

## The growth and optical properties of Bi<sub>12</sub>SiO<sub>20</sub> single crystals

ALEKSANDAR GOLUBOVIĆ<sup>1\*#</sup>, SLOBODANKA NIKOLIĆ<sup>1</sup>, RADOŠ GAJIĆ<sup>1</sup>, STEVAN ĐURIĆ<sup>2</sup> and ANDREJA VALČIĆ<sup>3</sup>

<sup>1</sup>Institute of Physics, Pregrevica 118, P. O. Box 57, YU-11001 Belgrade, <sup>2</sup>Faculty of Mining and Geology, Đušina 7, P. O. Box 162, YU-11000 Belgrade and <sup>3</sup>Faculty of Technology and Metallurgy, Karnegijeva 4, YU-11000 Belgrade, Yugoslavia

(Received 11 May 2001)

Single crystals of Bi<sub>12</sub>SiO<sub>20</sub> were grown from the melt by the Czochralski technique. The critical crystal diameter  $d_c = 10$  mm and the critical rate of rotation  $\omega_c = 20$  rpm were calculated by equations from the hydrodynamics of a melt. The rate of crystal growth was experimentally obtained to be 5 mm/h. The crystal growth was in the [111] direction. The lattice parameter  $a = 1.0096$  nm was determined by X-ray powder diffraction. The reflectance spectra were recorded in the wave numbers range 20–5000 cm<sup>-1</sup> at different temperatures. For all the recorded spectra the values of the vibrational TO and LO modes were found using the Kramers-Kronig analysis (KKA). Twentyfive TO and LO modes were found at 70 K, and eighteen at 295 K. The obtained results are discussed and compared with published data.

*Keywords:* bismuth silicon oxide single crystals, Czochralski technique, critical diameter, critical rate of rotation, optical properties.

### INTRODUCTION

Crystals with the nominal chemical formula of Bi<sub>12</sub>MO<sub>20</sub>, where M is Si, Ti, Ge, Mn or some other four-valente ion, or a combination of two ions are known as sillenites. Lars Gunar Sillen uncovered Bi<sub>12</sub>SiO<sub>20</sub> 1941, in Durango, Mexico and latter the whole group were named after him. All compounds with the Bi<sub>12</sub>MO<sub>20</sub> structure crystallize in the cubic system with I23 space group.<sup>1</sup>

Bismuth silicon oxide (BSO), due to its photoconductive and electro-optical properties, has found application in a number of technologically important optical devices. It demonstrated unique properties for use in Pockels Readout Optical Memories (PROM).<sup>2</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>3</sup> real-time interferometry,<sup>4</sup> image amplification,<sup>5</sup> etc. Bi<sub>12</sub>SiO<sub>20</sub> also belongs to the

\* Corresponding author, E-mail: galek@EUnet.yu.

# Serbian Chemical Society active member.

family of isomorphous compounds that could find broad application in integrated optics.<sup>6</sup> These applications demand the most stringent requirements on the optical quality of the material, including refractive index homogeneity,<sup>7</sup> uniformity of the optical density and freedom from light scattering defects such as inclusions.  $\text{Bi}_{12}\text{SiO}_{20}$  crystals are produced mainly by the Czochralski technique,<sup>8–12</sup> but recently also by the Bridgman method.<sup>13</sup> However, intrinsic defects such as core, striations and inclusions appear during crystal growth, degrading their optical quality and, thus, requiring a means for their elimination. The aim of the research presented here was to obtain high quality single crystals and determine their optical properties.

#### EXPERIMENTAL

$\text{Bi}_{12}\text{SiO}_{20}$  single crystals were grown by the Czochralski technique using a MSR 2 crystal puller controlled by a Eurotherm. The temperature fluctuations were typically lower than 0.2 °C. The crystal diameter was set and automatically kept constant by an additional weighing assembly that continuously monitored the crucible weight. The absolute value of the deviation from the given diameter was below 0.1 mm. The melt was contained in a platinum crucible ( $\varnothing$  4 cm, 4 cm depth), which was placed in an alumina vessel on 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>14</sup> The crystals were grown in an air atmosphere. An iridium wire was used as the crystal seed for the first experiment. A seed cut from the produced  $\text{Bi}_{12}\text{SiO}_{20}$  crystals was used for the next crystals.

