Journal of Crystal Growth 245 (2002) 56–62

JOURNAL OF CRYSTAL GROWTH

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Zone-melting Czochralski pulling growth of $Bi_{12}SiO_{20}$ single crystals

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Received 8 July 2002; accepted 31 July 2002
Communicated by D.T.J. Hurle

Abstract

In this report the zone-melting Czochralski (ZMCz) growth of $Bi_{12}SiO_{20}$ (BSO) single crystals is presented and its growth stability is discussed. With a careful starting up of the melt level, the growth was found always self-stabilized leading to an excellent diameter control. Due to the zone-leveling nature, the grown crystals showed good optical uniformity. Nevertheless, it was found that bubble inclusion was a serious problem. By using an inner crucible, bubble-free crystals could be easily grown. This double-crucible ZMCz technique was found to be useful and could be used for other oxides as well.

PACS: 44.25.+f; 47.27.Te; 81.10.Fq; 68.60.Dv; 44.30.+v

Keywords: A1. Diameter control; A1. Stability; A2. Zone-melting Czochralski method

1. Introduction

Bismuth silicon oxide ($Bi_{12}SiO_{20}$-BSO) is a good photorefractive material. Its high photorefractive sensitivity and fast response time, either for writing or erasing processes, make the material particularly attractive in applications such as optical data processing, image amplification and phase conjugation devices [1]. The photorefractive effect in BSO involves the photoexcitation and trapping of charge from and to interband states. BSO should be transparent in visible light with a large band gap [2] of 3.25 eV, but an intrinsic defect producing interband states limits the minimum absorption in the visible spectrum [3].

BSO crystals have been grown by Czochralski, Vertical Bridgman and Floating Zone methods [4–6]. In the present investigation the zone-melting Czochralski (ZMCz) technique combined with double crucibles has been employed for growing oxide crystals of BSO for the first time in the literature. The growth characteristics of zone melting of BSO with excellent diameter control have been described in detail. The ZMCz process without using an inner crucible was first employed by Barlic for the growth of Ge in 1965 [7]. Kou and Lin also used, with some modifications by including shapers, the ZMCz technique to grow Sn, InSb, and GaAs [8–10]. Although there is no

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0022-0248/02/$ - see front matter
PII: S0022-0248(02)01688-3

report of the ZMCz growth of oxide crystals, it can be anticipated that bubble inclusion could be a serious problem due to the solid feeding, which will be illustrated shortly. In order to avoid gas bubble inclusion into the growing crystal, the combination of double crucible with the ZMCz technique is considered here for the growth of BSO crystals. Due to the zone-leveling nature, with a suitable adjustment in the molten zone and pre-doping, uniform crystal diameter and composition in the growth direction can be obtained. Interestingly, for oxide growth, due to the lower thermal conductivity, this process is believed to have a better performance in the diameter control due to its continuous nature. Once the diameter, as well as the zone size, reaches a pseudo-steady state, compositional uniformity could be obtained.

The setup of the growth furnace and the experimental procedure are presented in the next section, followed by results and discussion.

2. Furnace design and crystal growth

Fig. 1 shows a schematic diagram of the double-crucible ZMCz method developed for the growth of BSO with continuous feeding. The apparatus consists of a resistive heating furnace, rotation and translation assemblies which are controlled by micro-stepping motors and interfaced with a computer. Each assembly is controlled by an individual motor. The charged outer platinum crucible (150 mm × 50 mm × 1 mm) is held on a crucible holder (Alumina tube) and finely perforated (side wall) inner platinum crucible (20 mm × 40 mm × 0.1 mm) is placed inside the outer crucible of the top portion. The outer crucible can be moved up and down inside the furnace using a motor so that the molten zone level can be maintained at the center of the furnace. By adjusting the outer crucible inside the furnace the zone leveling can be controlled for constant diameter crystal growth. The furnace is designed to have a maximum temperature at the center of the furnace, but sufficient thermal gradient at the top is necessary. As will be discussed shortly, this temperature profile is critical to have a controlled diameter crystal. Kanthal wire has been used as a resistance heater in the furnace and the temperature of the furnace is sensed by a Pt–Pt:Rh thermocouple at the inner wall of the furnace. A PID closed-loop control was used to keep the setting point controlled at ±1°C. The temperature gradient of the furnace is about 40°C/cm.

