Growth and characterization of Bi$_{12}$SiO$_{20}$ and Bi$_{12}$GeO$_{20}$ crystals

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The photorefractive bismuth silicon oxide (Bi$_{12}$SiO$_{20}$) and bismuth germanium oxide (Bi$_{12}$GeO$_{20}$) crystals were synthesized and Czochralski growth performed in a resistive heating furnace having a vertical temperature gradient of 20°C/cm. Several crystals with <100> orientation were grown. The effect of rotation rate was studied from the fluid flow point of view and the growth parameters were optimised to yield crystals free from the central core and bubbles. The UV-VIS spectra revealed optical absorption edge and transmission in these crystals. The quality of the crystals was analysed by chemical etching studies. The Vickers microhardness studies were also carried out on the (100) plane of the BSO crystal.

Bismuth Silicon Oxide (BSO) and Bismuth Germanium Oxide (BGO) crystals are widely used as photorefractive materials finding applications in optical information processing, optical computing and information storage due to their high sensitivity and quick response$^{1-4}$. For these purposes, high optical quality crystals are required, which means, from the crystal growth point of view, the crystals with planar or slightly curved interfaces must be grown. Nevertheless, any change in the solid-liquid interface shape will produce a variety of defects in the crystal, such as dislocations, core formation, stresses, impurity segregation, etc.

There is a general agreement regarding the interaction between the forced convection arising from the crystal rotation and the thermal free convection due to the temperature difference in the melt bulk, which produces a resultant flow whose rate and direction determine the shape of the solid-liquid interface. Thus, a perfect control of growth parameters such as rotation rate, the pulling rate, the temperature gradients, etc., are very important. In the particular case of sillenite compounds (Bi$_{12}$SiO$_{20}$, Bi$_{12}$GeO$_{20}$ and Bi$_{12}$TiO$_{20}$), there are several papers devoted to the study of the solid-liquid interface shape and its consequences on the crystal properties$^{5-7}$.

In this paper, we report the growth of bubble and core-free crystals of Bi$_{12}$SiO$_{20}$ crystals, under low temperature gradients, with reduced dislocation densities and the optical property variation due to non-stoichiometry in BGO. In addition, the results on the optical absorption spectra and the measured Vickers microhardness values of BSO are also discussed.

Experimental

The experimental set-up consists of a normal Czochralski crystal pulling apparatus consisting of two motors for rotation and translation of the seed. The motors are driven by a microprocessor based control units using which the pulling rates and the rotation rates can be varied between 0.01 mm/h and 0.01 and 99.99 rpm, respectively. The assembly containing the motors on the guide rods is placed on top of a double walled water cooled, non-magnetic stainless steel, square cross-section chamber with a door opening, fabricated in our laboratory. The chamber has provision for inlet and outlet connections for gas purging, water circulation and evacuation. The water-cooled door contains a separate water-cooled view port, situated at an angle 45° with respect to the crucible position, to monitor the growth process. The size and design of the chamber was made in such a way that the chamber can be used for growing crystals by employing home made resistive heated and induction heated systems. However, in this report we present the growth of BSO crystals using resistive heating system. The resistive heated furnace is a kanthal wire wound mullite tube. By adjusting the space between the windings and the placement of the crucible in the furnace, the required temperature gradients (10-15, 15-20 and 20-25 °C/cm) can be achieved. The entire furnace is placed inside the chamber. The heating system is interfaced with an Eurotherm temperature controller for the smooth and stable heating and cooling and temperature maintaining processes. The control thermocouple is placed just below the crucible such that the thermocouple junction is as close as possible to the crucible bottom. The control accuracy of the temperature controller is ±0.1°C.
Synthesis and growth of BSO and BGO crystals

The starting materials [6 mole Bi$_2$O$_3$ (99.9995%) and 1 mole SiO$_2$ (99.999%)] from Johnson and Matthey, were mixed thoroughly and stuffed into a platinum crucible (4.5 cm diameter and 5 cm height). The crucible containing the charge is then placed inside the furnace having vertical temperature gradient of 15°C/cm. The charge is then heated to 825°C and kept there for about 48 h. As there is a gradient in the furnace, much care is taken to ensure that the sintering temperature is well within the region of formation of the desired phase in the phase diagram of Si$_2$O$_3$ and SiO$_2$ system.

