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SCIENTIFIC PAPER

535-15.543.42.548.55

## THE OPTICAL PROPERTIES OF BISMUTH GERMANIUM OXIDE SINGLE CRYSTALS IN INFRARED SPECTRA

*Bi<sub>12</sub>GeO<sub>20</sub> single crystals were grown from the melt by the Czochralski technique. The critical diameter and the critical rate of rotation were calculated using the hydrodynamic equations for the melt. Suitable polishing and etching solutions were determined. The reflectance spectra were recorded in the wave numbers range 20–5000 cm<sup>-1</sup> at different temperatures. For all recorded spectra, the values of the vibrational TO and LO modes were found using the Kramers–Kronig analysis (KKA). The obtained results are discussed and compared with published data.*

Bi<sub>12</sub>GeO<sub>20</sub> (BGO) crystal belongs to the sillenite family with the formula Bi<sub>12</sub>MO<sub>20</sub>, where M=Si, Ge, Ti, Tl, Fe, etc. Bismuth germanium oxide also belongs to the large family of photo refractive materials, which are very attractive because of their high electro-optical coefficient, very high resistivity, large photo sensibility, memory effect and their capability to modulate refraction indices by a non-uniform illumination [1]. BGO crystals find a lot of application in the field of optics, for example as holographic storage [2,3], two-dimensional commutation [4], phase conjugation and real-time interferometry [5]. For these purposes, high optical quality crystals are required, which means that crystals with flat interfaces between the liquid and solid must be grown. All change in the interface shape produces a variety of defects in the crystals, such as dislocation, core formation, stresses, impurity segregation, cracks, and gas-bubble entrapment [6,7]. Sillenite single crystals are typically produced by the Czochralski technique, and the aim of the research presented here was to obtain high quality single crystals and determine their optical properties.

### EXPERIMENTAL

Bi<sub>12</sub>GeO<sub>20</sub> single crystals were grown by the Czochralski technique using a MSR 2 crystal puller controlled by a Eurotherm. This system keeps the crucible temperature constant within 0.2 K. 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 (ø 4 cm, depth 4 cm), 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 [8]. An air atmosphere was used. An iridium wire was used as the crystal seed.

Bi<sub>2</sub>O<sub>3</sub> was synthesised in our laboratory from pure Bi (purity 99.5 %) and concentrated HNO<sub>3</sub>. The purity of the GeO<sub>2</sub> was also 99.5 %. All crystals were grown from synthesised Bi<sub>2</sub>O<sub>3</sub> and GeO<sub>2</sub> [9]. The starting materials were mixed together in the stoichiometric ratio (6:1). The melt was contained in a platinum crucible (ø 4 cm, depth 4 cm). The crucible was not rotated during the growth. The conditions for the growth of Bi<sub>12</sub>GeO<sub>20</sub> single crystals by the Czochralski technique were optimised mainly on the hydrodynamics in the melt. The pull rates were experimentally determined. After the growth run, the crystal boule was cooled at a rate of about 50 K/h down to room temperature.

Attempts were made to find the optimal solution for the chemical polishing and etching of Bi<sub>12</sub>GeO<sub>20</sub> single crystals. These combinations were for the etching solution: HF + HNO<sub>3</sub> in the ratio 2:1, HCl + H<sub>2</sub>O in the ratio 1:2, and HCl + H<sub>2</sub>O in ratio 1:5. For the chemical polishing of the bismuth germanium oxide crystals a solution of HCl + HNO<sub>3</sub> + H<sub>2</sub>O in the ratio 1:1:5 was tried.

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

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 cm<sup>-1</sup>) and a standard KBr (400–5000 cm<sup>-1</sup>) beamsplitter for the infrared region. All the spectra were obtained for the near normal incidence configuration at different temperatures (T=77 K, and 298 K). For both spectral regions Globar (SiC) was used as the source and, in addition a Hg lamp for the far infrared region. 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

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Paper received: October 21, 2000

Paper accepted: December 4, 2000

(LN<sub>2</sub>) was used as the coolant. A Lake Shore 330 temperature controller provided a temperature error within 0.1 K.