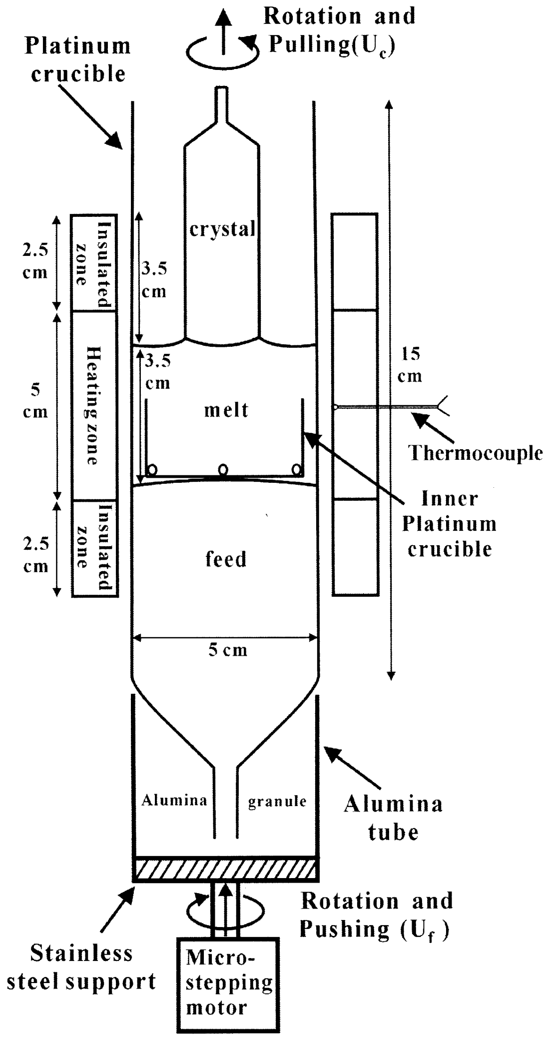

Fig. 1. Schematic of zone-leveling Czochralski method.

Commercial Bi_2O_3 (99.9%) and SiO_2 (99.995%) powders were used as starting materials with 6:1 mole ratio. The mixed powder was calcined twice at 800°C for 24 h in air and then ground with an agate mortar and used as feed material. In order to have a dense feeding material small pieces of the feed material was loaded in the bottom of the outer crucible and continuous solidification of the powder from the bottom was performed. Again the feed powder needs to be loaded into the crucible melt and melted. This process was repeated many times to obtain dense feed material for the growth. The growth was performed with the pulling speed of 2–5 mm/h and the rotation rate of 10–30 rpm. The crucible was counter rotated at 6 rpm with respect to the crystal rotation. The power used for the furnace was only 800 W (100 A and 8 V).

3. Results and discussion

3.1. Diameter control

The experiment was started using an inner crucible in order to have continuous feeding during growth. The temperature was measured outside the crucible and correspondingly controlled to meet the charge material. The ⟨1 0 0⟩ seed crystal was slowly brought closer to the melt by applying a 10 rpm rotation rate and was made to touch the melt. After forming a solid–liquid interface between the melt and seed, the growth was started. The outer crucible was moved upward after necking and shouldering. The temperature was reduced to get the desired diameter and the crystal was pulled. As soon as the required diameter was reached, the temperature of the melt was increased to control the increasing diameter. The temperature was kept constant when the required diameter was obtained. With a careful starting up of the melt level, the growth was found always to be self-stabilized leading to excellent diameter control (Fig. 2a). After necking the growth was continuous with a constant diameter and good quality BSO crystal was obtained by adjustment of the thermal fields (Figs. 2b and c).

