CHAPTER 3

GROWTH OF BGO AND BSO CRYSTALS BY FLOATING ZONE TECHNIQUE

3.1 INTRODUCTION

Floating zone method is essentially zone melting in a vertical configuration without a container. Zone melting is a generic term introduced by Pfann for a family of crystallization techniques. Different zone melting techniques have in common the following feature: "A zone is created by melting a small amount of material in a relatively large or long solid charge or ingot and it is then made to traverse through a part or whole of the charge". The stunning simplicity of this concept makes it responsible for many of the spectacular advances in almost every branch of solid state science.

Zone melting is one of the most powerful non-conservative techniques (the dissolution of the source compensates the consumption of a crystallizing material) that is used for purification and growth of single crystals of several materials.

The two commonly used variations of temperature gradient zone melting (TGZM) are the travelling solvent method (TSM) and Travelling heater method (THM). In both the methods, a liquid zone bounded by two solid layers moves in the direction of increasing temperature. The basic difference between these two methods of zone migration is in the application of heating source to the growth configuration. In TSM a temperature
gradient is applied across the entire slab configuration and the liquid zone migrates under its own driving force. In THM a temperature gradient is applied across the liquid zone and migration is sustained through slow motion of the heating source. From the physical arrangements of both systems, it follows directly that the THM should lend itself to the growth of much larger crystals than that the TSM would, since the material is always at a lower temperature than is the zone during the THM experiment. The THM has been applied to the growth of a range of materials. A good example of successful crucibleless THM growth is the preparation of single crystals of Calcite from their solution in CaCO₃, LiCO₃ eutectic melt as reported by Brissot and Belin (1971). In their experiments the eutectic solvent zone is heated and moved upwards through a sintered calcium carbonate rod by means of a perforated platinum heater strip embedded in the solvent zone. Modification of the travelling heater method is a heating strip which moves with the molten zone through the crystal bowl. A travelling strip heater was first used by Gasson et al (1967) to grow calcium tungstate crystals doped with neodymium and the method was modified to work as a travelling solvent zone method by Belin (1976) to grow calcite crystals using lithium carbonate flux.

The advantages of resistance heating or metal strip heater technique are its low capital cost (compared to other heating sources), the ability to make self-supporting heaters of complex shapes. In travelling zone method, the molten zone will be maintained between the feed rod and the seed crystal. The seed may be either a single crystal grown from pure melt using some other technique or a highly sintered rod (more than 75% of the density of the crystal). To maintain a flat interface at the growing end, a platinum heating strip with holes in a circular configuration, located at the centre is used. By very slow movement of either the heater or the seed-feed system, the materials get melted (dissolved in the molten solvent), and
growth takes place over the seed. In this technique, crystals can be grown at temperatures well below their melting point.

3.2 THEORY OF ZONE MELTING

The successful zone melting process depends on the understanding of the mechanism responsible for solute's (a soluble impurity) redistribution in processes involving a solid-liquid interface. During the zone melting process, the solute particles travel through the sample either in the same or opposite direction to the motion of zone. It depends on whether the distribution coefficient is less or greater than one. So the key parameters which need to be defined first are distribution coefficients.

The distribution of an impurity between the melt and the crystal is usually expressed by the equilibrium distribution coefficient $k_0$. The equilibrium distribution coefficient, defined first by Pfann, is the ratio of the concentration of the solute in the solid $C_s$ to that in the liquid $C_l$ when the solid and liquid phases are in equilibrium at temperature $T$. It follows that the first solid to appear would have the composition

$$C_s = k_0 C_l$$

(3.1)

The value of $k_0$ is less than unity when the addition of solute raises the melting point.

The expression for the equilibrium distribution is applicable only when (i) mixing of the solute with molten liquid zone is complete (ii) there is no diffusion in the liquid (iii) a steady growth rate is employed and (iv) the solid-liquid interface is planar and normal to the macroscopic direction of solidification. But in real zone melting process, the solidification does not take place at equilibrium conditions and hence it is pertinent to define two more distribution coefficients.
When the mixing in the liquid solution is imperfect and $k_0 < 1$, it is necessary to define the interface distribution coefficient separately because the rate of rejection of the solute with advancing solidification is much higher than the rate of diffusion of the solute in the liquid. The interface distribution coefficient $k^*$, defined as the ratio of the solute concentration in the solid to that in the liquid, at the interface is given as

$$k^* = \frac{C_s}{C_{l(0)}}$$

where $C_{l(0)}$ is the concentration of solute adjacent to the interface. Carruthers and Nassau (1968) have experimentally shown that in general, at non-zero growth velocities, the interface coefficient $k^*$, which is a function of the velocity of solidification, is different from the equilibrium coefficient.

