

## Single crystals of bismuth silicon oxide grown by the Czochralski technique and their characterisation

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Single crystals of  $\text{Bi}_{12}\text{SiO}_{20}$  were grown by the Czochralski technique. The critical diameter and the critical rate of rotation were calculated. Suitable polishing and etching solutions were determined. X-Ray measurements were performed on powdered samples to obtain the lattice parameters. The optical properties of the bismuth silicon oxide single crystals were investigated. The obtained results are discussed and compared with published data.

**Key words:** bismuth silicon oxide single crystals, Czochralski technique, critical diameter, critical rate of rotation, etching solution, optical properties.

Metastable  $\gamma\text{-Bi}_2\text{O}_3$  can be stabilised by the addition of small amounts of one of a number of oxides in the form  $\text{Bi}_{12}\text{MO}_{20}$ , where M is Si, Ti, Ge, Mn or some other four-valence ion, or a combination of two ions.<sup>1</sup> These oxide compounds have a congruent melting point. All compounds with the  $\gamma\text{-Bi}_{12}\text{MO}_{20}$  structure have cubic I-centred cells, the space group 123 with a unit cell parameter of about 1.0 nm. These materials have a composition which can be approximated by the formula  $\text{Bi}_x\text{MO}_{1.5x+2}$ , where it is known that  $x$  can vary from  $11.77 \pm 0.03$  to  $12.05 \pm 0.10$  in the crystal while  $x$  in the melt is changed from 10 to 14.<sup>2</sup>

Bismuth silicon oxide (BSO), due to its photoconductive and electrooptical properties, has found application in a number of technologically important optical devices. It has demonstrated unique properties for use in Pockels Readout Optical Memories.<sup>3</sup> As the material with the highest known photorefractive sensitivity, it has found application in read-write volume holographic storage with an associated high-quality image reconstruction.<sup>4</sup>  $\text{Bi}_{12}\text{SiO}_{20}$  also belongs to the family of isomorphic compounds that could find broad application in integrated optics.<sup>5</sup> These applications demand the most stringent requirements on the optical quality of the

material, including refractive index homogeneity, uniformity of the optical density, and freedom from light scattering defects such as inclusions.  $\text{Bi}_{12}\text{SiO}_{20}$  crystals have been produced mainly by the Czochralski technique,<sup>2,6-8</sup> but recently also by the Bridgman method<sup>9, 10</sup> and by the floating-zone technique.<sup>11</sup>

### EXPERIMENTAL

$\text{Bi}_{12}\text{SiO}_{20}$  single crystals were grown by the Czochralski technique using a MSR 2 crystal puller controlled by an Eurotherm. This system kept the crucible temperature constant to within 0.2 °C. The melt was contained in a platinum crucible ( $\varnothing$  4 cm, 4 cm depth) which was placed in an alumina vessel on the zircon oxide wool. The whole system forms a kind of protection against excessive radiative heat loss. To reduce thermal gradients in the crystal and the melt, a cylindrical silica glass afterheater was installed around the system with the crucible.<sup>12</sup> The atmosphere used was air. An iridium wire was used as the crystal seed in our first experiments. A seed cut from the produced  $\text{Bi}_{12}\text{SiO}_{20}$  crystals was used for the next crystals.

All crystals were grown from synthesised  $\text{Bi}_2\text{O}_3$  and  $\text{SiO}_2$ . The starting materials were mixed together in the stoichiometric ratio (6:1). Various pull rates were examined and the best results were obtained using pull rates in the range 5–6 mm h<sup>-1</sup>, in accordance with published data.<sup>13</sup> The rate of crystal rotation was calculated to be 20 rpm. The crucible was not rotated during the growth. After the growth run, the crystal boule was cooled at a rate of about 50 °C/h down to room temperature.

A solution of  $\text{HCl} + \text{HNO}_3 + \text{H}_2\text{O}$  in the ratio 1:1:5 was found to be suitable for the chemical polishing of the bismuth silicon oxide crystals. Many experiments were performed to find a suitable etching solution. Etching solutions of  $\text{HF} + \text{HNO}_3$  in the ratio 2:1, 0.1 M  $\text{NaOH}$ ,  $\text{HCl} + \text{H}_2\text{O}$  in the ratio 1:2 were found to be unsuitable, but  $\text{HCl} + \text{H}_2\text{O}$  in ratio 1:5 was satisfactory.