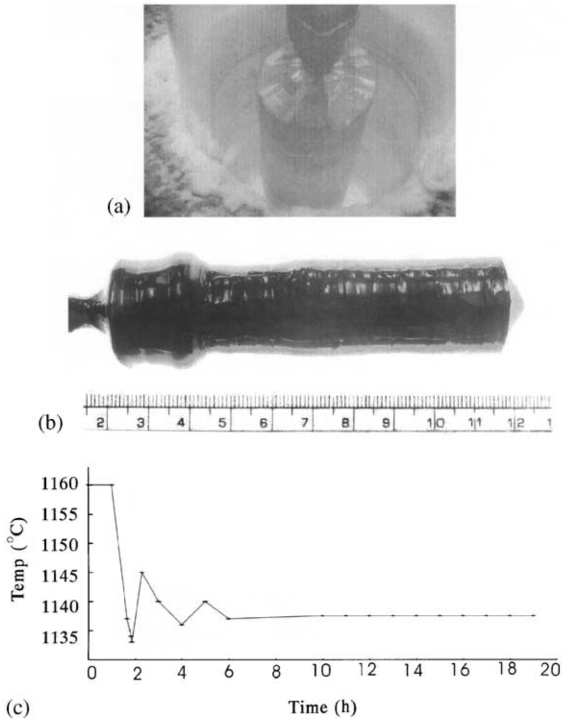

Fig. 2. (a) ZLCz growth of 1″ BSO single crystal; (b) an as-grown crystal and (c) relationship between the crystal diameter and temperature during growth.

3.2. Transmittance spectra

Cut and polished crystal plates of equal thickness from the top, middle and bottom portion were prepared for optical studies. The optical transmission spectra were recorded using a Spectrophotometer (JASCO V-570, JAPAN) in the wavelength range of 300–800 nm. It is evidenced from the transmittance spectra (Fig. 3) that the middle portion of the crystal has better transparency than the other portions. The optical uniformity of the crystal was found by measuring the optical transmittance of the crystal at different portions of the crystal wafer. The optical transmittance is found to be the same in all portions of a wafer. This optical homogeneity is owing to the compositional uniformity of the crystal.

3.3. Bubble inclusion

In the growth of oxide crystals like BSO certain difficulties arise that do not often occur in the growth of semiconductors. We can expect two types of difficulties during the growth of BSO crystals. One is caused by a fluid flow transition from free convection to forced convection. On

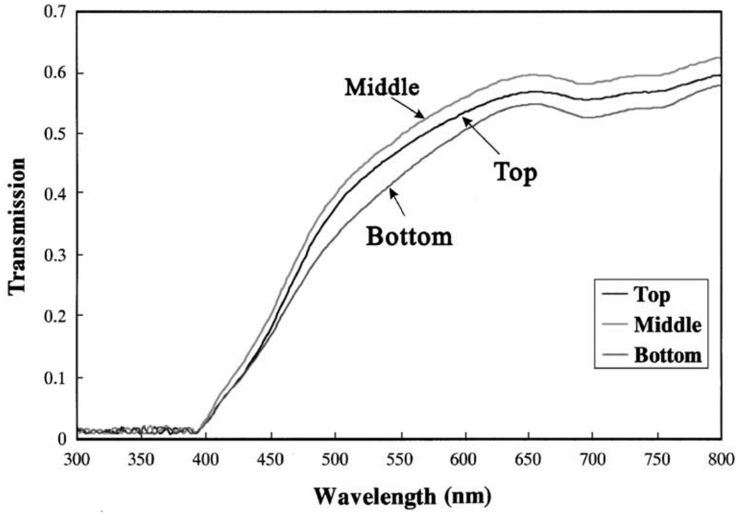

Fig. 3. Optical transmittance at different portions of the grown crystal.

transition the interface shape changes from convex to concave in the melt [11].