The relation for the solute incorporation into the solid by means of exchange reactions across the solid-liquid interface is given as

$$k^* = \frac{k_0 + f(1-k^*)}{\beta v} \quad (3.2)$$

where $f$ is the velocity of growth, $\beta$ is the dissociation coefficient of the observed solute molecule at the interface which describes the molecules leaving the interface and incorporating into the liquid and $v$ is the molecular velocity of diffusion of the solute.

At non-zero growth velocities in practical crystal growth methods, the overall incorporation of solute into the solid can be defined by the effective distribution coefficient $k_{eff}$ or $k$. The $k_{eff}$ is defined as the distribution coefficient, that is measured after solidification under a given set of experimental conditions. Hence $k_{eff}$ must be the function of such parameters as growth rate, the degree of mixing (or the degree of stirring), diffusion of the solute in the liquid and the concentration of the solute. The
Burton, Prim and Slichter (BPS) equation relating $k_{\text{eff}}$ to the conditions of crystallization based on solid-liquid reaction is mainly dependent on diffusion governed transport process (Burton et al., 1953).

$$k_{\text{eff}} = \frac{k_0}{[k_0 + (1+k_0)e^{-\Phi}]}$$

where $\Phi = \frac{\delta D}{\delta}$, $\delta$ is defined as the thickness of a layer in which solute transport is diffusion controlled and $D$ is the diffusion coefficient of the solute assumed to be independent of concentration. As the quantity $(\delta/D)$ characterizes the nature of an experimental crystallization process, the above equation has been widely used in the analysis and interpretation of solidification process. While the diffusion coefficients are not generally known accurately, the quantity $\delta/D$ can be obtained experimentally by measuring $k$ for crystals grown at different velocities with identical stirring conditions. Such experiments are analysed by plotting $\ln(1/k_{\text{eff}})$ against the growth velocity $f$, giving a straight line whose slope is $(-\delta/D)$.

3.3 EXPERIMENTAL ASPECTS OF ZONE MELTING

The essential experimental characteristics of the zone melting apparatus are

i) a means of mounting or holding the charge

ii) a heat source to melt the sample

and

iii) a traverse mechanism for the transport of molten zone.

In addition, the apparatus may incorporate a device meant for stirring the liquid, to maintain constant or controlled ambient atmosphere and temperature conditions particularly at the solid-liquid interface. The work chamber with easy access for setting up good visibility during growth, permanent and accurate alignment of the upper and lower chucks and the power source are also essential.
3.3.1 Container

With respect to the container, the zoning may be divided into two categories, as zoning within a container and zoning without a container.

3.3.1.1 Zoning within a container

In this method zone melting is possible with container made up of a suitable material. The container should be selected in such a way that it does not react with the melt, and is capable of withstanding the strain developed by the molten charge during solidification and is available for holding the charge.

3.3.1.2 Zoning without a container

There are two methods, Verneuil and Floating zone melting (FZM) which are not having any container for the growth of a variety of crystals. The complete absence of container eliminates the melt - crucible interface that causes spurious nucleation and contamination due to differential expansion of single crystal and crucible.

The well perfected method in zone melting is that one without a container as is the Floating zone method. An idealised floating zone is a cylindrical column of melt with free cylindrical surface held by surface tension forces between two solid rods of the same material. The floating zone technique was originally developed by Keck and Golay (1953) and was then used by others (Balbashov and Egorov 1981; Kun et al., 1982) for the preparation of high purity oxygen free silicon, for a variety of high melting refractory materials (Field and Wagner 1968) and semiconducting compounds (Johnson 1963). Recently floating zone melting technique has proved to be an effective method in growing single crystals of metals (Hayashi et al., 1974), transition metal compounds
(Nrlund Christensen 1976), refractory borides (Tanaka et al., 1975) carbides (Otani et al., 1983) and peritectic compounds (Shindo et al., 1979).