The sintered material was then melted and after allowing the melt for homogenisation for about 4 h, the growth was attempted with <100> and <110> oriented seeds obtained from previous growth experiments. Initially, the rotation rate and pulling rate were fixed to be 10 rpm and 1 mm/h, respectively. The crystal thus grown was square in shape and the interface shape was convex with respect to the melt. On analysing the crystal plate cut perpendicular to the growth direction, a dark central coloured core of diameter 2-3 mm was observed and bubbles were rarely seen in the central part of the crystal.

When the rotation rate was increased to 25 rpm, the growth process was smooth in the seeding. When the attempt to increase the diameter of the crystal was made, a sudden increase in the diameter of the crystal was noticed. It was very difficult to continue the growth in this rotation rate range of 20-35 rpm.

A further increase in the rotation rate to 35-45 rpm makes the experiment more smooth except for a small difficulty in the initial stages of seeding which could be controlled by a proper reduction of the rotation rate as the diameter increased. The crystal thus obtained has a flat/ flat to concave interface. We could not observe any core in the crystal plate cut perpendicular to the growth axis and the bubbles are seen only in the shoulder portion of the crystal. With very high rotation rates (50-60 rpm), many times the interface cut and the crystal cracking were observed, and the bubbles were present in the shoulder portion only.

After the growth period, the crystals were annealed at a temperature 100°C less than the crystallization temperature and cooled to room temperature at a rate of 15°C/cm. The crystal that was grown with rotation rate 5-9 rpm and pulling rate of 1 mm/h is shown in the Fig. 1. When the cooling rate was increased, the crystal tended to crack.

Bi$_2$GeO$_2$ single crystals with different (Bi$_2$O$_3$-GeO$_2$) melt compositions with starting materials Bi$_2$O$_3$ (99.9999 % pure) and GeO$_2$ (99.9999 % pure) were grown by Czochralski method. They were mixed in proper ratios (8,12,14.3, 20, 24 mol % of GeO$_2$) to have 700 g mixture for each run. They were melted in the platinum crucible of 50 mm diameter and 50 mm height. Crystals weighing around 100 g were grown along the <100> direction using an automatic diameter controlled growth chamber.

Characterization Studies

Powder X-ray diffraction studies

The formation of the phase was confirmed by powder X-ray diffraction pattern obtained from the powder prepared from the grown crystals. The calculated cell parameter value for BSO is $a = 10.158$ Å.

Chemical etching studies

To analyse the quality of the grown crystal, classical chemical etching studies were carried out according to the procedure described by Tu et al. The crystal plate of 1 mm thick was cut from the crystal that was grown in the rotation rate range of 35-45 rpm for this study. The crystal was immersed in 30% NaOH solution kept at 75-80°C for 5 min, and then in 50% diluted nitric acid heated to 80-85°C for 25 sec. The crystal was then taken out and dipped in deionised water maintained at the same temperature and cold water added slowly to cool the crystal down to room temperature to prevent its cracking. Subsequently, the crystal was put in acetone and observed under a microscope. Fig. 2 shows the etch pits pattern obtained on the crystal and the measured etch pit density was approximately 1500/cm$^2$.

Optical absorption spectra

The optical absorption spectra of the cut and polished crystal plate (of area 1 cm$^2$ and 2 mm thick)

Fig. 1 — Bi$_2$SiO$_2$ crystal
was recorded using Hitachi 3200 spectrophotometer as shown in Fig. 3, and is in agreement with the reported value. The spectra recorded for the core part of the crystal reveal that the lower cut-off value shifts to the longer wavelength region.

The colour of the as-grown BGO samples differed from reddish brown for the bismuth rich (8 GeO$_2$ mol %) to transparent pale yellow for germanium rich (24 GeO$_2$ mol %) melt compositions. The absorption strongly depended on the melt composition from which the crystal was grown. Bismuth rich melt grown crystals have strong absorption than the germanium rich melt grown BGO crystals (Fig. 4).

Photoconductivity measurements for BGO crystals indicate that the non-stoichiometry in the melt composition, either bismuth rich or germanium rich, results in quenching of the photoconductivity.

**Vickers microhardness studies**

Hardness is an important solid-state property: As hardness properties are basically related to the crystal structure of the material, microhardness studies have been applied to understand the plasticity of the crystals.

The crystals with polished (100) were subjected to static indentation tests in air at room temperature (300 K) using Leitz Wetzlar hardness tester fitted with a Vickers diamond pyramidal indenter and attached to a Leitz incident light microscope. Loads of different magnitudes (5, 10, 25 and 50 g) were applied over a fixed interval of time. Fig. 5 shows the variation of Vickers microhardness with applied load. The hardness is found to decrease as the load is increased.