All crystals were grown from synthesized  $\text{Bi}_2\text{O}_3$  and  $\text{SiO}_2$ . The starting materials were mixed together in the stoichiometric ratio (6:1), or 14.28 mol %  $\text{SiO}_2$ . Various pull rates were examined and the best results were obtained using pull rates in the range 5–6 mm/h. 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.

All the obtained crystal plates were checked in polarized light to reveal strains.

The chemical compositions of the products were determined by the XRD powder technique. All samples were examined under the same conditions, using a Philips PW 1729 X-ray generator, a Philips 1710 diffractometer and the original APD software. The radiation source was an X-ray LLF tube with copper radiation and a graphite monochromator. The radiation was  $\lambda_{\text{CuK}\alpha_1} = 0.15405$  nm. The anode tube load was 40 kV and 30 mA. Slits of 1.0 and 0.1 mm were fixed. The samples were pressed into standard aluminium frames and measured in the  $2\theta$  range from 4° to 100°. Each  $1/50^\circ$  (0.02°) was measured for 0.5 s. The MPDS program and JCPDS (ASTM) card files were used for product identification.

The infrared spectra were recorded on a Bomem DA8 Fourier-transform spectrometer. A new hyper splitter was used for the far infrared region (from 20–700  $\text{cm}^{-1}$ ) and a standard KBr (400–5000  $\text{cm}^{-1}$ ) beamsplitter for the infrared region. All the spectra were obtained for a near normal incidence configuration at different temperatures ( $T = 70$  K, and 295 K). A Global (SiC) source was used in both regions of the infrared spectra. All measurements were performed using a Janis STDA 100 cryostat, which enabled the precise exchange of the sample and the mirror in the same position of the cold finger. At the lower temperature, a polyethylene (far IR) and ZnSe (mid IR) window were used. Liquid nitrogen ( $\text{LN}_2$ ) was used as the coolant. The temperatures below 77 K were obtained through additional pumping-out of  $\text{N}_2$ . A Lake Shore 330 temperature controller provided a temperature error within 0.1 °C.

#### RESULTS AND DISCUSSION

The hydrodynamics of a melt are governed by buoyancy-driven convection, by forced convection due to crystal rotation and by thermo-capillary surface convection.

Three dimensionless numbers can describe all these flows, where the Grashof number ( $Gr$ ) depends on the depth of the melt, the Reynolds number ( $Re$ ) on the rotation rate of the crystal and the Marangoni number ( $Ma$ ) on the temperature gradients over the surface of the melt act. The  $Ma$  number will not change significantly if a small temperature gradient exists over the surface of the melt, and can be neglected. So, the hydrodynamics will be governed mainly by the  $Re$  and  $Gr$  numbers. These dimensionless numbers can be written as

$$Re = \omega d^2/4\nu, \quad (1)$$

$$Gr = g \beta \Delta T R^3 \nu^{-2}, \quad (2)$$

where  $\omega$  – rotation rate in  $\text{rad s}^{-1}$ ,  $d$  – crystal diameter,  $\nu$  – kinematic viscosity,  $g$  – acceleration due to gravity,  $\beta$  – volumetric expansion coefficient of the melt,  $\Delta T = T_{\text{crucible}} - T_{\text{mp}}$ ,  $R$  – crucible radius.<sup>15,16</sup>

As has been pointed out by different authors,<sup>11,17</sup> the crystal rotation rate and the axial temperature distribution are two very important parameters which affect the shape of the crystal/melt interface and these two growth parameters must be taken into account in order to understand the shape of the crystal/melt interface. Conduction and convection caused by pulling are included in the crystal and rod pull rod. To simplify the current analysis, it was chosen to neglect the effects of internal radiation through the crystal. It was presumed, as Carruthers<sup>18</sup> did, that there was no change in the kinematic viscosity at the interface melt/crystal during the growth process and that there was equilibrium  $Gr = Re^2$ . There is, during this time, a flat crystal/melt interface with a critical rotation rate  $\omega_c$  and a critical diameter  $d_c$ . According to published data for the physical properties of BSO,<sup>11</sup> the critical rotation rate  $\omega_c$  and the critical diameter  $d_c$  were found to be 10 mm, and 20 rpm, respectively.