Gas bubble entrapment is the other serious problem encountered in Czochralski pulling of a wide range of oxide crystals, creating optical inhomogeneity in the crystal [12]. This problem is particularly severe in ZMCz growth. When the concentration of the gaseous component, which is coming from the feed rod into the melt, becomes sufficiently high, gas bubbles nucleate. Most of the time, the bubbles form directly during the melting of the feeding rod. They are often small and can be carried around by the melt flow. The bubbles may grow due to coalescence and may escape from the melt surface. However, very often, especially due to crystal rotation, they are likely to be incorporated into the growing crystal. By using an inner crucible, bubble-free BSO crystals have been grown with controlled diameter. The inner crucible has a very fine perforation in the side wall and hence it is continuously fed with molten material for growth. The bubble incorporation into the growing crystal is avoided by the use of the inner crucible because surface tension prevents the bubbles from passing through the fine perforations in the crucible wall. Although a taller inner crucible could be used, the shorter one had less effect on the thermal condition. Fig. 4 shows the

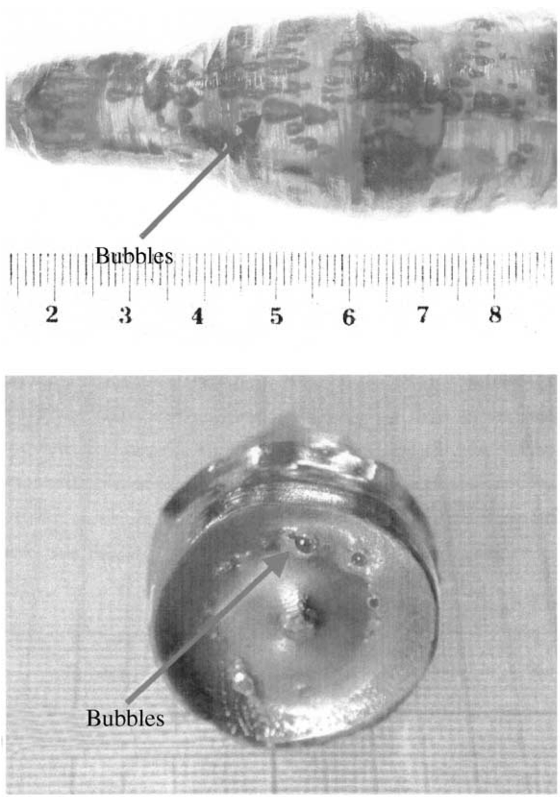

Fig. 4. Gas bubbles and voids at the outer edge of the crystal at high rotation speed (30 rpm).

gas bubbles observed in the outer edge of the crystal while the crystal was grown with a rotation rate of 30 rpm. With a low rotation rate, the bubbles transported by natural convection can accumulate near the edge of the crystal, when the growth interface is convex. Some spiral striation lines were observed on the crystal surface owing to the continuous rotation of the gas bubbles around the crystal.

3.4. Thermal fields

The heating zone of the furnace is 50 mm in length and the starting melt level was kept at 15–20 mm above the center of the heater by adjusting the outer crucible. The temperature of the melt increases when the melt level reaches just below the above-stated fixed level and the diameter of the crystal decreases. On the other hand, the tempera-