**Discussion**

It has been observed that formation of the core is unavoidable when low rotation rates are employed (<20 rpm). Under such conditions, only the flow due to the temperature gradient (the so called natural convection due to gradient) is dominant over the forced convective flow due to crystal rotation. In this case, the interface shape will be convex with respect to the melt and the gas surplus melt or impurities in the melt will go down along the axis of rotation and concentrate in the central part adjacent to the
interface. Due to higher bubble or impurity concentration or compositional changes, the freezing point of melt ahead of the interface becomes supercooled and so a layer freezes in an abrupt manner once the melt composition reaches a critical value\(^\text{10}\). Also, any interface instability will result in incorporation of bubbles or concentrated impurities at the centre of the crystal. In addition, there is also preferential absorption of photochromic impurities at the impurity segregated areas\(^\text{11}\). Hence, the formation of the core or incorporation of bubbles along the axis of the crystal is unavoidable under low rotation rates.

When the rotation rate is increased to 35-45 rpm, the forced convection becomes effective. It drags the hot fluid from the bottom of the crucible, along the axis of the crystal, and pushes it out to the periphery of the crystal. Hence, the interface shape is concave with respect to the melt. Since the flow is from the centre to the periphery of the crystal, the concentration of impurities is defused and the bubbles carried away from the centre of the crystal. Hence, the crystals grown in this rotation rate can be free from core and bubbles.

When very high rotation rates are employed (>50 rpm), the interface shape becomes more concave and the hot liquid velocity beneath the axis of the crystal is high. A very deep concave interface is the characteristic of this rotation rate range. Also, owing to the dark nature of the crystal, the thermal energy gets accumulated at the centre of the interface. As the heat energy is not transferred much through the crystal, the interface tends to melt and results finally in the disintegration of the crystal from the melt.

At a medium rotation rate range of (20-30 rpm), both the natural and forced convective flows have equal magnitudes but in different directions. Physical simulation studies\(^\text{12}\), under such conditions, suggest that there exists a wide supercooled region at the junction of these two flows (which is normally at the periphery of the crystal). Hence, when the temperature is reduced to increase the diameter of the crystal, this large supercooled region gets attached to the crystal and hence the increase in diameter could not be controlled. This rotation rate range has been identified as ‘Middle danger rotation rate range’\(^\text{13}\). It is very difficult to obtain good quality crystals in this rotation rate range.

For uniformity of the results, the pulling rate for all through the study was kept at 1 mm/h and the diameter of the crystal maintained in the body portion of the crystal was approximately 15 mm.

The etch pit results also suggest that quality of the crystal is fairly good when it is grown under the rotation rate range of 35-45 rpm. Hence, by employing this rotation rate range one can obtain fairly good crystals free from core and crystals of low dislocation densities suitable for optical applications. The optical absorption spectra also show a good transparency. The dark central core, which is assumed as clusters of Bi\(^{3+}\) and Bi\(^{5+}\), shifts the lower cut off wavelength to the higher wavelength region. Improvement in transparency is observed for increase in germanium/silicon contents in BGO and BSO respectively due to improved occupancy in the lattice and hence, lower optical defects.

The initial higher value of the hardness value may be attributed to the surface hardening effect due to polishing of the sample. Since the magnitude of the applied load (5 g) is not enough to make indentation beyond this layer thickness, the high value of hardness is observed. As the magnitude of the load increases, the dimensions of the indentation mark reach beyond the hardened surface with respect to the crystal lattice. Hence, the hardness value attains saturation after 25 g of load is reached. The hardness values of Bi\(_2\)SiO\(_5\) crystals are nearly comparable with the hardness values of lead molybdate\(^\text{14}\) and twice the values of bismuth tellurite\(^\text{15}\) crystals under similar experimental conditions.

Conclusions
The compound Bi\(_2\)SiO\(_5\) was synthesized from the basic constituent oxides. The formation of the phase was confirmed by powder X-ray diffraction pattern. The crystals were grown with <100> and <110> seed orientations using the home made furnace. To obtain crystals free from central core and bubbles, and crystals of low dislocation densities, a rotation rate range of 35-45 rpm and a pulling rate of 1 mm/h must be employed. The optical absorption spectrum of the core free crystal is in agreement with the reported one. The variation in Vickers hardness value against different loads is plotted. In BGO, the optical absorption varies with the non-stoichiometry in the melt composition from which the crystal is grown. Germanium rich melt grown crystals have better conductivity for storage applications.

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References