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The influence of temperature gradient and rotation rate on $Bi_4Ge_3O_{12}$ crystal growth by czochralski method

In Kook Bae and Chin Myung Whang*

Korea Institute of Geology, Mining and Materials, Taejon 305-350, Korea
**Department of Ceramic Engineering Inha University, Inchon 402-751, Korea*

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쵸크랄스키법에 의한 $Bi_4Ge_3O_{12}$ 단결정 육성에서 온도구배와 회전속도가 미치는 영향

배인국, 황진명*

한국자원연구소 지질연구부, 대전, 305-350
*인하대학교 무기재료공학과, 인천, 402-751

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Abstract In order to grow $Bi_4Ge_3O_{12}$ crystals by the Czochralski method equipped with the auto-diameter control system, we used the resistance heater of our own design. We measured the temperature gradients under various thermal configurations. The relation between the critical rotation rate corresponding to the flat interface and the temperature gradient was investigated, and the importance of the axial temperature gradient was pointed out. The results from this work were compared with those obtained by other authors when RF heating was used. The optimal conditions for the crystal growth were determined as follows; under O_2 atmosphere with the pulling rate fixed at 2 mm/hr, rotation rate changed from 30 to 23 rpm as the crystal growth proceeded, radial and axial temperature gradients were 50 and 40°C/cm near melts respectively, and the composition was chemically stoichiometric.

요 약 자동직경제어방식이 부착된 쵸크랄스키법에 의해 $Bi_4Ge_3O_{12}$(BGO) 단결정을 육성하기 위해 저항발열식로를 자체설계로 제작하여 사용하였다. 로 내의 온도 구배는 열적구조를 변화하면서 측정하였다. 각각의 변화된 온도구배와 평평한 계면을 갖는 임계 회전속도의 의존성에 대해 연구하였고 또한 저항발열식 가열에서 수직온도구배의 중요성을 지적하였다. 그것은 RF 가열방식을 사용하였을 때 다른 저자들에 의해 얻어진 결과와 비교되었다. 단결정 육성을 위한 최적조건은 다음과 같다. 산소 분위기하에서 2 mm/h로 인상속도를 고정하고 성장이 진행함에 따라 회전속도를 30에서 23 rpm으로 변화하였고, 수평 및 수직 온도구배는 용액근처에서 각각 50과 40°C/cm이었고, 조성은 화학양론 조성이었다.

1. Introduction

$Bi_4Ge_3O_{12}$ (BGO) is a cubic crystal with space group $I\bar{4}3d$ whose crystal structure is isomorphous to the mineral eulytite $Bi_4Si_3O_{12}$ [1, 2]. The unit cell contains four formula units and 78 atoms. The advantages of BGO crystal are non-hygroscopicity, high effective atomic number and density, and large absorption coefficient. And another advantage is that it is more homogeneous than other impurity-doped materials because the luminescence center of scintillator is Bi itself [3]. Compared to other commercial detectors, e.g., NaI (Tl) and CsI (Na), much smaller detector assemblies with the same efficiency can be fabricated.

Also, BGO crystals have emerged as a scintillation material of choice for medical application in present and future instrumentation of XCT and PCT diagnostic imaging [4, 5]. Furthermore, the electro-optic crystal BGO can be doped with rare earths for laser application [6]. However, one of the drawbacks of BGO is its relatively lower luminescence efficiency and the resultant poorer energy resolution. Recently, in order to improve the energy resolution of BGO crystal, many attempts to improve the quality of crystal by the Czochralski method [7, 8] have been made.

Many authors [9-11] have carried out studies to examine the shape of the interface in terms of various growth parameters such as pulling rate, temperature gradients and rotation rate. The interface shape influences many crystal properties such as dislocation density, homogeneity of impurities and strains. High-quality crystals are obtained when a flat interface is maintained during their growth. The flat interface is dependent upon the critical rotation rate of the crystal immersed in the melt, which is attained when an upflow of forced convection arises in the melt along the crucible axis below the crystal. Berkowski *et al.* [12] presented the dependence of the critical rotation rate N_{crit} with a flat interface on various growth parameters in the RF heating. In the RF heating, axial temperature gradient can be neglected because radial temperature gradient is very high. However, Lukasiewicz *et al.* [13] emphasized the importance of axial temperature gradient in the resistance heating. Therefore, in the resistance heating, it is necessary to consider both temperature gradients at a critical rotation rate with the flat interface.

