CHAPTER 2

GROWTH OF BGO AND BSO CRYSTALS BY CZOCHRALSKI TECHNIQUE

2.1 INTRODUCTION

The growth of large oxide crystals by Czochralski technique has attracted attention since 1960 for use in electronics industry. Several oxide crystals have been grown by Czochralski technique and this technique has the advantage of producing large, bulk, single crystals in a relatively short time with high degree of perfection. The parts fabricated from oxide crystals are used as active components in laser systems (Nd:YAG and ruby), as substrates for silicon epitaxy (Al₂O₃), for optical components (LiNbO₃ and LiTaO₃), for magnetic bubble devices (Gd₃Ga₅O₁₂), for high atomic number scintillation materials (Bi₁₂Ge₃O₁₂ and Bi₁₂Si₃O₁₂) and for holographic recording materials (Bi₁₂GeO₂₀ and Bi₁₂SiO₂₀) (Brandle 1985).

A better understanding of growth process and the material system will help in transferring the growth technology from laboratory to industry. The growth of oxide crystals requires, crystal pulling unit, large amount of power for r.f heating and use of refractory metal crucibles such as platinum or iridium to contain the molten oxide. Melting points range from a low value of 930°C for BGO and BSO to value more than 2000°C for Al₂O₃, while growth times can be as short as two days or as long as one month. Because of these factors, oxide substrates usually cost 5 to 50 times more than that of a comparable size silicon substrate.
2.2 BASIC CONSIDERATIONS

The oxide crystal growth using Czochralski technique is dependent upon

(i) a detailed understanding of the materials system and the phase relationship in the region of interest
(ii) the combination of heating system, molten oxide-crucible
(iii) the role of fluid dynamics in establishing the thermal environment and fluid flow patterns of the liquid and
(iv) the limitations imposed on the growth process

2.3 MATERIAL LIMITATIONS

When considering a material to be grown into a single crystal, by pulling technique, it should have the following properties

(i) the material should have a congruent melting point, i.e the material should not decompose upon or before melting
(ii) it should have a relatively low vapour pressure
(iii) it should not have any first order solid-solid phase transition or reconstructive phase transitions and
(iv) there must be a crucible material, which is non-reactive with the material above its melting point

2.3.1 Selection of Crucible

Once the material is chosen to be grown into single crystals by the pulling technique, the first equipment selection which must be made is the choice of a crucible and its size. Selection of crucible is based upon
(i) compatibility with the melt
(ii) melting point of the crucible material versus that of the compound
(iii) type of heating
(iv) chemical stability and
(v) mechanical properties

Fused silica is the most commonly used crucible material for growing semiconductor materials such as silicon, germanium, gallium arsenide and gallium phosphide etc. It provides the most suitable compromise between chemical stability and cost and ease of fabrication. Normally, these crucibles are used only once and are then discarded, because upon cooling, expansion of the freezing liquid causes the crucible to fracture.

For oxide crystals, which generally have higher melting points, refractory materials or the noble metal crucibles are used. The use of platinum or iridium and in special cases tungsten or molybdenum, provides the most reasonable compromise between chemical stability, ease of fabrication and mechanical strength. In oxide crystal growth, the crucible is cleaned and reused repeatedly because of the initial expenses. Some of the more commonly used materials are listed in Table 2.1
Table 2.1
Crucible materials and operating temperatures

<table>
<thead>
<tr>
<th>Material</th>
<th>Maximum Operating Temperature °C</th>
<th>Melting Point °C</th>
<th>Heating System</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum</td>
<td>1400</td>
<td>1773</td>
<td>resistance, rf</td>
</tr>
<tr>
<td>Iridium</td>
<td>2150</td>
<td>2452</td>
<td>resistance, rf</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>2300</td>
<td>2620</td>
<td>resistance, rf</td>
</tr>
<tr>
<td>Tungsten</td>
<td>2800</td>
<td>3370</td>
<td>resistance, rf</td>
</tr>
<tr>
<td>Carbon</td>
<td>3000</td>
<td>---</td>
<td>resistance, rf</td>
</tr>
<tr>
<td>Silica</td>
<td>1550</td>
<td>1700</td>
<td>resistance</td>
</tr>
<tr>
<td>Alumina</td>
<td>1800</td>
<td>2050</td>
<td>resistance</td>
</tr>
</tbody>
</table>

