the Bridgman growth. However, some cracks were observed in the end of the crystal. These cracks always had an inclination angle of about 20° with the growth direction. They were mainly induced by the residual having different thermal properties in comparison with the crystal. The inclination of the crack may be attributed to the existence of cleavage plane, which will be discussed in the next section. Table 1 shows the optimal growth parameters for the Bridgman growth of 1-inch Bi_2TeO_5 crystals. The growth of 2-inch Bi_2TeO_5 crystals had been tried several times but some problems were often encountered. One of the problems was the leakage of the melt from the shouldering part of the crucible, as shown in figure 3. The platinum crucible might be etched by Bi_2O_3 component during crystal growth. It is better

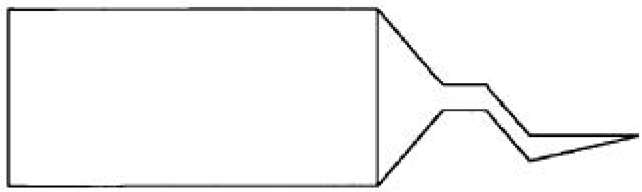

Figure 1. Schematic of the platinum crucible for the nuclei competition.

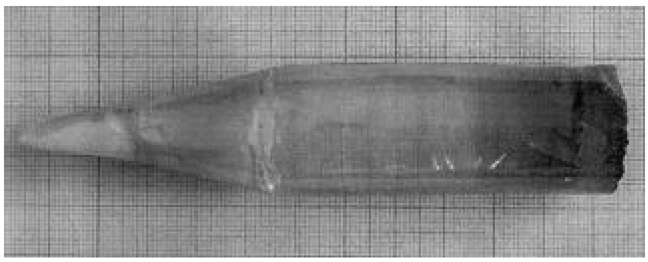

Figure 2. As-grown Bi_2TeO_5 crystal by the modified Bridgman method.

to grow Bi_2TeO_5 crystal using polycrystalline Bi_2TeO_5 powder.

3.3 *Crystal characterization*

Powder X-ray diffraction (XRD) data of Bi_2TeO_5 crystal sample were collected on a Rigaku D/Max-2250 V diffractometer with CuK*a* radiation of wavelength *l* = 1·5418 Å at room temperature (28 kV, 20 mA, fixed scattering and divergence slits of 1° and a receiving slit of 0·15 mm). Intensities for the diffraction peaks were recorded in the 10–70° (2*q*) range with a step size of 0·02° and a scan speed of 10°/min as shown in figure 4. The XRD experiments agreed well with JCPDS card No. 76-1971. Bi_2TeO_5 crystal belongs to orthorhombic symmetry of space group C_{2v}^{15} and the lattice constants were calculated as a = 1·155 nm, b = 1·640 nm and c = 0·550 nm.

The as-grown crystals were cut by a diamond saw and polished mechanically with 0·1 μm diamond paste. X-ray orientation showed that crystallographic direction <213> was the preferable growth direction of Bi_2TeO_5 crystal. In order to check single crystallinity of as-grown crystal, the cross-section was polished and immersed in hydrochloric acid solution (volume ratio of HCl: water = 1 : 3) for 5 min. No crystal boundary or twin was observed in the section.

As described in the above section, cracking always occurred in the top part with an inclination angle of about 20° to the growth direction, which is shown as figure 5. All of the cracking planes looked smooth and were determined as (100) face by X-ray orientation. So the cracking plane was suggested to be a cleavage plane of Bi_2TeO_5 crystal. The same problem was also met in Czochralski growth of Bi_2TeO_5 crystal (Foldvari *et al* 1990). In fact, Bi_2TeO_5 crystal is easy to crack during cutting and polishing process as well as crystal growth. A small temperature gradient was employed in the growth and an *in situ* annealing system was assembled in the lower temperature zone of the furnace. As-grown crystal was moved to this zone and annealed for several hours when the crystal growth finished. By this way, the occurrence of cracking was reduced considerably.

Table 1. The technical parameters for Bridgman growth of Bi_2TeO_5 crystals.