X-Ray measurements of the  $\text{Bi}_{12}\text{SiO}_{20}$  powders were recored on a Philips PW 1710 instrument in the  $2\theta$  range from 10° to 90° using the Cu anthocathode wavelength  $\lambda_{\text{CuK}\alpha_1} = 0.154051$  nm. The anode load was 40 kV and 30 mA. The diffractograms were recorded in 0.02° steps with a recording time of 0.5 s for each step.

Infrared spectra were recorded using a Fourier-transform spectrometer Bomem DA8. For the far infrared region a beamsplitter was used (hyper splitter for the spectral region 30–1000 cm<sup>-1</sup>) and for the infrared the standard KBr (400–5000 cm<sup>-1</sup>). All spectra were obtained for a near normal incidence configuration at room temperature.

### RESULTS AND DISCUSSION

The Czochralski growth of crystals of bismuth silicon oxide sometimes results in a darkened core with an unusual microstructure. The formation of the core is not well understood, but there have been several proposals. Picone<sup>14</sup> proposed that, at low peripheral speeds, compositional variations ahead of the interface are coupled with rapid temperature fluctuations, which are responsible for the suddenly freezing these variations into the crystal. Increasing the rotation rate leads to the growth of highly faceted crystals at a critical peripheral speed and the disappearance of the central core. Tanguary *et al.*<sup>15</sup> suggested that very low angle facets are found on the solid/liquid interface which could lead to the preferential absorption of photochromic impurities at these sites. Microprobe measurements on bismuth silicon oxide<sup>5</sup> have shown no evidence of higher impurity concentrations on the facets. Some crystals of bismuth silicon oxide exhibited photochromatism even though not a single impurity was reportedly found at levels above 1–2 ppm.<sup>15</sup>

Crystals of bismuth silicon oxide show an obvious tendency towards faceting. For growth along [111] axes, {110} facets are usually observed.<sup>15</sup> The polar nature of the [211] direction was evidenced by noticeable differences in the size of prominent ridges oriented along the opposite ends of the [211] axes. On the other hand, for growth along the [001] direction, primary facets observed were always {100}, usually accompanied by less well-developed {110} facets. It has been reported in the literature<sup>16</sup> that a concave interface shape was observed in a crystal when the crystal diameter was larger than a critical diameter  $D_c$ . The inversion occurred when the flowing melt caused by rotation overcame natural convection.<sup>17</sup> When the crystal diameter reached the value of  $D_c$  some parts of the crystal melted and the interface became nearly flat.<sup>18</sup> Applying the Grashof and Reynolds numbers, Carruthers<sup>16</sup> gave an equation for  $D_c$ :

$$D_c = (g\alpha\Delta TR^3 \pi^{-2})^{0.25} \nu^{-0.5} \quad (1)$$

where  $D_c$  – critical diameter,  $g$  – acceleration due to gravity,  $\alpha$  – volume expansion coefficient,  $\Delta T$  – the radial temperature gradient at the melt,  $R$  – the melt radius, and  $\nu$  – kinematics viscosity.

It was found from the literature<sup>2,19</sup> that  $\alpha = 7 \times 10^{-5} \text{ C deg}^{-1}$ ,  $\Delta T = 80 \text{ }^\circ\text{C}$ ,  $\rho = 7.65 \text{ g/cm}^3$ ,  $\eta = 23 \text{ kPa s}$  at 1173 K, and  $\eta = 15 \text{ kPa s}$  at 1223 K. In our case  $R = 2 \text{ cm}$ . From Eq. (1), the value  $D_c = 0.94 \text{ cm}$  was obtained. The value  $D_c \approx 1.0 \text{ cm}$  was assumed to be suitable for experiments of crystal growth.