The purpose of our studies is to find out the optimal conditions required to obtain high quality $Bi_4Ge_3O_{12}$ crystals grown by the Czochralski method. We used the resistance heating apparatus of our own design, the details of which are presented in section 2, and measured temperature gradients under various thermal configurations. We determined the optimum condition for the flat interface in terms of temperature gradient and rotation rate. We reformulated the equation of the critical rotation rate with RF heating by taking both temperature gradients into account, and compared the theoretical and experimental values.

2. Experimental

2.1. *Crystal growth*

As shown in Fig. 1, BGO single crystal is grown by the Czochralski apparatus equipped with the auto-diameter control system. Especially, we used the frequency-weighing sensor, developed by Korea Institute of Geology, Mining and Materials [14], as the auto-diameter control system. We adopted the resistance heater, because melting temperature of BGO (1044) is relatively low, and resistance heater has higher electric efficiency and finer temperature control than RF heater.

Melt composition was stoichiometric. Sintered material was made from Bi_2O_3 (99.99 %, CERAK CO.) and GeO_2 (99.99 %, CERAK CO.), and was placed into the platinum crucible, which was 57 mm in depth and 53 mm in diameter. Oxygen was used as the growth atmosphere to prevent the melt from decomposing, the pulling rate was 2 mm/h and the growth direction was <110>. The crucible was not rotated. From necking to shouldering manual temperature control was employed based on data from the sensor, e.g. diameter, weight signal and so on, and the automatic procedure was initiated when the predetermined desired diameter had been reached. The interface was investigated by withdrawing the crystals and looking at the interface shape, and studying crystal slices cut parallel to the growing direction with the naked eye.

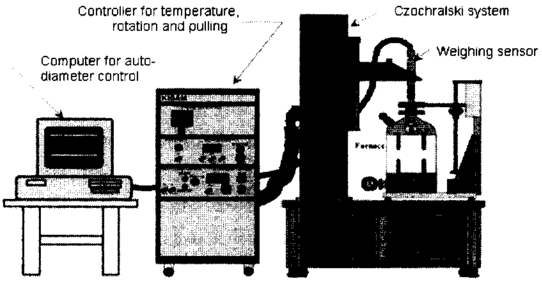

Fig. 1. Schematic diagram of Czochralski system used in this study.

2.2. *The configuration of furnace*

As shown in Fig. 2, the furnace consisted of six U type superkantal heating elements placed in radial form. Two thermocouples were used. One (CTC) controlling temperature was placed close to the heater, the other (BTC) in the bottom of crucible in order to measure the real temperature of the melt. The internal size of furnace was 110 mm in height and 110 mm

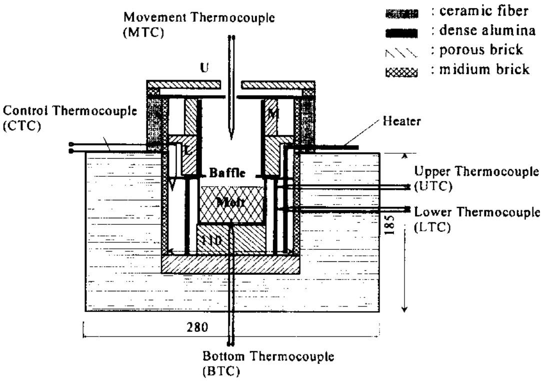

Fig. 2. Thermal configuration and structure of furnace used in this work.

in diameter. We placed alumina tube around the crucible in order to protect the crucible from the heater, and placed insulating bricks (supporter) under the crucible to control the height of the crucible from the furnace bottom. Generally, there are two types of afterheaters, passive or active [15]. We adopted the passive heater. Passive afterheater consisted of alumina tubes, insulating bricks and ceramic fibers, and could control mainly the axial temperature gradient. The afterheater consisted of lower (L: porous bricks), medium (M: porous brick and alumina tube), and upper (U: two layers of porous and alumina plate) part. Baffle consisted of the ring type of alumina or metal plate, and controlled mainly the radial temperature gradient.