It has been found<sup>19</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 that for larger diameters a lower growth rate is needed. If the diameter changes rapidly, there is a possibility of inclusions forming in the center 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.

Bi<sub>12</sub>SiO<sub>20</sub> crystals grown by Bridgman method<sup>13</sup> were initiated on seed crystals oriented along the [001], [110], [111], or [112] directions, where a core appeared when grown along the [001] and [110] directions. This is in accordance with published data<sup>20</sup> where different facets for various growth directions were observed. Recently it was found<sup>21</sup> that the core is formed when the crystal/melt interface is convex towards the melt and the (110) and/or (100) planes are tangential to the interface. The obtained crystals grew in the [111] direction and no core was observed. In this work the [111] direction was also used for crystal growth, although some authors<sup>11,17</sup> used the [001] direction. Before necking application was tried, as the first step in the crystal run, of extended seed as the BSO crystals have a great tendency towards faceting. The aim was to pro-

duce an effect similar to the remove dislocations before necking in dislocation-free silicon when pulling the crystal in the [111] direction. Pulling the crystal from a melt by the Czochralski technique is a process essentially governed by the shape of the meniscus and the thermal gradients on both sides of the growth interface. It is a well-known practical fact that in order to produce a crystal in the shape of a right cylinder some kind of regulation of the external conditions, like the supplied heating power or the pulling speed, has to be implemented. From the hydrodynamics equations one obtains  $\omega_c$  about 21 rpm, and we used a value 20 rpm, as many approximations were applied. When a higher  $\omega_c = 25$  rpm was used, the single crystal had a core although the other conditions were the same.<sup>14</sup> It was supposed that the solid/melt interface was not flat and hence a core was formed although pulling in the [111] direction. When  $\omega_c = 20$  rpm was used, the obtained crystals were without core. These crystals were checked by taking slices from different parts of the crystals: beneath the neck, two from the central part, and the last one near the bottom. None had a core. As a result of these experiments, pale yellow crystals 10 mm in diameter were produced with a length of about 40 mm. The rate of crystal growth was experimentally obtained to be 5 mm/h. The colour of the crystals is in accordance with published data.<sup>20,22</sup>

The absence of a core was confirmed by viewing polished crystal slices in both normal and polarised light. The polarised infrared reflectance spectrum of a  $\text{Bi}_{12}\text{SiO}_{20}$  single crystal in the region from 1000 to 2000  $\text{cm}^{-1}$  revealed several small peaks for the sample which had a rotation rate of 25 rpm.<sup>14</sup> These peaks disappeared in the spectrum of the sample with rotation rate of 20 rpm and it was concluded that these peaks originate from the core in the  $\text{Bi}_{12}\text{SiO}_{20}$  single crystal.<sup>14</sup> The reflectance spectra of  $\text{Bi}_{12}\text{SiO}_{20}$  single crystals in the region from 400 to 2000  $\text{cm}^{-1}$  for both rotation rate are given in the Fig. 1. Fig. 2 represents a magnification of the region from 900 to 1800  $\text{cm}^{-1}$ .

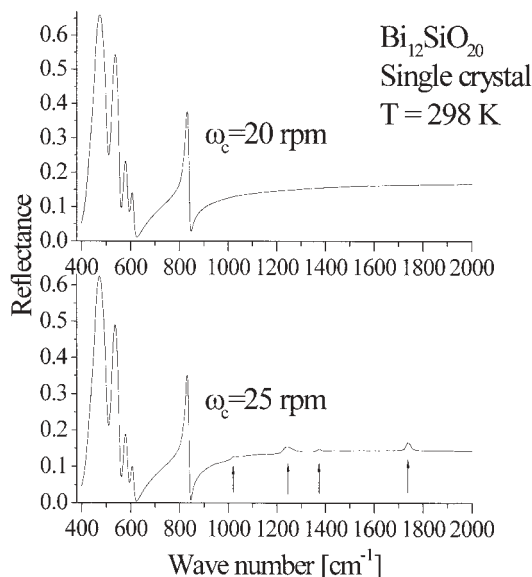


Fig. 1. The compared polarised reflectance spectra of a  $\text{Bi}_{12}\text{SiO}_{20}$  single crystals for  $\omega_c$  20 and 25 rpm, in the range 400–2000  $\text{cm}^{-1}$  at 298 K.