It is known that a disc rotating on a fluid introduces instability with vortex formation when the Reynolds number exceeds a critical value. Similarly, Couette flow, which might be expected to occur between the rotating crystal and the stationary crucible, also produces instability followed by vortex formation when the critical value of the Taylor number is exceeded.<sup>2</sup> A rotating disc could approximate the crystal, and an equation for vortex formation at the surface of the melt is<sup>2</sup>

$$R_1^2 \omega / \nu = 2.5 \quad (2)$$

where  $R_1$  – the crystal radius,  $\omega$  – the rate of rotation, and  $\nu$  – kinematic viscosity.

It was calculated from the Eq. (2) that  $\omega$  is 23.4 rpm. With the formation of vortices the streamlines stop to have circular symmetry. It was assumed crystal growth would be better with a melt without vortices, and so  $\omega = 20 \text{ rpm}$  was selected.

It is well known that the main criterion for the flow regime is the Reynolds number. For stirring, the Reynolds number is given by

$$\text{Re} = \omega d \rho / \eta \quad (3)$$

where is  $\text{Re}$  – Reynolds number,  $\omega$  – rotation rate,  $d$  – crystal diameter,  $\rho$  – specific gravity, and  $\eta$  – viscosity.

For the laminar regime,<sup>20</sup>  $\text{Re}$  has to be less than 10, and from Eq. (3)  $\text{Re}$  was calculated to be 9.5.

It has been found<sup>2</sup> that crystals up to 15 mm in diameter can be grown from the melt without inclusions provided that the growth rate is always less than  $6 \text{ mm h}^{-1}$ , and for larger diameters a lower growth rate is needed. If the diameter changes rapidly, there is a possibility of inclusions forming in the centre of the crystal. It was supposed that crystals with 10–12 mm diameters would be suitable for crystal growth at a growth rate of  $5\text{--}6 \text{ mm h}^{-1}$ . They should not have inclusions in the centre of the crystal. In our case, it was found from Eq. (2) that  $\omega$  (rotation rate) would be 20 rpm. Our proposal for the diameters of the crystals and the growth rate is in accordance with the published data.<sup>2,15,19</sup> As a result of our experiments, pale yellow crystals 10–12 mm in diameter were produced with a length of about 40 mm. The colour of the crystals was in accordance with published data.<sup>15,21</sup> Some of the obtained crystals are shown in Fig. 1.

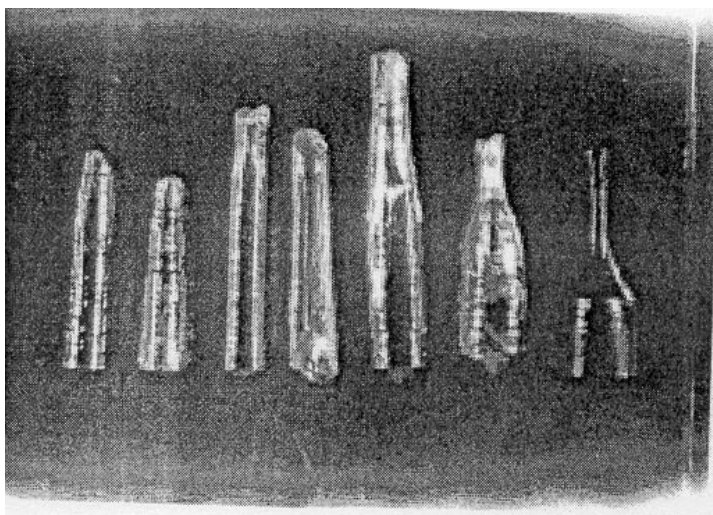


Fig. 1. A view of some obtained crystals of  $\text{Bi}_{12}\text{SiO}_{20}$ . The last crystal in the row was obtained using a crystal seed.