3.3.2 Heating source

Since the temperature gradient at the interface is an important factor in solute distribution, the design of heating system assumes a greater significance as it determines the efficiency of the overall zoning apparatus. The heating source is of central importance in zone melting. A wide variety of heating systems such as electron beam heating, laser / infrared heating and resistance heating have been used for producing a small molten zone.

3.3.3 Traverse mechanism

The movement of a liquid zone along the length of a charge may be effected either by keeping the charge stationary and moving the heater or by keeping the heater stationary and moving the charge to produce a molten zone. The main requirements to be satisfied by different kinds of drive mechanism are the flexibility (e.g., variable speed) and constancy of motion. While growing single crystals, smooth motion must be maintained.

For oxides and other materials, a resistive metal strip heater with holes has been used to maintain a molten zone in a sintered rod. By allowing the passage of the melt through the holes of the strip, the molten zone can be made to traverse up or down the sintered rod by moving the strip. Gasson et al. (1967) have successfully grown CaWO₄:Nd³⁺ using iridium strip with a circular depression having two holes as a heating source to melt the materials. Later, Brissot and Belin (1971) and Belin (1976) have grown optical quality large synthetic calcite (CaCO₃) single crystals by this method, using platinum strip as a heater. Similarly Henson and Pointen (1974) and Turner (1982) have grown large size Ba₀.₆₅Sr₀.₃₅TiO₃ and BaTiO₃ single crystals using the strip heater.
3.4 STABLE GROWTH CONDITIONS

The unstable growth conditions affecting the quality of the crystal can be eliminated by establishing stable growth condition either by trial and error or by the application of theoretical principles. The conditions for stable growth of a crystal by floating zone melting depends on many factors such as, solid-liquid interface, constitutional supercooling, rotation rate, pulling rate and zone length.

3.4.1 Solid-liquid interface

The shape of the freezing and melting interface critically influences the kinetics and morphology of the growing crystal. The shape of the melt-interface varies with various growth parameters such as the nature of heat flow pattern and growth and rotation rates. The interface shape reflects the radial temperature profile at the crystallization front. For example, when the temperature at the centre of the interface is higher than that at the periphery, the interface becomes concave towards the melt. But, when the temperature at the centre of the interface is lower than that at the periphery, the interface becomes convex towards the melt. A highly curved interface results in a large thermal stress in the pulled ingots and also a non-uniform dopant distribution across the interface. A large thermal stress in a pulled ingot results in plastic deformation and the generation of dislocations. Hence the growth of large crystals of good quality from melt requires flat solid-liquid interface.

3.4.2 Constitutional supercooling

The growth conditions are very stable when the melt is everywhere above its equilibrium liquidus temperature. If the actual temperature gradient is less steep, a region in the melt could exist where the actual temperature is below the equilibrium liquidus temperature and this region
is said to be constitutionally supercooled. The planar growth surface becomes unstable under these conditions. Due to this constitutional supercooling, the crystalline perfection rapidly degenerates into massive array of dislocations, grooves (dendritic growth) and striations. For a given solute concentration in the melt, a slow growth rate, good stirring, uniform heating and steep temperature gradient above the equilibrium liquidus temperature avoid the constitutional supercooling.

3.4.3 Effect of rotation and growth rates

In crystal growth from the melt using the floating zone technique, rotation of the rods is normally applied in order to achieve an axisymmetric temperature distribution and liquid mixing of the zone. The tungsten and molybdenum crystals grown by floating zone technique with electron beam heating under high vacuum without crystal rotation have shown axial and radial inhomogeneities. The effect of rotation has been studied by many authors (Chun 1980; Eyer and Leiste 1985; Fowlis and Roberts 1986). Kobayashi (1984) has studied the effect of fluid rotation on thermocapillary convection for various combinations of the crystal and feed rod rotation. Rotation induces forced convection in the floating zone which interacts with thermocapillary convection. In the presence of a high fluid rotation, thermocapillary convection is confined to a thin layer near the free surface, whereas forced convection due to rotation occupies the zone interior. A suppression of oscillatory thermocapillary convection achieved either by single rotation, iso-rotation or counter rotation leads to the growth of homogeneous crystals.

Normally lower pulling rate is adopted for the growth of single crystals of oxides by floating zone technique (Gopalakrishnan and Ramasamy 1994). The multielemental compounds require a longer time to attain equilibrium condition, that is possible only at lower pulling rates. At higher growth rates, a large amount of latent heat is evolved and hence the
large amount of supercooling is required. This obviously represents an unstable situation since any protrusion on the solid-liquid interface can grow more readily than neighbouring regions.