Crucible material	Platinum
Crucible size (mm)	Φ10 × 60 + Φ25 × 250
Furnace temperature (°C)	950–1000
Precision of temperature controlling (°C)	0·5
Growth rate (mm/h)	0·2–0·6
Temperature gradient (°C/cm)	15 ~ 30
Period of growth (day)	15

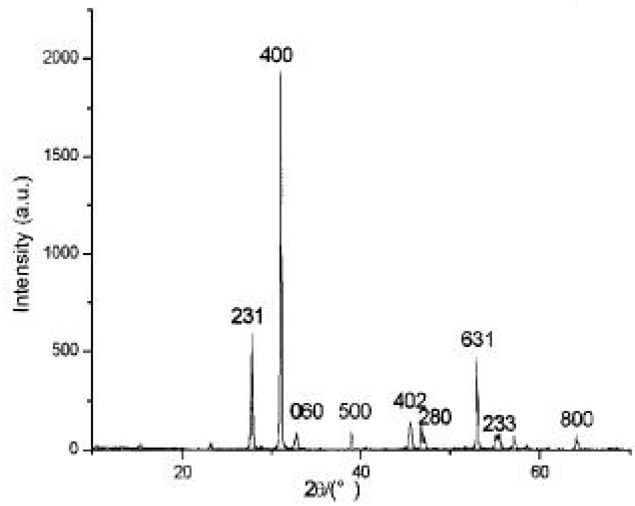

Figure 4. The XRD pattern of the as-grown crystal.

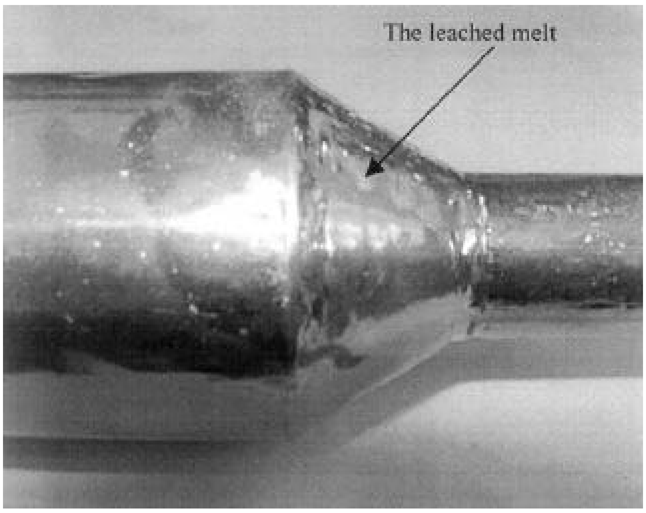

Figure 3. The platinum crucible etched by the melt.

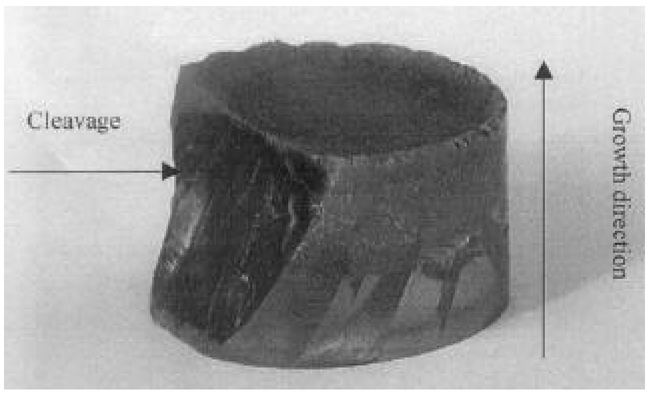

Figure 5. The cleavage in the top part of Bi_2TeO_5 crystal.

4. Conclusions

Bi_2TeO_5 crystals were grown by the modified vertical Bridgman method from its stoichiometric melt. The melt was sealed in the limited space of the Pt crucible and the evaporation of TeO_2 was controlled effectively. Small temperature gradient and *in situ* annealing process were employed during crystal growth and the occurrence of cracking was reduced considerably. Transparent and crack-free Bi_2TeO_5 crystal up to 25 mm in diameter and 40 mm in length had been grown successfully.

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