It is very difficult to observe the behaviour of the melt during Czochralski growth. The flow, generally, cannot be visualised, although some features of the surface flow can be seen in materials with a temperature dependent emissivity. Model experiments, with water as the working fluid, have been used in some investigations of the flow.<sup>16,22</sup> Since the value of the water viscosity is near to the viscosity of many melts, these experiments correctly modelled the effect of rotation. However, large temperature differences, commonly occurring in the melt, cannot be treated by this model. Some authors explained the rotational instability by a coupling of the flows due to the rotation and the convection caused by the radial temperature gradient,<sup>19</sup> but their system is valid only for the surface flow. For this reason, we decided to take into consideration only a combination of the Taylor, Grashof and Reynolds numbers instead of combinations of the Ekman, Grashof, Prandtl and Rosby numbers,<sup>22</sup> or a combination of the Grashof and Reynolds numbers.<sup>23</sup> The

method based on the combination of the Taylor, Grashof and Reynolds numbers is simple and does not introduce a speculative picture derived from any of the theories describing the flow of the melt. Besides, this combination gave very good results for many crystals, like sapphire, ruby and YAG.<sup>24</sup>

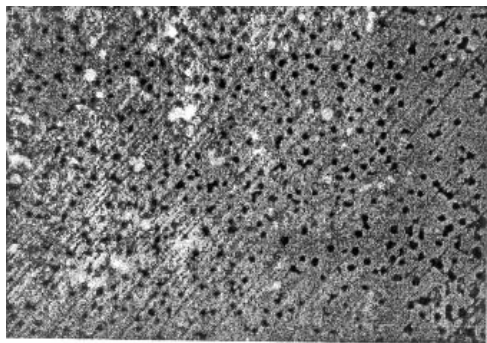


Fig. 2. A view of an etched plate of  $\text{Bi}_{12}\text{SiO}_{20}$  crystal with triangles of dislocations. Magnification 24x.

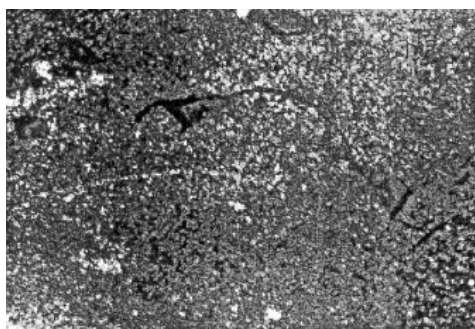


Fig. 3. A view of an etched plate of  $\text{Bi}_{12}\text{SiO}_{20}$  crystal with triangles of dislocations in the  $[111]$  plane. Magnification 48x.

An etching solution suitable for  $\text{Bi}_{12}\text{SiO}_{20}$  was not found in the literature. Bismuth silicon oxide is not a very hard material, with a hardness of 5 degrees on the Mohs scale<sup>21</sup> and it is very important to find a suitable etching solution for the chemical removal of surface damages after mechanical polishing.<sup>12</sup> The first examined etching solution was the mixture  $\text{HF}:\text{HNO}_3 = 2:1$ , but this solution was too strong for the considered material. The reaction was very quick and violent, but without the expected results. The obtained surface was neither flat nor smooth. The

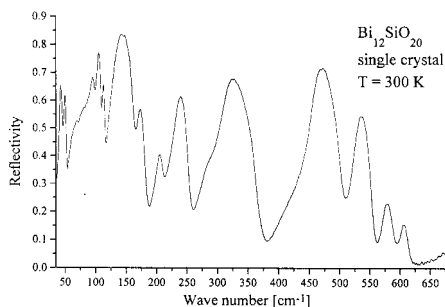


Fig. 4. The polarised infrared reflectance spectrum of  $\text{Bi}_{12}\text{SiO}_{20}$  obtained at a rotation rate of 20 rpm in the range  $35\text{--}650\text{ cm}^{-1}$  at  $T=300\text{ K}$ .