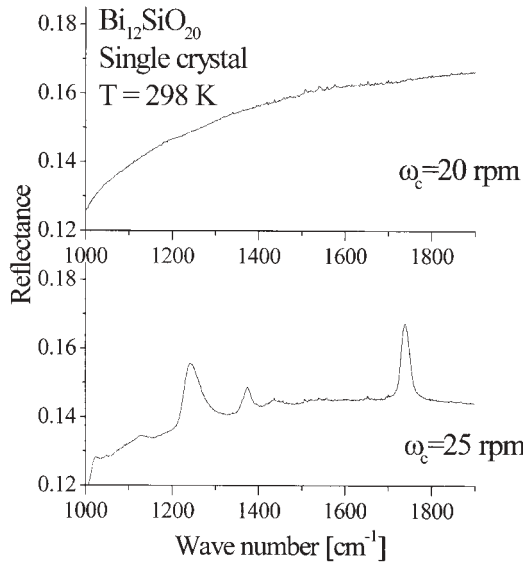


Fig. 2. The compared polarised reflectance spectra of a Bi<sub>12</sub>SiO<sub>20</sub> single crystals for  $\omega_c$  20 and 25 rpm, in the range 1000–1800 cm<sup>-1</sup> at 298 K.

The observed peaks between 1000 and 1800 cm<sup>-1</sup>, denoted by arrows at Fig. 1 and magnified in Fig. 2, are in direct correspondence with the appearance of a core in the crystal. The nature of these peaks is not clear. It is obvious that the presence of a core in BiSiO single crystals does not change the normal phonon structure. To the best of our knowledge, the appearance of these peaks in IR spectra has not been noticed previously.

The structure properties were obtained using X-ray analysis of powdered samples. A Philips PW 1710 diffractometer was used in the  $2\theta$  ranges from 4° to 100°. The unit cell of bismuth silicon oxide was calculated by the least square method using 32 reflections including more  $K\alpha_2$  for 5 reflections. All reflections correspond to Bi<sub>12</sub>SiO<sub>20</sub> crystals with the parameter of the cubic I-centred cell  $a = 1.01067$  nm. Some divergence from the compared results can be explained by the fact that X-ray powder diffraction analysis gives a statistical result. Our calculated result for the lattice parameter is  $a = 1.0096$  nm, which is in good agreement with published data.<sup>19,20,23</sup> An X-ray diffractogram for powdered Bi<sub>12</sub>SiO<sub>20</sub> was given in a previous article.<sup>14</sup> It has been reported<sup>24</sup> that only almost perfect single crystals can split X-ray reflections into  $K\alpha_1$  and  $K\alpha_2$  and the presence of doublets is one more confirmation of the high quality of the produced crystals.

The infrared reflectance spectra of the Bi<sub>12</sub>SiO<sub>20</sub> single crystals at 70 K and 295 K in the region 30–900 cm<sup>-1</sup> are presented in Fig. 3.

The spectra were recorded in the wave numbers range from 20 to 5000 cm<sup>-1</sup>, but are only presented in the range from 30 to 900 cm<sup>-1</sup>, as below 30 cm<sup>-1</sup> the noise level was large, and above 900 cm<sup>-1</sup> the reflectance curve were almost flat. The small peak at 3451 cm<sup>-1</sup> belongs to the stretching mode of OH groups, as the Bi<sub>12</sub>SiO<sub>20</sub> single crys-