The second factor which must be considered is the size and shape of the crucible, for these dimensions can strongly affect the results of any crystal growth equipment. In any heated system the primary source for fluid motion within the crucible is due to liquid density changes resulting from temperature gradients. Carruthers (1976) has examined the effects of crucible geometry and orientation on convective flow and has shown that the type of fluid flow present is determined by the aspect ratio of the crucible and the thermal and viscous properties of the liquid.

The other factor which must be considered is the crystal size which can be grown from a crucible of given dimensions. Generally the final crystal diameter should be approximately 50% of the crucible diameter. When this value is exceeded, growth becomes more difficult for several reasons:

(i) Small irregularities in the crucible can produce large changes in the growth rate
the rotating crystal has a much stronger influence on the fluid flow and the stability regions for different flow types become increasingly narrow giving rise to abrupt flow transitions and consequently large temperature fluctuations (Brandle 1978; Carruthers 1976; Brice et al., 1974).

2.3.2 Heating Sources

In all crystal pulling techniques, the material from which the crystal is to be grown must be kept in the molten state. Although various unique power systems have been developed (Field and Wagner 1968; Reed and Pollard 1968) today two common sources are based on resistance heating and induction heating.

2.3.2.1 Resistance heating

Resistance heated furnaces are usually limited to the lower temperature ranges (less than 1500°C). Because of temperature and ambient gas limitations, resistance heating usually finds use in the growth of semiconductor materials and a few low melting oxides, e.g. LiNbO₃, Bi₁₂SiO₂₀, Bi₁₂GeO₂₀ and TeO₂. Higher temperatures require either special elements such as platinum-rhodium alloys or a hard vacuum operation to protect refractory metal elements from oxidation.

A special advantage of resistance heated furnaces over other types is greater electrical efficiency and therefore reduced operation costs. Also power input to the furnace, can easily be accomplished without the need for elaborate control equipment.
2.3.2.2 R.F heating or Inductive heating

The second source of heating is r.f or inductive heating and is used for the higher melting oxide crystals such as sapphire (Al$_2$O$_3$) and Gd$_3$Ga$_5$O$_{12}$ (GGG). However it can also be used for the growth of semiconductor materials. R.F generators operate in the frequency range of 250-500 kHz and a wide power range (20-100 kW). For laboratory use, a 20 or 25 kW r.f generator is suitable and provides the capability of growing crystal upto about 3 cm in diameter.

The use of an r.f generator places an additional constraint on the crucible in that it must be conductive since r.f heating induces a current flow in the crucible. The depth of current flow or penetration of the r.f field into the crucible walls is determined by the frequency and is given by

$$D = \frac{3570\rho}{\sqrt{f\mu}} \text{ cm}$$ \hspace{1cm} (2.1)$$

where
- $\rho$ is the resistivity in ohms
- $\mu$ is the permeability
- $f$ is the frequency in Hz
- $D$ is the penetration or skin depth

Of those materials listed in Table 2.1, platinum is the only one which has to be operated far below its melting point because of large changes in its resistivity with temperature as one approaches its melting point. This causes localised 'hot spots' to develop in the crucible wall which can result in crucible failure. Because, such crucible defects as small cracks, impurities in grain boundaries, and variation in wall thickness can cause localised resistivity changes, the physical condition of the crucible is much more important in r.f heating than in resistance heating. One method of reducing these effects is to use lower frequencies and thereby increase the
'skin depth'. This reduces the effect on resistivity of crucible imperfections and therefore provides more uniform heating of the crucible.