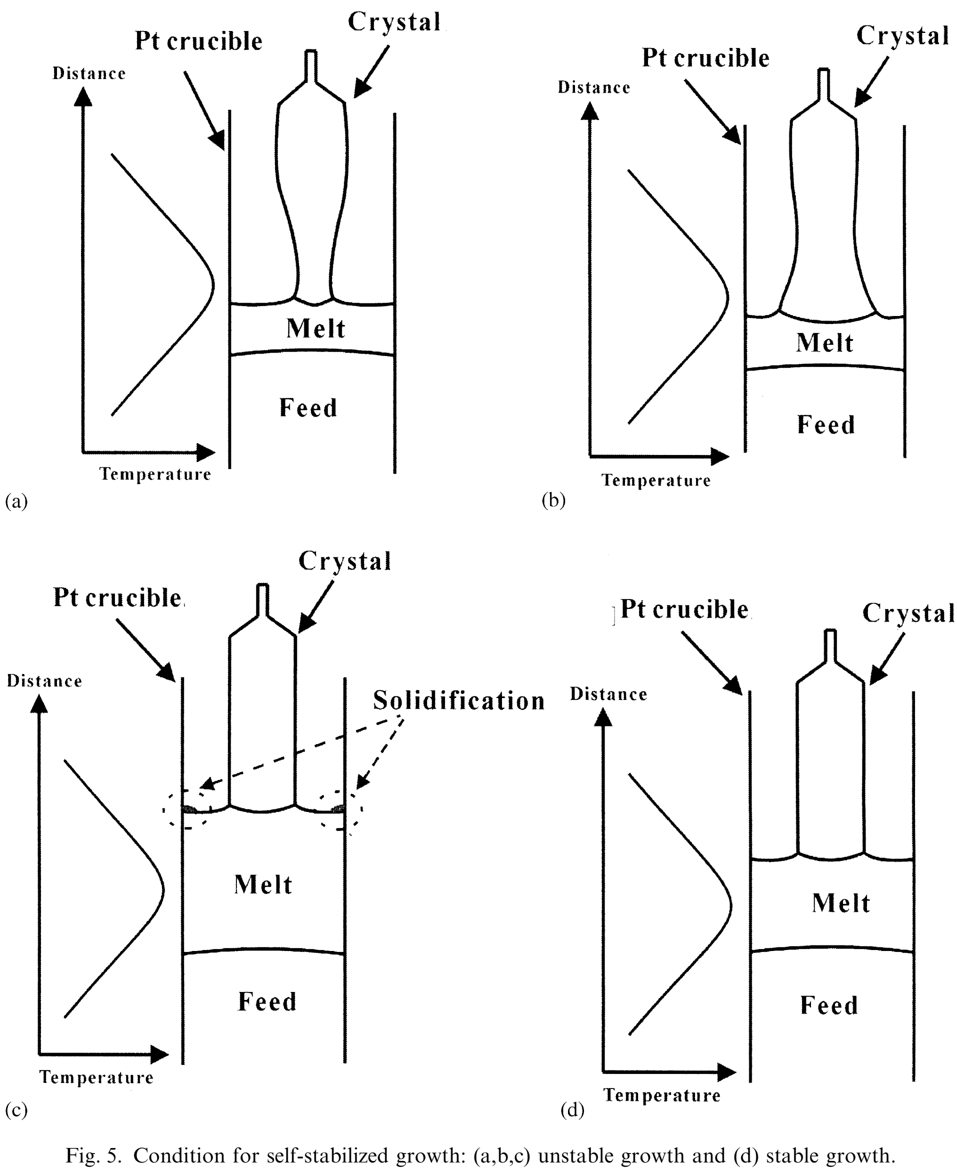

Fig. 5. Condition for self-stabilized growth: (a,b,c) unstable growth and (d) stable growth.

ture of the melt decreases while the liquid level reaches above the fixed level (> 20 mm from the center of the heater) and then the crystal diameter increases. It is proposed that by properly adjusting the melt level the diameter of the crystal can easily be controlled. The conditions for different growth modes are shown in Fig. 5. We have found unstable and self-stabilized modes in our system. They can be explained in the following way: If we consider ρ_c, A_c, U_c are the density, cross-sectional area and velocity of the growing crystal and ρ_f, A_f, U_f are the density, area and velocity of the feed, respectively, then by the mass balance at steady state $\rho_c A_c U_c = \rho_f A_f U_f$ and the steady growing cross section $A_c^* = \rho_f A_f U_f / \rho_c U_c$.

There are two unstable modes that have been observed where the melt level is lower than the position having the maximum temperature. The first case is illustrated in Fig. 5a; that is, a decrease of the crystal diameter. When the diameter of the crystal starts decreasing, the amount of material growing (pulling) is less than that of feeding. Then the melt level increases due to the mass balance. Due to the positive temperature gradient, the increase in melt level towards the maximum temperature point increases the melt temperature and, in turn, the crystal diameter again decreases, i.e., the diameter is getting smaller and smaller. The second case is illustrated in Fig. 5b; that is, the increase in the crystal diameter. When the crystal diameter starts increasing (the material pulled out is larger than that being fed), the melt level decreases and the melt gets cooler. This causes the crystal diameter to increase further; the diameter is getting larger and larger.