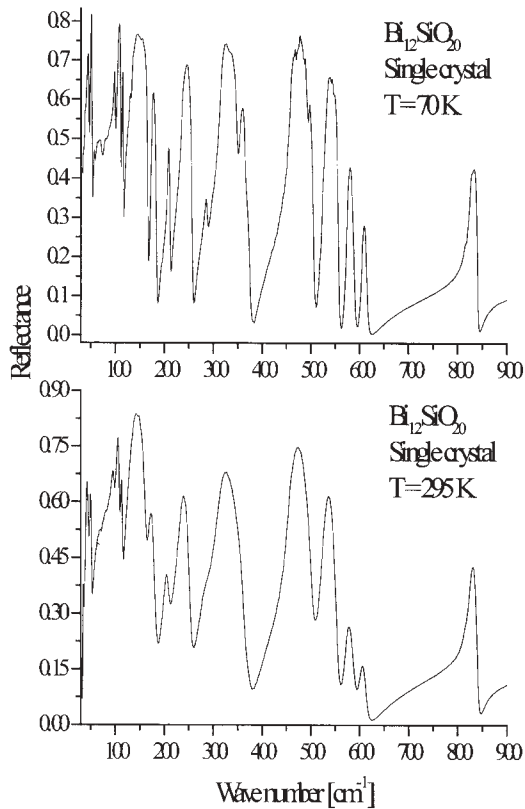


Fig. 3. The infrared reflectance spectra of a  $\text{Bi}_{12}\text{SiO}_{20}$  single crystal at  $T = 70 \text{ K}$  and  $T = 295 \text{ K}$ .

tals were grown in an air atmosphere. The position of the OH group at  $3451 \text{ cm}^{-1}$  is in accordance with that found in the literature.<sup>25</sup>

Crystal  $\text{Bi}_{12}\text{SiO}_{20}$  has a cubic unit cell with parameters  $a = 1.01067 \text{ nm}$ ,  $Z = 2$  (two identical motives in the unit cell), and space group  $I23 (T^3)$ . Factor group analysis yields:<sup>26</sup>

$$\Gamma = 8A + 8E + 25F \quad (3)$$

Among these modes, only the F modes are infrared active.

After Kramers-Kronig analysis of the spectra of a  $\text{Bi}_{12}\text{SiO}_{20}$  single crystal at 70 K and 295 K (Fig. 4), the positions of TO modes were obtained. This analysis of the 70 K spectrum gave all 25 infrared active modes, which were predicted for the mentioned symmetry relation (3). At 295 K only 18 TO modes were revealed. In the literature,<sup>27</sup> 10 active modes for a  $\text{Bi}_{12}\text{SiO}_{20}$  single crystal at room temperature were reported and our results for  $\text{Bi}_{12}\text{SiO}_{20}$  single crystals could be very useful for understanding of the assignment of the normal modes and the overall characterization of these crystals.

The values of TO and LO modes at 70 K and 295 K are presented in Tables I and II, respectively.

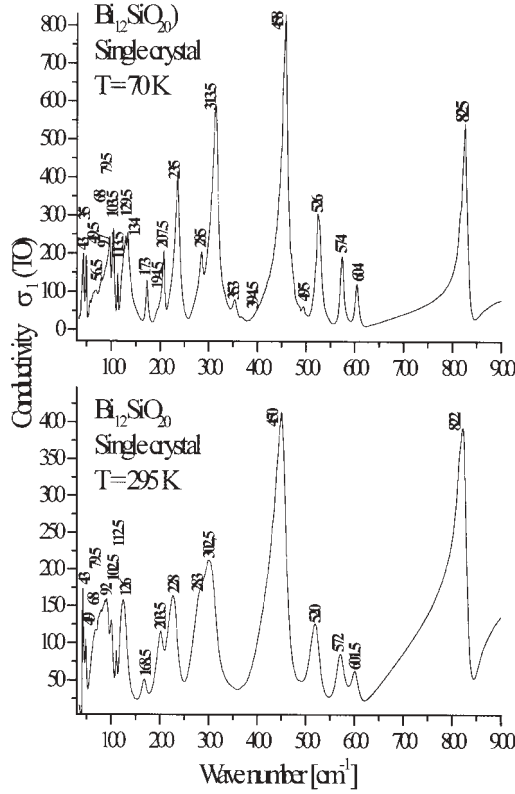


Fig. 4. TO modes ( $\omega_{TO}$ ) of a Bi<sub>12</sub>SiO<sub>20</sub> single crystal at 70 K and 295 K.