Another factor which must be considered in r.f heating is load matching. Improper matching of the loaded work coil to the tank circuit can cause an enormous loss of efficiency.

2.3.3 Furnace Construction

The furnace which is used for crystal pulling can vary from the very simple, e.g., a resistance wound heating element, to one which is extremely complex, because of thermal and chemical constrains placed upon it by the crystal. These furnaces can also be divided into two types. The first type is for oxide crystal growth and is generally composed of ceramic and noble metal parts whereas the second type is the semiconductor growth and is usually composed of graphite and fused silica parts.

2.3.3.1 Resistive heating furnace

A typical resistive heating furnace which is used by the author, for the growth of oxide crystals Bi₁₂GeO₂₀, Bi₁₂SiO₂₀, Bi₄Ge₃O₁₂ and Bi₄Si₃O₁₂, is shown in figure 2.1. The furnace mounted on a ceramic base is the outer sleeve, loose granular insulation followed by an inner ceramic tube (Al₂O₃ or ZrO₂). The choice of Al₂O₃ or ZrO₂ depends on the operating temperature. A second base or pedestal is placed inside this inner tube to position the crucible within the furnace. A coil (Kanthal or Nichrome) outside the silica sleeve completes the assembly. An enclosure is then placed around the furnace to provide atmosphere control. The detailed growth procedures for growing Bi₁₂GeO₂₀, Bi₁₂SiO₂₀, Bi₄Ge₃O₁₂ and Bi₄Si₃O₁₂ are discussed in the proceeding portions of this chapter.
Figure 2.1 Resistive Heating Furnace
2.3.3.2 R.F heating furnace

In contrast to the furnace discussed above, a typical rf semiconductor furnace is shown in figure 2.2. An outer sleeve of fused quartz is placed between the rf work coil and the carbon susceptor. The susceptor has been machined so that a fused quartz crucible will fit inside. A thermocouple for temperature control is kept in the centre of the carbon susceptor. The entire assembly can be raised or lowered and rotated within the work coil of the rf generator.

2.3.4 Growth Rate or Geometric Effect

The successful growth of a crystal using a crystal pulling technique is dependent upon the interaction of many variables such as pulling rate, rotation rate and thermal geometry to produce the desired crystals.

The growth of an oxide crystal in the Czochralski geometry is schematically represented in figure 2.3. Unlike semiconductor growth, the crucible and furnace remain stationary during the growth cycle, therefore the effect of the liquid level drop on the actual growth rate of the crystal must be considered. Using a mass balance and assuming a flat crystal growth interface with a circular cross section, one can obtain the variation of crystal growth rate with crucible diameter and density (Brandle 1985).

\[ \frac{h}{P} = \frac{x}{x-D^2} \]  

(2.2)

where  
\[ h = \text{actual growth rate} \]  
\[ P = \text{pull rate} \]  
\[ x = \text{ratio of liquid to solid densities} \]  
\[ D = \text{ratio of crystal diameter to the crucible diameter} \]
Figure 2.2  Radio frequency semiconductor furnace
Figure 2.3  Parameters for calculating the crystal growth rate for an oxide Czochralski system (Brandle 1985)

Figure 2.4  Dependence of the relative growth rate on the crystal/crucible (D) ratio for various values of x (Brandle 1985)
The relative change in growth rate \((h/p)\) as a function of the crystal/crucible diameter ratio \((d)\) is shown in figure 2.4 for various values of \(x\). As can be seen from the figure 2.4, \(h/p\) begins to increase quickly as \(D\) exceeds 0.5 for \(x\) values in the range 0.7 to 0.9 (typical oxides). For this reason, typical values of \(D\) for oxide growth are usually 0.5 or less in most commercial operations so that problems associated with growth rate fluctuations are minimised.

Using the equation (2.2) the actual growth rate \((h)\) of the crystal can be estimated. This estimate can be used as a guideline for changes in pull rate due to a change in the crucible size. In this manner, one is assured that the linear growth rate of the crystal will be the same when the growth is scaled from one crucible size to another.