3.4.4 Zone length

The molten zone length 'l' is one of the most important operational parameters as it appears in nearly all the equations of zone melting. It is often desirable to express the total ingot length 'L' in terms of a multiple 'm' of the zone length, i.e

\[ L = lm \] (3.4)

In practice the values of m less than 5 are not very useful for the growth of single crystals.

3.5 APPARATUS DESCRIPTION

A schematic diagram of the floating zone apparatus using platinum strip heating element adopted for the growth of Bi₄Ge₃O₁₂, Bi₄Si₃O₁₂, Bi₁₂GeO₂₀ and Bi₁₂SiO₂₀ single crystals, is shown in figure 3.1.

The floating zone apparatus consists of a growth chamber ‘A’ enclosed either by stainless steel bell jar or glass bell jar. The bell jar, resting on a rigid metal base ‘B’ can be tightly fitted with the base. The sectional view of the growth chamber enclosed with stainless steel bell jar and the expanded growth regions with hole configuration in the platinum strip are shown in figures 3.2 and 3.3 respectively. The stainless steel chamber is provided with two windows to observe the growth. The good visibility of the bell jar enables one to have a close watch at the growing crystal.
Figure 3.1 Schematic diagram of floating zone apparatus
Figure 3.2 The cross-sectional view of a growth chamber of floating zone apparatus
Figure 3.3 The growth region and the best strip hole configuration of the FZ apparatus
The most important part of the growth chamber is the copper electrodes 'R' fixed on ebonite insulator at the base to which a high current/low voltage source is connected by thick copper bars through a step down transformer. The platinum strip with holes 'P' is firmly clamped by screws 'Q' to these copper electrodes. The holes made at the centre of the platinum strip connect the molten zone 'm' on both sides of the strip thereby providing facility for material transport from the feed zone to the growth zone. The entire growth chamber is surrounded by a copper tube with inlet and outlet facility for water circulation which cools the chamber which otherwise would be heated by heat radiation. A teflon ring is kept in between the bell jar and metal base to act as a good seal when the chamber is evacuated. The provisions for gas inlet 'M' and outlet 'N' help to carry out growth in desired atmosphere.

A vertical column 'C' with one millimeter pitch screw in between two copper electrodes is fitted to a revolving nut at the base so that the column can be raised or lowered by means of the revolving nut. The column is also prevented from rotating about its axis by a suitable sliding key. The revolving nut is driven by means of a sprocket wheel 'S'. The vertical column 'C' has a thorough hole at its centre running down its axis. Through this hole, a vertical shaft 'D' is fitted so that it is free to rotate inside the hole. The vertical shaft 'D' is driven by means of a belt driven wheel 'E'. The belt 'f' drives the wheel 'E'. The vertical shaft 'D' carries at its top a small circular platform 'G' with screws for carrying the seed crystal 'O' of required dimension.

The sintered feed rod 'F' is supported at the top by means of a light cap 'H' attached to a stirrup guide 'J'. The stirrup guide slides freely on two rigid vertical pillars 'K', so that the top of the sintered rod is kept aligned in a vertical direction. The stirrup guide can be fixed using a metal stand 'b' which is held in between the two freely movable screws 'S' at the vertical column. The sintered rod moves up or down ensuring axial alignment. The
The top cap can be loaded with weights 'L' if required. The feed holder can accommodate feed rods of various dimensions ranging from less than 5 mm to 12 mm in diameters. The downward movement of the vertical column can either be varied from 1 mm to 10 mm per hour or 1 mm to 10 mm per day. The axial rotary movement of the seed material support 'G' of the vertical shaft can be varied from 1 rpm to 20 rpm. The vertical downward movement of the column and rotary movement of the seed platform are obtained from two independent multiple speed reduction gear electric motors.

The electrical driving unit consists of two variable reduction gear DC motors. One motor 'T' drives the rotating nut through a multiple speed reduction gear system 'U' for obtaining the downward motion of the threaded column 'C'. The very high speed reduction is obtained by a compound gear box worm and worm wheel drives, which eventually reduce the rpm of the motor shaft. The motor speed is controlled by a dimmerstat and a suitable power supply 'V' to enable the rate of movement of the column. The rate of movement of the column is read from the axial movement meter. Since the axial movement of the column is very slow, for all practical purposes of the initial positioning, pull out the thumb clutch 'W' to disengage the entire gear train from the column 'C'. Then by turning the hand wheel 'X' the column could be moved quickly to the required position for starting. Once the growth system is positioned properly the thumb clutch 'W' is engaged by connecting the gear train and motor for the run. A limit switch 'V' is provided to prevent the exceeding of the downward movement beyond the safe limit and jamming the system.