2.3. *The measurement of temperature gradients*

In order to measure the axial (Δt_A) and radial (Δt_R) temperature gradients, three thermocouples were setup in the furnace as shown in Fig. 2. For example, one (UTC) is placed on the furnace wall at a distance of 30 mm from the crucible bottom which is the same level as the melt, another (LTC) at a distance of 10 mm from the crucible bottom. The other (MTC) is placed at the seed holder level at a distance of 120 mm from the crucible bottom. We carried out temperature measurements at one hour after melting to make the thermal equilibrium. MTC was lowered by 5 mm in many steps, and the temperature was measured at each step after waiting for 20 minutes. All thermocouples are of Pt-Pt10 % Rh type. The temperature gradients were measured at various thermal configurations by modifying the afterheater structure.

3. Results and discussion

3.1. *Temperature gradients in the furnace*

The measured Δt_A values are shown in Fig. 3. In the thermal configuration attained (Fig. 3-ATD20) when all afterheaters are used (e.g. L, M and H in Fig. 2), the observed Δt_A and Δt_R were ~30°C/cm near melt. Crystallization did not occur, indicating that Δt_A was too small. After we removed porous brick from M and U afterheater, or porous part from M and alumina plate from U afterheater, Δt_A increased (ATD-60 or ATD-50 of Fig. 3, respectively). In ATD-60 case, the Δt_R near melt is 43°C/cm, Δt_A 60°C/cm, and the slope is steep. The rotation rate of the flat interface is 35 rpm. In ATD-50 case, Δt_R and Δt_A is 40°C/cm and Δt_A 50°C/cm near melt respectively, and the slope is gradual. The rotation rate with flat interface is 30 rpm. Under both these conditions, we could easily grow crystals without cracks.

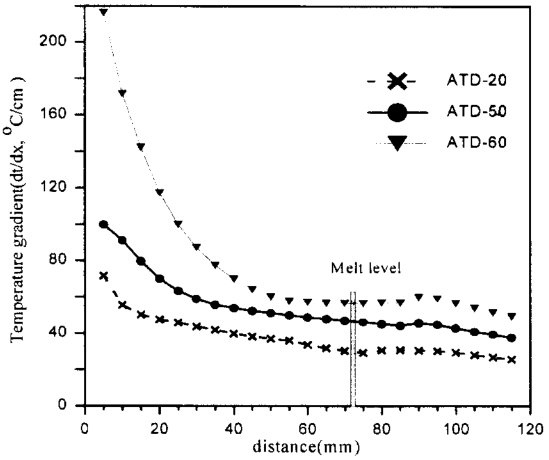

Fig. 3. Distribution of axial temperature gradient under the various thermal configurations.

Berkowski *et al.* [12] proposed the dependence of the critical rotation rate N_{crit} on growth parameters for RF heating with a flat interface by the following formula:

$$N_{crit} = 3.18\ (g\beta\Delta t_R)^{0.44}\ D^{0.245}\ h^{0.155}\ v^{0.12}\ d^{-1.08} \qquad (1)$$

where g denotes the acceleration due to gravity, β is the volumetric expansion coefficient of the melt, Δt_R the radial temperature gradient between the crucible wall and crystal, D the crucible diameter, h the height of melt in the crucible, v the kinematics viscosity of melt and d the crystal diameter. Under such conditions, Δt_R was very high and Δt_A could be neglected.

For TeO_2 crystal growth with resistance heating, Lukasiewicz *et al.* [13] proposed to introduce the axial temperature gradient in the dependence between the diameter of the crystal corresponding to the inversion of the flows in the melt and the rotation rate. In our experiments with resistance heating, both Δt_R and Δt_A play a significant role in the dependence of the critical rotation rate N_{crit}. The conditions in our experiments are described by the following equation.

$$N_{crit} = 3.18\ \{g\beta(\Delta t_A + \Delta t_R)\}^{0.44}\ D^{0.245}\ h^{0.155}\ v^{0.12}\ d^{-1.08} \qquad (2)$$

Results of calculations with the parameters (β and

Table 1
The calculated and experimental N_{crit} values from this work

Parameter	Values			
D (cm)	5.3	5.3	5.3	5.3
d (cm)	3.0	3.0	3.0	3.0
β (K^{-1})*	0.8×10^{-4}	0.8×10^{-4}	0.8×10^{-4}	0.8×10^{-4}
Δt_R (K/cm)	43	40	40	37
Δt_A (K/cm)	60	57	50	48
H (cm)	3.0	1.0	3.0	1.0
v (cm^2/sec)*	12.82×10^{-2}	12.96×10^{-2}	12.82×10^{-2}	12.96×10^{-2}
Cal. (Eq. 2) N_{crit} (rpm)	~33	~28	~31	~25
Exp. N_{crit} (rpm)	35	30	30	23

*Data from Berkowski *et al.* [12].

v) used by Berkowski *et al.* [12], and the experimented data such as the temperature gradients and so on obtained from our study are in good agreement the experimental results as shown in Table 1.