In most Czochralski geometries used in oxide growth, an aspect ratio (height to diameter) of approximately one for the crucible appears to be a good compromise between thermal geometry, melt volume and metal utilisation. The crucible aspect ratio produces a liquid depth which is approximately 0.8 times the crucible diameter. As pointed out by Whiffin and Brice (1971), this ratio has the most pronounced effect on thermal oscillations in the liquid and flow structure.

### 2.3.5 Thermal Gradient Effect

Once a power supply and heat source have been selected along with the crucible material, the placement of the crucible within the 'hot zone' of the furnace can result in success or failure. One of the prerequisites for good control of the growth operation is a suitable thermal gradient. This thermal gradient is classified into external and internal thermal gradients. An external thermal gradient is defined as one which is outside the crystal or crystal growing medium whereas an internal thermal gradient is within the crystal or crystal growing medium. For example, the vertical gradient in an
after-heater would be an external gradient and that present in the liquid or crystal is an internal gradient.

It is not completely possible to separate the internal from the external gradients; however, some degree of independence can be achieved by a proper selection of the method of heating. Most resistance heated furnaces tend to have a long hot zone since heat is supplied not only to the crucible but to the surrounding furnace parts as well. This leads to fairly uniform heating of the crucible and therefore low liquid thermal gradients. Small changes of the position of the crucible within a resistance furnace have little effect on the internal or liquid gradient since all gradients are determined by that produced from the resistive elements.

In r.f. heating, heat is supplied only to the crucible walls and any heating of the furnace bottom and walls is by conduction or radiation from the hot crucible. This results in much higher internal and external thermal gradients. It also gives a certain degree of independence which cannot be achieved using a resistance furnace. This independence has been shown by Brandle and Miller (1974) in the growth of LiTaO₃. By changing the position of the crucible with respect to the coil, they were able to alter the vertical liquid gradient without appreciably changing the external vertical and radial gradients. They also found that this liquid gradient greatly affected the quality of the resultant crystal. Thus crucible placement, particularly in the rf furnace system, can significantly alter the growth environment of the crystal.

One of the concerns in a crystal pulling system is that of thermal gradients. As a direct result of the liquid thermal gradients, density gradients are generated and bulk fluid flow results within the crucible. Fluid flow can be classified into two broad areas: (1) natural convection wherein the driving forces for fluid motion are density gradients created by local temperature differences. (2) forced convection wherein the driving
forces for the fluid flow are mechanical in origin and are usually due to crystal/crucible rotation. In all crystal pulling systems, either one or both of these convective forces exist and it is the interaction of these forces which can determine the growth and perfection of the crystal (Gopalakrishnan et al., 1993a, 1993b, 1993c, 1995; Krishnamurthy et al., 1993; Yin Chun Hou 1991; Gabriel Gevay 1987; Miyazawa 1980).

The height of the fluid within the crucible also have pronounced effects on thermal oscillations. This is the common phenomena in all oxide crystal growth. Krishnamurthy et al. (1994) studied the change in the temperature in the crucible when the melt depth is reduced as the crystal is being pulled. According to their measurements (45 mm diameter and 50 mm height platinum crucible) the temperature gradually rises until a critical melt height \( h_c' \) is reached, then decreases until a second critical melt height \( h_c'' \) is reached, after which a slight rise occurs. Whiffin and Brice (1971) have pointed out that the thermal stability of the fluid can be increased considerably by positioning baffles within the liquid. The most stabilizing effect resulted when the baffle was positioned between \( h = d_1/3 \) and \( h = 2d_1/3 \), (\( d_1 \) = liquid depth and \( h \) = baffle depth). Taking into considerations of all above discussed factors the author has optimised the growth conditions for BGO and BSO crystals.