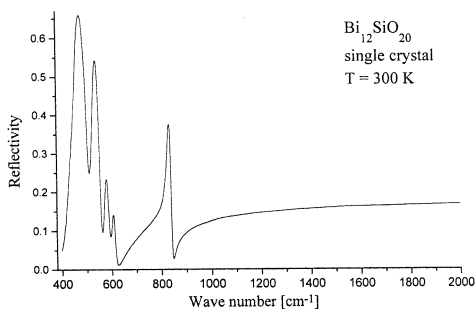


Fig. 5. The polarised infrared reflectance spectrum of  $\text{Bi}_{12}\text{SiO}_{20}$  obtained at a rotation rate of 20 rpm in the range  $400\text{--}2000\text{ cm}^{-1}$  at  $T=300\text{ K}$ .

other examined etching solution was a 0.1 M NaOH solution. This solution did not show any reaction even after a long time (20 h) at the room temperature, nor at a higher temperature (323 K). The next examined etching solution was  $\text{HCl}:\text{H}_2\text{O} = 1:2$ . This solution did not give the expected results, but using the ratio 1:5 instead of 1:2 did after 55 s. However, the surface was not completely flat, as the samples had not been chemically polished before etching. A suitable solution for chemical polishing,  $\text{HCl}:\text{HNO}_3:\text{H}_2\text{O} = 1:1:5$ , was found after several attempts. The  $\text{Bi}_{12}\text{SiO}_{20}$  crystal was first chemically polished using the solution  $\text{HCl}:\text{HNO}_3:\text{H}_2\text{O} = 1:1:5$ , and then etched by the solution  $\text{HCl}:\text{H}_2\text{O} = 1:5$ . Part of a polished slice of a  $\text{Bi}_{12}\text{SiO}_{20}$  single crystal with etched pits of dislocations is shown in Fig. 2, and at a higher magnification in Fig. 3.

The structure properties were obtained by X-ray analysis of powdered samples. The diffractometer PW 1710 was used in the  $2\theta$  range from  $15^\circ$  to  $90^\circ$ . The unit cell of  $\text{Bi}_{12}\text{SiO}_{20}$  was calculated by the least square method using all 18 reflections including more  $K\alpha_2$  for 5 reflections.

Many of the reflections correspond to  $\text{Bi}_{12}\text{SiO}_{20}$  crystals<sup>1</sup> with the parameter of cubic I-centred cell  $a = 1.01067$  nm, and  $x = 12$ . Our calculated result for the lattice parameter is  $a = 1.0096$  nm, which is in good agreement with published data. It should also be mentioned that a value of  $x = 12$  for crystals  $\text{Bi}_x\text{SiO}_{1.5x+2}$  where the diameters are 10 to 12 mm for a crucible diameter of about 4 mm, have been reported in the literature.<sup>2</sup> This is in accordance with the dimensions of the crystals obtained in this work.

The polarised infrared reflectance spectra of  $\text{Bi}_{12}\text{SiO}_{20}$  in the region from 35 to  $650\text{ cm}^{-1}$  and 400 to 1000 are presented in Figs. 4 and 5, respectively. The spectra were recorded in the region  $25\text{--}5000\text{ cm}^{-1}$ . The absence of a core was confirmed by viewing polished crystal slices in both normal and polarised light.

The reflectance spectrum of a  $\text{Bi}_{12}\text{SiO}_{20}$  single crystal is presented in Fig. 6 in the region from 400 to  $1000\text{ cm}^{-1}$  of  $\text{Bi}_{12}\text{SiO}_{20}$  obtained using rotation rate of 25 rpm during the process of crystal growth. This value of rotation was higher than the calculated value of 20 rpm where some estimations were made. We wanted to know what could happened with the optical spectra as a consequence of higher rotation rates and the beginning of turbulent regime flow.

It is very clear from Fig. 6 that a rotation rate of 25 rpm is not appropriate for the growth of single crystal with good optical properties. Several small peaks, decreasing the optical quality, appeared in the region from 1000 to  $2000\text{ cm}^{-1}$ . In polarised light a stain could also be seen in the central part of the polished crystal slice.

The transverse (TO) and longitudinal (LO) frequencies of the optical phonons were obtained using Kramers-Kronig (KK) analysis. The results were shown in Tables I and II.