The positions of the TO modes at 49.5 and 394.5 cm<sup>-1</sup> are not entirely reliable. In comparison with the TO modes of a Bi<sub>12</sub>GeO<sub>20</sub> single crystal,<sup>28</sup> the TO mode at 49.5 cm<sup>-1</sup> has its corresponding well-defined mode at 52 cm<sup>-1</sup>, and the mode at 394.5 cm<sup>-1</sup> has the mode at 352 cm<sup>-1</sup>. For this reason these not absolutely defined modes were included. It should be pointed that we revealed 20 TO modes at 70 K in our previous article,<sup>29</sup> but after more precise measurements of both the infrared reflectance spectra and the Kramers-Kronig analysis, the mentioned 25 TO modes were obtained.

Comparing with previous results<sup>28</sup> on the infrared spectra of Bi<sub>12</sub>GeO<sub>20</sub>, the main difference concerns the modes at 680 cm<sup>-1</sup> (Bi<sub>12</sub>GeO<sub>20</sub>) and 825 cm<sup>-1</sup> (Bi<sub>12</sub>SiO<sub>20</sub>). According to the literature,<sup>25</sup> these vibrations consist entirely of Ge–O (Si–O) vibrations. This assumption can be confirmed using the simple formula for a diatomic molecule.:

$$\frac{\omega_{Si-O}}{\omega_{Ge-O}} = \sqrt{\frac{m_{Ge-O}}{m_{Si-O}}} = 1.14 \quad (5)$$

where  $\omega = \frac{m_{Ge(Si)} m_0}{m_{Ge(Si)} + m_0}$ . Taking  $\omega_{Ge-O} = 680$  cm<sup>-1</sup>, one obtains  $\omega_{Ge-O} = 775.2$  cm<sup>-1</sup>, which is in fairly good agreement with the experimental value at 825 cm<sup>-1</sup>.

TABLE I. The transverse (TO) frequencies of the optical phonons of  $\text{Bi}_{12}\text{SiO}_{20}$  single crystal in the range  $30\text{--}900\text{ cm}^{-1}$  at  $T = 70\text{ K}$  and  $T = 295\text{ K}$

Number of phonon mode	Position of phonon mode at $T = 70\text{ K/cm}^{-1}$	Position of phonon mode at $T = 295\text{ K/cm}^{-1}$
1	35	
2	43	43
3	56.5	49
4	52	
5	68	68
6	79.5	79.5
7	97	92
8	103.5	102.5
9	113.5	112
10	129.5	126
11	134	
12	173	
13	194.5	
14	207.5	203.5
15	235	228
16	285	283
17	313.5	302.5
18	353	
19	394	
20	458	450
21	495	
22	526	520
23	574	572
24	604	601.5
25	825	822



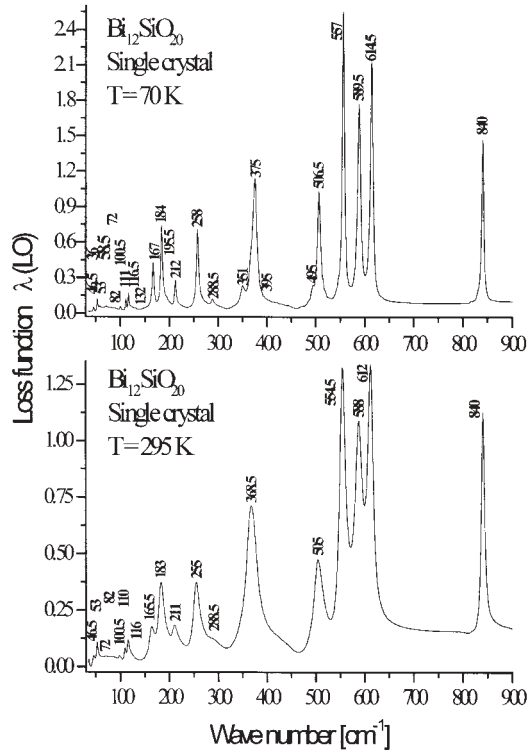


Fig. 5. LO modes ( $\omega_{LO}$ ) of a Bi<sub>12</sub>SiO<sub>20</sub> single crystal at 70 K and 295 K.