Another DC variable geared motor 'Z' drives the rotating shaft 'D' through the belt 'F'. The motor speed is controlled by a dimmerstat and suitable power supply 'I' to enable the rpm of the shaft 'D' and the rotating circular platform 'G' to be varied. The rpm of the seed holder can be read from the rpm meter.
Provisions are also given at the base plate for connecting thermocouple to record the temperature at the strip. The power for heating the foil is derived from a 40:1, 240V step down transformer, capable of delivering up to 250A. The maximum operating temperature up to 1100°C can be attained with the heating strip.

3.5.1 Heating strip configuration

Pure platinum and platinum (10%) rhodium strips have been used for the growth process. The strip heater has been fabricated from 0.5 mm thick foils of 20 mm breadth and 110 mm length (figure 3.3). The strip is perforated with 1 mm diameter holes with a circumference of 7 mm diameter at its centre to transport the solute from the feed zone to the growth zone. The geometry of the hole configuration made on the strip plays a vital role for temperature stability. Gopalakrishnan et al (1991) have designed a strip heater configuration using stainless steel strip to study the thermal stability of the transporting zone. The configuration in which holes of 1 mm diameter spreading along the circumference of 7 mm diameter with single array of holes at the two edges of the strip has been found to be the best configuration with better thermal stability in the transporting zone compared to other configurations. Using this strip, sodium nitrate single crystals have been grown with low dislocation density. The same strip heater configuration has been made on the platinum strip for growing Bismuth germanium oxide and Bismuth silicon oxide single crystals. The circular hole configuration is found to be useful for stable growth. A 2mm step close to each side is provided to overcome the problem of warping of the foil due to thermal expansion. A single array of 1 mm diameter holes is drilled at the two extremities to allow for a homogeneous distribution of temperature on the total surface by locally increasing the current density.
3.5.2 Seed perfection

In all Crystal Growth methods, the seed perfection decides the quality of the growing crystal. In float zone melting technique, the concentration of point and linear defects of the crystals grown under stable conditions are mainly dependent on the seed perfection.

In addition to the above mentioned parameters, two experimental conditions must be met for a stable growth. They are (i) intrinsic crystallization rate should be high enough to allow a practical rate of zoning. The crystallization rate can be increased by increasing the difference between dissolution and crystallization temperature, but it should be remembered that efficiency of purification is reduced if this difference is too large, and (ii) the solute, impurity and solvent must all be chemically compatible with materials of construction and not be mutually reactive.

3.5.3 Phase formation during growth

The phase formation during float zone growth occurs due to the following properties of zone melting

(i) the molten zone is in contact with the freezing solid and the melting rod with which it is in equilibrium

(ii) the composition of the molten zone is adjusted by the continuous feeding, so that the freezing solid will be in the same composition as the feed rod (excluding losses due to volatilization)

(iii) the melt automatically adjusts itself exactly to the right composition as demanded by the thermodynamic properties of the system

and (iv) in principle, the zone melting configuration can allow steady growth of incongruently melting phase over the bulk of the sample, provided a planar interface is maintained.
3.5.4 Advantages of Immersed heater Floating zone

The IHFZ configuration confers several important advantages over any other conventional floating zone technique. They are

(i) low capital cost of the heating source compared to other sources and the source has the ability to make self supporting heaters of complex shapes
(ii) the immersed heater gives efficient heat transfer so that the energy requirement is small
(iii) since it is a crucible free technique the contamination due to container reaction and the container breakages are essentially eliminated
(iv) the system is simple with only moving part
(v) the melt zone is stable due to much shorter melt region of the order of 0.5 mm to 1 mm
(vi) heating strip makes the growth interface flat throughout the growth which is essential for the bulk growth
(vii) growth initiation with a seed crystal is easy
(viii) uniform melting of the feed material aids complete reaction. It avoids the segregation of secondary phase material along with the solidified material
(ix) large temperature gradient in the melt region of the order of 100°C/mm avoids constitutional supercooling
(x) transport of a directly heated solvent zone through a prefabricated ceramic rod makes the composition of the crystal similar to that of the feed rod
(xi) a priori knowledge of the actual melt composition required to produce the appropriate steady state growth condition is not necessary

and (xii) it is one of the most suitable techniques for growing single crystals of incongruently melting compounds
3.5.5 **Drawbacks and rectification**