When the melt level is well above than the center of the heater, having the highest temperature, diameter control is self-stabilized. However, if the melt level is too high, as illustrated in Fig. 5c, the growth is still unstable due to solidification at the surface rim. Since the BSO melt wets the Pt crucible very well, the contact line is well above than the melt level and its temperature is lower. Sometimes the growth can be stable, but the grown crystal diameter is smaller. With a suitable melt level, though still well above the position with highest temperature, as illustrated in Fig. 5d, a self-stabilized growth without solidification at the wall is possible. The self-stabilized mechanism can be easily understood. When the diameter of the growing crystal decreases from a steady state, the amount of material growing (pulling) is less than that of feeding. Then the melt level increases and the melt gets cooler causing the crystal diameter to increase, i.e., back to the steady-state value. On the other hand, if the diameter of the growing crystal happens to increase, the amount of material growing (pulling) is larger than that of feeding. The melt level will decrease, and the increased melt temperature (at the edge) will force the crystal to grow smaller. Because of this self-stabilized nature in the negative temperature gradient region, the crystal grows to a required constant diameter. Fortunately, we have found that the window (melt level) for a stable growth is large enough to be of practical value. Therefore, with some care at the beginning, stable growth could be easily obtained.

Fig. 6a shows the decrease in diameter of the crystal owing to increase of temperature in the melt. That is because the concentration of gas

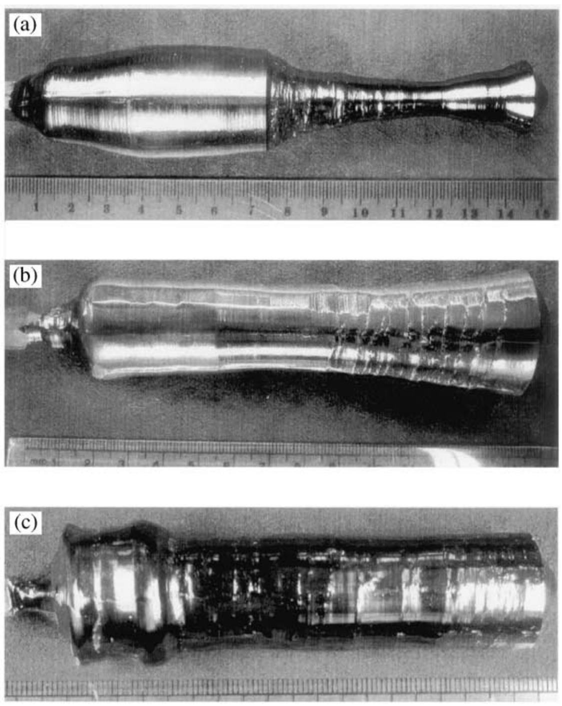

Fig. 6. (a,b) Unstable growth and (c) stable growth.

bubbles coming from the feed rod to the melt interface is increased which affects the mass balance and hence, the heat energy coming from the melt to the crystal is more than the heat energy liberated from the growing crystal. Fig. 6b illustrates the increase in diameter of the crystal due to decrease of temperature in the melt and change in the melt level. Fig. 6c shows stable growth, which is attained by the zone leveling. It is evidenced from the crystals shown in Figs. 6a–c that a proper initial melt level is important. Too low is dangerous, and when too high there is a problem of solidification at the outer melt surface.

4. Conclusions

A zone-melting Czochralski growth technique combined with a double crucible has been designed and fabricated for the growth of $Bi_{12}SiO_{20}$ (BSO) single crystals. With a careful zone leveling of the melt, a number of excellent diameter-controlled BSO crystals have been grown. The unstable growth modes were found, and they occurred when the melt level was too low or too high. The self-stabilized mode was obtained by zone leveling. The optical uniformity of the crystals has been verified using the transmittance spectra recorded at different positions of the wafers obtained from different portions (top, middle and bottom) of the grown crystals. Gas bubble incorporation into the crystal has been avoided in the center portion of the crystal by introducing an inner crucible. Though the use of inner crucible avoids the gas bubble incorporation into the growing crystal, it is not possible to grow all the feed material as crystal. The removal of the inner crucible is very difficult after the growth. This can be overcome by using a lengthy inner crucible with a holder.

Acknowledgements

This work was supported by the National Science Council of the Republic of China under Grant No. 89-2214-E-002-040. CWL would like to thank Prof. Hurle for his careful review and comments. Assistance and comments by Dr. R. Gopalakrishnan are appreciated.

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