2.4 GROWTH OF BGO AND BSO CRYSTALS

2.4.1 Growth of \( \text{Bi}_{12}(\text{Ge},\text{Si})\text{O}_{20} \) crystals

The imperfections, yellow colour formation and precipitation, which are the inherent properties of BGO and BSO crystals, affect the device performance of the crystal considerably. Takagi et al. (1981) refer to the precipitates as shrinkage voids, but according to them the number of voids increases when the deviation from stoichiometry is as small as 0.6 mol\% and certain impurities have ionic radii different from those of Bi\(^{3+}\) and Ge\(^{4+}\).
Barnes (1984) showed that the incorporation of impurities into the BGO crystal is strongly dependent on geometrical considerations.

In principle, BGO and BSO crystals are grown using the melt technique. Since the RF heating gives rise to sharp temperature gradients at the interface (Martinezlopez et al., 1993), single crystals of Bi$_{12}$GeO$_{20}$, Bi$_{12}$SiO$_{20}$, Bi$_4$Ge$_3$O$_{12}$ and Bi$_4$Si$_3$O$_{12}$ were grown by indigenously developed Czochralski puller (shown in figure 2.5 and 2.6) using resistive heating furnaces with platinum crucibles (45 mm diameter and 50 mm height) that contained the charge and were placed in the centre of the ceramic core wound with Kanthal wire. A chromel-alumel thermocouple was placed at the base of the crucible and temperature was maintained by the temperature controller.

The starting materials were of high purity bismuth trioxide (Bi$_2$O$_3$) (99.99%) and germanium dioxide (GeO$_2$) (99.999%) or silicon dioxide (SiO$_2$) (99.999%). They were mixed in the mole ratio Bi$_2$O$_3$:(Ge,Si)O$_2$ = 6:1 and melted (930°C) in the platinum crucible. The molten liquid has been soaked for 12 hours for homogenisation. To confirm the melting temperature of the synthesised materials (homogeneity) of BGO and BSO, differential thermal analysis (DTA) was performed (figure 2.7). After verifying the homogenisation of these materials, single crystals were first obtained on a platinum wire, which were then pulled to small diameters. After growing the small size crystal, the necking process was adopted and the growth continued. Specific orientations, such as <100>, <110> and <111> were obtained using seeds cut from grown boules. Different rotation rates of the seed were employed. The effect of rotation rate on the quality of the crystals has been studied in the light of existing literature.

In the growth of oxide crystals like BGO and BSO, certain difficulties arise that do not occur in the growth of semiconductors. Thus, we can expect two types of difficulties during the growth of BGO and BSO.
Figure 2.5  Schematic arrangement of the experimental set up of Czochralski technique
Figure 2.6 Czochralski crystal puller
SCAN RATE: 10 c/min.
ATMOSPHERE OXYGEN 50 cc/min.

A = Bi$_2$SiO$_{20}$
B = Bi$_2$GeO$_{20}$

Figure 2.7 DTA spectrum of Bi$_2$GeO$_{20}$ and Bi$_2$SiO$_{20}$
crystals. One is caused by fluid flow transition from free convection to forced convection. On transition, the interface shape changes from convex to concave in the melt. The other difficulty is caused by a thermal asymmetry around the crystal, assisted by a low temperature difference between the crystal and crucible when the forced convection is dominant in the melt. To overcome the interface shape change from convex to concave, the crystals should be grown under the conditions where either free convection or forced convection is dominant in the melt. The interface shape will be convex for the former and concave for the latter.

Gas bubble entrapment is another serious problem encountered in the Czochralski pulling of a wide range of oxide single crystals, creating optical inhomogeneity in the crystal. The oxide materials have high viscosity and low diffusivity (Miyazawa 1980, Kobayashi 1981), and so gas diffusion into the liquid is much less. When the concentration of the gaseous particles becomes sufficiently high, gas bubble may nucleate. The bubble will then grow and may either be incorporated into the crystal or float away. According to Miyazawa (1980), when forced convection is made dominant in the melt, bubbles will not get incorporated into the crystals. Fluid flow convection modes were recognised from simulation experiments (Miyazawa and Kondo 1973) when the rotation rate is relatively low, the natural convection going downward just near the interface is predominant. On the other hand, when the crystal rotation rate is high, forced convection stronger than the natural convection is produced. The forced convection is caused by a stream of hot liquid inside the melt forcing towards the interface.