The gas released from the porous sites of the polycrystalline feed rod upon melting would produce gas bubbles in the melt region. The formation and breakage of such bubbles generate vibrations at the growth interface. The melt equilibrium, affected by these vibrations, leads to the trapping of solvent materials and gas bubbles into the growing solid. The formation of bubbles can be eliminated using highly densified or premelted source rods.

3.6 **PREPARATION OF Bi₄(Ge,Si)₃O₁₂ FEED RODS**

The starting materials were of high purity bismuth trioxide (Bi₂O₃) (99.99%) and germanium dioxide (GeO₂) (99.999%) or silicon dioxide (SiO₂) (99.999%). They were mixed in the mole ratio Bi₂O₃ : (Ge,Si)O₂ = 2:3 and then melted in the platinum crucible (45 mm diameter and 50 mm height) using resistive heating furnace. A chromel-alumel thermocouple was placed at the base of the crucible and the temperature was maintained (1050°C) by the temperature controller. The molten materials of Bi₄(Ge,Si)₃O₁₂ were soaked for 24 hours in the molten stage for homogenisation and cooled to room temperature very gradually.

The synthesised materials were powdered and subjected to Differential thermal analysis (DTA) and X-ray powder analysis. The DTA spectrum and X-ray diffraction pattern of synthesised materials of Bi₄Ge₃O₁₂ and Bi₄Si₃O₁₂ were as already shown in chapter-2. The observed X-ray data (powder analysis) coincide with the ASTM data. These differential thermal analysis and X-ray data agreement show, the synthesised materials of Bi₄Ge₃O₁₂ and Bi₄Si₃O₁₂ are of fully homogenised nature.
3.7 PREPARATION OF Bi$_{12}$GeO$_{20}$ AND Bi$_{12}$SiO$_{20}$ FEED RODS

The starting materials were of high purity bismuth trioxide (Bi$_2$O$_3$) and germanium dioxide (GeO$_2$) or silicon dioxide (SiO$_2$). They were mixed in the mole ratio Bi$_2$O$_3$ : (Ge,Si)O$_2$ = 6:1 and melted in the platinum crucible (45 mm diameter and 50 mm height) using resistive heating furnace. A chromel-alumel thermocouple was placed at the base of the crucible and the temperature was maintained (930°C) by the temperature controller. The molten materials of Bi$_{12}$(Ge,Si)O$_{20}$ were soaked for 24 hours in the molten stage for homogenisation and cooled to room temperature very gradually.

The synthesised materials were powdered and subjected to differential thermal analysis (DTA) and X-ray powder analysis. The DTA spectrum and X-ray diffraction pattern of synthesised materials of Bi$_{12}$GeO$_{20}$ and Bi$_{12}$SiO$_{20}$ were as already shown in chapter-2. The observed X-ray data (powder analysis) coincide the ASTM data. These differential thermal analysis (DTA) and X-ray data agreement show that the synthesised materials of Bi$_{12}$GeO$_{20}$ and Bi$_{12}$SiO$_{20}$ are of fully homogenised nature.

The materials to be grown into single crystals were sintered into rods of 10 mm dia and 100 mm length using hydraulic press with stainless steel dye at an applied pressure of 6 tonnes/cm$^2$. The triple distilled water has been used as the binder. The prepared rods of Bi$_4$(Ge,Si)$_3$O$_{12}$ and Bi$_{12}$(Ge,Si)O$_{20}$ were sintered at temperatures 900°C and 800°C respectively for eight hours to get the less porous rods and to remove the moistures in the materials. The density of feed rods was found to be 7.02 g/cm$^3$.