3.2. *The relation of rotation rate and interface*

Figure 4 shows the photographs of crystals grown with various rotation rates and fixed pulling rate of 2 mm/hr under different thermal configurations, and we observed the inclusions distributed in polished plates which had been cut parallel to growth axis. The crystals of (b), (c), (d) and (e) were grown under the conditions of ATD-60, and the crystal (a) was grown under those of ATD-50.

Crystals of (e) and (d) were grown at constant rotation rate, and we could observe the gradual change from convex to flat interface as the growth process proceeded. The crystal of (e) was grown at the rotation rate of 30 rpm. Because crystal diameter was small and rotation rate was slow at shouldering part, natural convection was predominant and the interface became convex. The crystal of (d) was grown at the rotation rate of 35 rpm. At shouldering part, the interface is slightly convex. In the Czochralski process, the temperature gradient is not the same throughout the crystal growth process due to the lowering of the melt level and so on. Therefore it is necessary to change the rotation rate with the lowering of the melt.

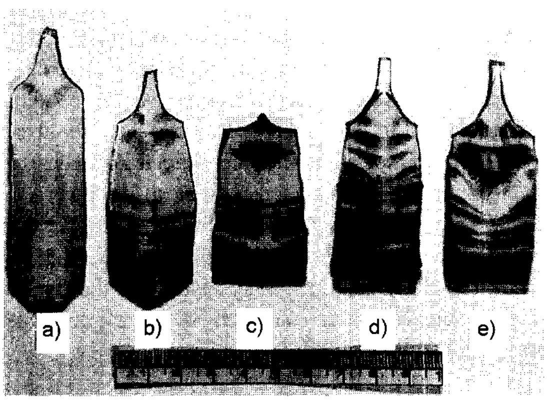

Fig. 4. Photographs of the vertically cut $Bi_4Ge_3O_{12}$ crystals grown with different rotation rates and under conditions of ATD-60 or ATD-50.

In crystals of (b) and (c), the rotation rates were changed gradually from 35 to 25 rpm and from 35 to 30 rpm, respectively as the crystal growth proceeded. Crystals with relatively flat interface were obtained, but they contained many inclusions. Feng *et al.* [6]. grew BGO crystals by Bridgman-Stockbarger method. They argued that dark-colored layer attributed to constitutional supercooling. Because the mechanism of formation of Pt inclusions is different from that of inclusions in supercooling layers when the furnace temperature was suddenly cooled, a dark-colored layer appeared in the crystal.

Under the thermal configuration of ATD-50 and the

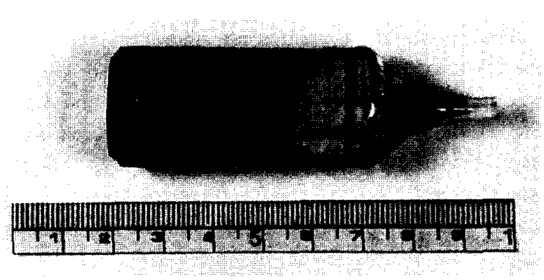

Fig. 5. Photograph of the grown $Bi_4Ge_3O_{12}$ crystal with rotation rates from 30 to 23 rpm and under conditions of ATD-50.

rotation rate change from 30 to 18 rpm, single crystal was obtained nearly without inclusions as shown in Fig. 4 (a). It was indicated that the restraining sudden cooling and the gradual slope of temperature gradient could grow free of dark-colored layer caused by the Pt inclusions. Fig. 4 (a) crystal has, however, slightly convex interface at the end part.

In summary, we could grow good crystals as shown in Fig. 5, and the growth conditions were as follows; under O_2 atmosphere with the pulling rate fixed at 2 mm/hr, rotation rate changed from 30 to 23 rpm as the crystal growth proceeded, Δt_R and Δt_A were 50 and 40°C/cm near melt respectively, the slope of Δt_A was gradual, and the composition was chemically stochiometric.

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