When the crystal rotation rate is relatively low, which results in a strong natural convection flow thereby making the interface convex, the gas surplus liquid goes down along the axis of rotation. The gas surplus liquid is concentrated in the central part of the melt adjacent to the interface. When the crystal rotation rate is increased, the gas surplus liquid spreads
a little bit over the growing interface and the resultant entrapment of gas bubbles is laid according to an alteration of supersaturation of rejected gases and nucleation of new gas bubbles acting as sinks. Further increase in the rotation rate causes the solid-liquid interface to become first flat, then concave (Miyazawa and Kondo, 1973). The gas surplus liquid is taken away from the interface by the increased rotation rate, thus bubble free crystals can be obtained (Gopalakrishnan et al., 1993a, 1993b, 1995c).

The crystal rotation rate and pulling rate employed during the growth determine the quality of the crystals (Gospodinov and Doshkova 1994). Crystals grown with the rotation rate of 5 to 15 rpm corresponding to free convection were found to have gas bubbles entrapped. These crystals were cut perpendicular to the growth axis and observed through the scanning electron microscope. The photographs (figures 2.8a and 2.8b) show the gas bubbles in the grown crystals of Bi$_{12}$GeO$_{20}$ and Bi$_{12}$SiO$_{20}$. These bubbles will lead to optical inhomogeneity in the crystal. But for the rotation rate between 15 to 35 rpm, the growth becomes very difficult. This rotation rate is called 'Middle danger rotation rate' (Yin Chun Hou 1991, Krishnamurthy et al., 1993). When the rotation rate is increased to the range 35 to 45 rpm, good quality crystals are obtained. We correlate this growth sequence with fluid flow simulated by Whiffin et al (1976) and attributed the existence of middle danger rotation rate to the coexistence of both free and forced convection which makes the flow not conducive for crystal growth. A further increase resulted in cracks. The diameter has been maintained at 15 mm and the growth rate 1-3 mm/hr. Thus in our case, Bi$_{12}$GeO$_{20}$ and Bi$_{12}$SiO$_{20}$ crystals of 15 mm diameter and 40 mm length have been grown (figures 2.9a and 2.9b) (Gopalakrishnan et al., 1993a, 1993b).

The grown crystals were characterised by Laue and powder X-ray diffraction analysis (figures 2.10 and 2.11) to confirm their single crystallinity and structure, respectively. The observed X-ray powder data for
Figure 2.8a SEM micrograph showing gas bubbles in Bi$_2$GeO$_2$O$_2$ crystal

Figure 2.8b SEM micrograph showing gas bubbles in Bi$_2$GeO$_2$O$_2$ crystal

Figure 2.9a Bi$_2$GeO$_2$O$_2$ crystal

Figure 2.9b Bi$_2$SiO$_2$O$_2$ crystals

Figure 2.12 Homogeneous distribution of bismuth in Bi$_2$GeO$_2$O$_2$ crystal

Figure 2.13 Non-uniform distribution of bismuth in Bi$_2$SiO$_2$O$_2$ crystal
B$_{12}$GeO$_{20}$ and Bi$_{12}$SiO$_{20}$ is in good agreement with the ASTM data. The stoichiometry of the grown crystals has been confirmed by electron probe microanalysis (EPMA). To establish the effect of rotation rate on the quality of the crystal, Electron probe microanalysis has been made with Bismuth germanium oxide (BGO) grown at rotation rate 35-45 rpm, which indicates homogeneous distribution of bismuth as shown in figure 2.12. Figure 2.13 shows the inhomogeneous distribution of bismuth in bismuth silicon oxide (BSO) grown at the rotation rate of 15-35 rpm. This may be due to the presence of fluid flow due to the coexistence of free and forced convections and non-uniform radial temperature distribution in the melt (Gopalakrishnan et al., 1993b).