3.8 GROWTH OF Bi$_4$(Ge,Si)$_3$O$_{12}$ AND Bi$_{12}$(Ge,Si)O$_{20}$ CRYSTALS

3.8.1 Growth of Bi$_4$(Ge,Si)$_3$O$_{12}$ crystals
The indigenously developed floating zone apparatus (shown in figures 3.4a and 3.4b) discussed at the beginning of this chapter, was employed for the growth of $\text{Bi}_4(\text{Ge,Si})_3\text{O}_{12}$ and $\text{Bi}_{12}(\text{Ge,Si})\text{O}_{20}$ single crystals. The Czochralski- grown crystals (Gopalakrishnan et al., 1993a, 1993b) have been cut and used as seed crystals. To start the experiment, sintered rod of $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ was made to touch the bottom of the strip heater. The strip heater temperature has been measured using the chromel-alumel thermocouple by touching the top of the transporting zone of the strip heater. The temperature of the strip heater was increased to reach the melting temperature of the crystal (1050°C). As soon as the sintered rod got melted the seed crystal was rotated slowly. A thin layer of the seed crystal was melted, so that the molten materials transported from the feed rod can be made to get into the liquid film between the strip and seed crystal. Now the seed crystal is rotated at the rate of 10-15 rpm and pulled down at the rate of 1-2mm/hr. While increasing the rotation rate beyond 15 rpm, the molten material lost its stability and the growth was not possible. By employing this technique, the crystals of $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ and $\text{Bi}_4\text{Si}_3\text{O}_{12}$ of 10 mm diameter and 15 mm length respectively, have been grown (figure 3.5a and 3.5b) (Gopalakrishnan and Ramasamy 1994). After-heaters maintained at a temperature well below the melting temperature of the material, were used to avoid the formation of cracks and thermal strains in the grown crystals. After the growth, strip heater temperature was slightly reduced and the crystals were annealed for two days.

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

The experimental procedure employed for $\text{Bi}_{12}(\text{Ge, Si})\text{O}_{20}$ is the same as that of $\text{Bi}_4(\text{Ge, Si})_3\text{O}_{12}$ crystals. The only variation is in the operating temperatures of strip heater and after-heater, since the melting point of $\text{Bi}_{12}(\text{Ge, Si})\text{O}_{20}$ is different. Figure 3.6a and 3.6b show the crystals of $\text{Bi}_{12}\text{GeO}_{20}$ and $\text{Bi}_{12}\text{SiO}_{20}$. 
Figure 3.4a Floating zone apparatus

Figure 3.4b Floating zone apparatus - Electrodes shown
Figure 3.7a SEM photograph of Bi$_4$Ge$_3$O$_{12}$ grown without after-heater (1000X)

Figure 3.7b SEM photograph of Bi$_2$Ge$_2$O$_{20}$ grown without after-heater (1000X)
Figure 3.8 Polycrystalline mass of $\text{Bi}_4\text{Ge}_3\text{O}_{12}$

Figure 3.9a SEM photograph of $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ grown with after-heater and with higher annealing rate (1000X)

Figure 3.9b Optical microscopic picture of $\text{Bi}_{12}\text{GeO}_{20}$ grown with after-heater and with higher annealing rate (250X)
3.8.3 Effect of variation in After-heater and strip heater temperatures

Experiments were also conducted without after-heaters and with faster annealing rate of the after-heater temperature. In order to find the effect of after-heater temperatures on the quality of the crystals, growth sequence at different annealing temperature rates were observed for Bi$_4$(Ge,Si)$_3$O$_{12}$ and Bi$_{12}$(Ge,Si)O$_{20}$ crystals.

Figures 3.7a and 3.7b show the SEM photographs of the sectional view of Bi$_4$Ge$_3$O$_{12}$ and Bi$_{12}$GeO$_{20}$, grown without after-heater. From the observation it is established that without after-heaters, the quality of the crystals is very poor, often we end up with polycrystalline mass and is shown in figure 3.8.

Figures 3.9a and 3.9b show the scanning electron microscopic and optical microscopic pictures of Bi$_4$Ge$_3$O$_{12}$ and Bi$_{12}$GeO$_{20}$ respectively, grown with after-heaters with higher annealing rate. The quality of the crystals is much better than the crystals grown without after-heaters. From the optical and scanning electron microscopic studies, it can be seen that the crystals are strained and voids are observed, when the crystals are grown without after-heater and with higher annealing rate. It is emphasised that the after-heaters are very much essential, in order to get strain free, good quality single crystals.

3.9 CONCLUSION

A strip heater configuration has been designed using platinum strip for better thermal stability. A number of good quality single crystals of BGO and BSO have been grown by Floating zone technique. The effect of strip heater and after-heater temperatures on the quality of the crystals has been discussed.