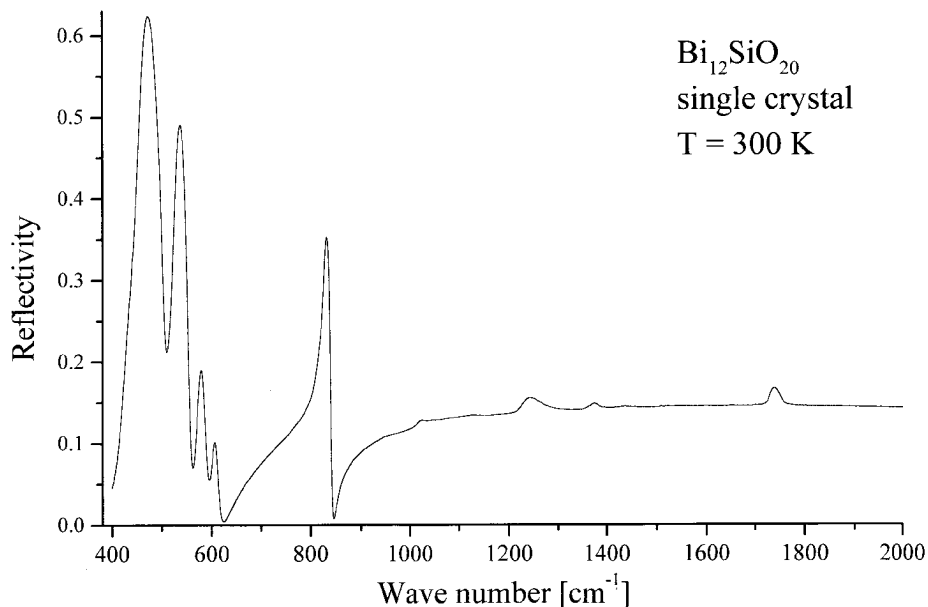


Fig. 6. The polarised infrared reflectance spectrum of  $\text{Bi}_{12}\text{SiO}_{20}$  obtained at a rotation rate of 25 rpm in the range  $400\text{--}2000 \text{ cm}^{-1}$  at  $T = 300 \text{ K}$ .

TABLE I. The transverse (TO) frequencies of the optical phonons for  $\text{Bi}_{12}\text{SiO}_{20}$  in the range  $35\text{--}1000 \text{ cm}^{-1}$  at  $T = 300 \text{ K}$

Number of phonon mode	Position of phonon mode/ $\text{cm}^{-1}$
1	44
2	50
3	99
4	106.5
5	114
6	135
7	169.5
8	206
9	234
10	310
11	486
12	538
13	581
14	608
15	834

TABLE II. The longitudinal (LO) frequencies of the optical phonons for  $\text{Bi}_{12}\text{SiO}_{20}$  in the range  $35\text{--}1000\text{ cm}^{-1}$  at  $T = 300\text{ K}$ 

Number of phonon mode	Position of phonon mode/ $\text{cm}^{-1}$
1	48
2	52
3	99
4	110
5	116.5
6	164
7	183.5
8	216
9	255.5
10	370
11	417.5
12	556
13	589
14	614
15	842

To the best of our knowledge no data on the parameters of TO nad LO modes have been published in the literature. A detailed analysis of the optical phonons of  $\text{Bi}_{12}\text{SiO}_{20}$  in the infrared and Raman spectra will be published in the next paper.

### CONCLUSION

The conditions for growing single crystals of  $\text{Bi}_{12}\text{SiO}_{20}$  were calculated by using a combination of the Reynolds, Taylor and Grashof numbers. The absence of a core was confirmed by viewing polished crystal slices in both normal and polarised light.

### ИЗВОД

#### РАСТ МОНОКРИСТАЛА БИЗМУТ СИЛИЦИЈУМ-ОКСИДА ПОМОЋУ ТЕХНИКЕ ЧОХРАЛСКОГ И ЊИХОВА КАРАКТЕРИЗАЦИЈА

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Монокристали  $\text{Bi}_{12}\text{SiO}_{20}$  су расли помоћу технике Чохралског. Израчунати су критични пречник и критична брзина ротације. Одређена су погодна средства за поли-



рање и нагризање. Рендгенска мерења спрашеног узорка су извршена да би се добили параметри решетке. Проучавање су оптичке особине бизмут силицијум-оксида. Добити резултати су дискутовани и поређени са литературним подацима.

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