2.4.2 Growth of Bi$_4$(Ge,Si)$_3$O$_{12}$ crystals

The starting materials were of high purity bismuth trioxide and silicon dioxide or germanium dioxide. They have been mixed in the mole ratio Bi$_2$O$_3$:(Si,Ge)O$_2$ = 2:3 and melted (1050°C) in the platinum crucible. To confirm the melting temperature of the synthesised materials (homogeneity) of Bi$_4$Ge$_3$O$_{12}$ and Bi$_4$Si$_3$O$_{12}$, differential thermal analysis (DTA) has been performed (figure 2.14). The growth procedure employed for these crystals is the same as that discussed earlier for Bi$_{12}$GeO$_{20}$ and Bi$_{12}$SiO$_{20}$ except the operating temperature of the furnace (1050°C) (Gopalakrishnan and Ramasamy 1995). The voids and gas bubbles observed in Bi$_4$Ge$_3$O$_{12}$ and Bi$_4$Si$_3$O$_{12}$ are shown in figures 2.15a and 2.15b. Figures 2.16a and 2.16b show the crystals of Bi$_4$Ge$_3$O$_{12}$ and Bi$_4$Si$_3$O$_{12}$. The X-ray diffraction pattern of the above crystals are shown in figures 2.17 and 2.18. For all the growth runs, the chemicals used, were purchased from the same manufacturer.
Figure 2.10 XRD Pattern of Bi$_2$GeO$_{2}$o
Figure 2.11 XRD Pattern of Bi$_2$SiO$_5$
SCAN RATE = 10.00 c/min
ATMOSPHERE: OXYGEN 50 cc/min

A = Bi$_4$Ge$_3$O$_{12}$
B = Bi$_4$Si$_3$O$_{12}$

Figure 2.14 DTA spectrum of Bi$_4$Ge$_3$O$_{12}$ and Bi$_4$Si$_3$O$_{12}$
Figure 2.15a SEM micrograph showing gas bubbles in $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ crystal

Figure 2.15b SEM micrograph showing gas bubbles in $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ crystal

Figure 2.16a $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ crystal

Figure 2.16b $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ crystal
Figure 2.17 XRD Pattern of Bi$_4$Ge$_3$O$_{12}$
Figure 2.18 XRD Pattern of Bi$_4$Si$_3$O$_{12}$
2.5 MICROSCOPY OBSERVATIONS OF BSO (Bi$_{12}$SiO$_{20}$) CRYSTALS

In order to study the effect of higher pulling and rotation rates on the quality of the crystals, Bi$_{12}$SiO$_{20}$ has been grown and microscopic observations made on this crystal.

An attempt was made to grow crystals (with the platinum crucible 45 mm diameter and 50 mm height) by employing a rotation rate of 65-70 rpm and pulling rate of 6-7 mm/hr. No crucible rotation was employed, and the (100) oriented crystals were grown in an open atmosphere. The transverse sections of the BSO crystals were investigated by optical and scanning electron microscopy (SEM). The SEM picture (figure 2.19) shows the existence of inclusions with a local change in colour in the metastable phases. These areas of the crystal were analysed by electron probe microanalysis (EPMA) which revealed compositional non-uniformity in various places. The dark bands are due to a higher impurity concentration or compositional change and imply a variation in the melt composition ahead of the interface, which suddenly freezes (Picone, 1988).

Optical microscopy reveals the presence of precipitates in the form of thin threads (figure 2.20). During growth the precipitates align with the melt flow direction at the solid-liquid interface. The precipitates that are continuous and aligned longitudinally, parallel to the growth axis, are due to constitutional supercooling during growth (Horowitz and Kramer, 1986). Unless the crystallisation and cooling are carried out very slowly, bismuth silicate (germanate) is likely to end up with crystals of higher SiO$_2$ (GeO$_2$) concentration. The density and viscosity of the melt determined as functions of the temperature and composition have been reported (Tananaev et al., 1978). The existence of two structural phases for the Bi$_2$O$_3$-GeO$_2$ system has been reported by Dickinson et al (1972). From these data and from the correlation between melt superheating and from the formation of metastable
Figure 2.19 SEM picture showing inclusions in Bi$_2$SiO$_2$O.