TABLE II. The longitudinal (LO) frequencies of the optical phonons of Bi<sub>12</sub>SiO<sub>20</sub> single crystal in the range 30–900 cm<sup>-1</sup> at  $T = 70$  K and  $T = 295$  K

Number of phonon mode	Position of phonon mode at $T = 70$ K/cm <sup>-1</sup>	Position of phonon mode at $T = 295$ K/cm <sup>-1</sup>
1	36	
2	46.5	46.5
3	53	53
4	58.5	
5	72	72
6	82	82
7	100.5	100.5
8	111	110
9	116.5	116
10	132	165.5
11	167	

TABLE II. Continued

Number of phonon mode	Position of phonon mode at $T = 70 \text{ K/cm}^{-1}$	Position of phonon mode at $T = 295 \text{ K/cm}^{-1}$
12	184	183
13	195.5	
14	212	211
15	258	255
16	288.5	288.5
17	351	368.5
18	374	
19	395	
20	506.5	505
21	495	
22	557	554.5
23	589.5	588
24	614.5	612
25	840	840

The found TO-LO splitting in  $\text{Bi}_{12}\text{SiO}_{20}$  is not very large pointing to a weak ionic bond in this material (Table II). The values of the LO modes are presented in Fig. 5.

#### CONCLUSION

The conditions for growing  $\text{Bi}_{12}\text{SiO}_{20}$  single crystals were calculated by using a combination of Reynolds and Grashof numbers. From the hydrodynamics of the melt, a critical crystal diameter  $d_c = 10 \text{ mm}$  and a critical rate of rotation  $\omega_c = 20 \text{ rpm}$  were calculated. The value of the rate of crystal growth was experimentally found to be  $5 \text{ mm/h}$ . The  $[111]$  direction is suitable for growth of a  $\text{Bi}_{12}\text{SiO}_{20}$  single crystal without a core.

The values of all 25 active infrared modes were revealed in the reflectance spectra at  $70 \text{ K}$  and  $295 \text{ K}$  by Kramers-Kronig analysis. We have some reserve about the lines at  $49.5$  and  $394.5 \text{ cm}^{-1}$  (TO modes at  $70 \text{ K}$ ) but more precise measurements in the far-infrared region could resolve this dilemma.

#### ИЗВОД

##### РАСТ И ОПТИЧКЕ ОСОБИНЕ МОНОКРИСТАЛА $\text{Bi}_{12}\text{SiO}_{20}$

АЛЕКСАНДАР ГОЛУБОВИЋ,<sup>1</sup> СЛОБОДАНКА НИКОЛИЋ,<sup>1</sup> РАДОШ ГАЈИЋ,<sup>1</sup> СТЕВАН ЂУРИЋ<sup>2</sup> и  
АНДРЕЈА ВАЛЧИЋ<sup>3</sup>

<sup>1</sup>Институт за физику, Предревница 118, бр. 57, 11001 Београд, <sup>2</sup>Рударско-геолошки факултет, Бушина 7, бр. 162, 11000 Београд и <sup>3</sup>Технолошко-металуршки факултет, Карнегијева 4, 11000 Београд

Монокристали  $\text{Bi}_{12}\text{SiO}_{20}$  су расли из растопа по методи Чохралског. Вредности критичког пречника кристала  $d_c = 10 \text{ mm}$  и критичне брзине ротације  $\omega_c = 20 \text{ o/min}$  су

израчунате коришћењем једначина динамике флуида. Брзина раста кристала од 5 mm/h је одређена експериментално. Кристал је растао у правцу [111]. Помоћу рендгенске дифракционе анализе спрашеног узорка одређен је параметер решетке  $a = 1,0096$  nm. Рефлексиони спектри су снимљени на различитим температурама у оспегу таласних бројева 20–5000 cm<sup>-1</sup>. Помоћу Крамерс-Крониг анализе одређене су вредности ТО и LO модова за све спектре. Нађено је 25 ТО и LO модова на 70 К и 18 ТО и LO модова на 295 К. Добијени резултати су дискутовани и поређени са литературним подацима.

(Примљено 11. маја 2001)

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