Figure 2.20 Precipitates in Bi$_2$SiO$_2$O (250X).

Figure 2.21 Surface of the as-grown Bi$_2$SiO$_2$O showing striations (250X).

Figure 2.22 Microcracks observed in Bi$_2$SiO$_2$O (250X).

Figure 2.23 Cracked and twinned Bi$_2$SiO$_2$O crystal.

Figure 2.24 Faceting morphology in Bi$_2$SiO$_2$O (400X).
phases (Tananaev et al., 1978, Dickinson et al., 1972) it was concluded that upon melt heating, crystallisable melt structural units - which are necessary for solidification of the stable phases- are destroyed, and high - temperature melt structural units favour the precipitation of the unstable phases (Tananaev et al., 1978; Zhereb et al., 1978; Van Enckevort and Smet 1987).

In the case of crystal growth of BGO and BSO, high growth rates and / or unstabilised thermal configuration cause metastable (non-stoichiometric) phases to precipitate (Gopalakrishnan et al., 1993c). For the higher rotation rate and for the faster pulling rate, the flow pattern in the melt is in different directions. The optical microscopic picture (figure 2.21) of the surface of the grown crystal shows growth striations, which indicate the absence of time-dependent convective flow in the melt.

When the rotation and pulling rates of the crystals are too high, microcracks appear in the crystals. Figure 2.22 shows the microcracks in the grown crystals, created owing to stress during fast solidification. The longitudinal cracks propagate during annealing. When the rotation rate is low, free convection is dominant and the solid-liquid interface becomes convex. If the rotation rate is increased further, the solid - liquid interface shape becomes flat owing to forced convection in the melt. Finally, when the rotation rate is very high, forced convection is dominant and the solid-liquid interface shape becomes concave; the solid-liquid interface shape changes from flat and slightly concave to more concave, and the possibility of getting cracks, twinning and core formation in the crystals is greater. The cracked and twinned crystal of Bi$_{12}$SiO$_{20}$ is shown in figure 2.23. If the pulling rate, rotation rate and temperature distribution of the furnace and crucible are not synchronised, the possibility of obtaining good quality crystals is low.

Bismuth silicon oxide crystals grown over a wide range of conditions show a pronounced tendency to facet. According to Kobayashi (1981), in crystals like BSO and BGO, if free and forced convection coexist
in the melt, a wide supercooled region spreading from the crystals toward the crucible walls will appear on the melt surface. Figure 2.24 shows the typical faceting morphologies of the BSO crystals observed through optical microscopy. When the rotation rate is low, cylindrical crystals are formed. When the rotation rate is greater than 35 rpm, faceted crystals with rectangular cross sections are predominant. According to Picone (1988), the solid-liquid interface gradually flattens out, owing to the change in the melt convection, when the rotation rate is increased. At the critical rotation rate, a flat interface occurs and the flow patterns are not regular, leading to instabilities in the core position. At high rotation rates the interface shape and convection patterns will tend to push the compositional variations toward the edge of the crystal, and highly faceted crystals are obtained. Correlating the results of the author with those of Picone (1988) and Tanguay et al (1977), it is concluded (Gopalakrishnan et al., 1993c) that the precipitation, metastable phases, core formation, faceting and microcracks observed, are due to very high pulling rate (6-7 mm/h) and rotation rate (60-70 rpm) employed.

2.6 CONCLUSION

A number of good quality single crystals of BGO and BSO have been grown by Czochralski technique. The effect of rotation rate and pulling rate on the quality of the crystals has been studied. The factors responsible for gas bubble incorporation into the crystal, precipitation, metastable phases, core formation, faceting and microcracks have been explained in the light of the existing literature.