## RESULTS AND DISCUSSION

Conduction and convection were considered in the melt and the fluid velocity was determined by solution of the Navier–Stokes equation and equations written for an incompressible Newtonian fluid [10]. Nonslip and nonpenetration boundary conditions were imposed at the crucible wall and the melt–crystal interface. The crucible was considered to be stationary, during crystal rotation at a constant rate. Tangential stresses generated by surface tension gradients were applied to account for Marangoni flow, while no flow was allowed normal to the melt meniscus. Marangoni flow is given by Eq. (1).

$$Ma = -(\partial\gamma/\partial T) \cdot \Delta T (R - r) (\rho \cdot \nu \cdot \alpha)^{-1} \quad (1)$$

where  $(\partial\gamma/\partial T)$  – is the temperature coefficient of the surface tension;  $\Delta T$  – the temperature difference ( $T_{\text{crucible}} - T_{\text{mp}}$ );  $R$  – the crucible radius;  $r$  – the crystal radius;  $\rho$  – the melt density;  $\nu$  – the kinematic viscosity, and  $\alpha$  – the thermal diffusivity of the melt.

Conduction and convection caused pulling are included in the crystal and rod pull rod. To simplify the current analysis, it was decided to neglect the effects of internal radiation through the crystal.

The hydrodynamics of a melt are governed by buoyancy–driven convection or free 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 rotation rate of the crystal modifies the Reynolds number ( $Re$ ), and the temperature gradients over the surface of the melt influences the Marangoni number ( $Ma$ ). The Reynolds and Grashof numbers can be written by

$$Re = \omega r^2 \nu^{-1}, \quad (2)$$

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

where  $\omega$  – is the rotation rate;  $r$  – the crystal radius;  $\nu$  – the kinematic viscosity;  $g$  – the acceleration due to gravity;  $\beta$  – the volumetric expansion coefficient of the melt;  $\Delta T$  – the temperature difference ( $T_{\text{crucible}} - T_{\text{mp}}$ ), and  $R$  – the radius of the crucible.

It was assumed, as Carruthers did [11], that there was no change in the kinematic viscosity at the melt/crystal interface during the growth process and there was equilibrium  $Gr = Re^2$ . There is, during this time, a flat melt/crystal interface with a critical rotation rate  $\omega_c$  and a critical diameter  $d_c$ .

The conditions for the growth of Bi<sub>12</sub>GeO<sub>20</sub> single crystals by the Czochralski technique were optimised [9, 12]. The crystals were pulled at a rate of 5 mm/h with a rotation of 20 rpm so that a flat solid/liquid interface was obtained at the required crystal diameter. The obtained

crystal boules were pale yellow and transparent, about 12 mm in diameter, and 40 mm long. The high quality of the obtained crystals was confirmed by X–Ray analysis [9, 12] as doublets of  $K\alpha_1$  and  $K\alpha_2$  appeared (only almost perfect single crystals can split X–Ray reflections into  $K\alpha_1$  and  $K\alpha_2$  [13]).

A solution of HCl + HNO<sub>3</sub> + H<sub>2</sub>O in the ratio 1:1:5 was found to be suitable for chemical polishing of the Bi<sub>12</sub>GeO<sub>20</sub> crystals, and an etching solution of HCl + H<sub>2</sub>O in ratio 1:5 was found satisfactory. Observation of each of the pits revealed that the Bi<sub>12</sub>GeO<sub>20</sub> single crystals grew in the [111] direction.

The infrared reflectance spectra of Bi<sub>12</sub>GeO<sub>20</sub> single crystals at 77 K and 298 K in the region 35–900 cm<sup>-1</sup> are presented in Figure 1.

The spectra were recorded in the wave numbers range from 20 to 5000 cm<sup>-1</sup>, but are presented in the range from 35 to 900 cm<sup>-1</sup>, as there was a lot of noise below 35 cm<sup>-1</sup>, and beyond 900 cm<sup>-1</sup> the reflectance curves were almost flat. There is a small peak at 3451 cm<sup>-1</sup> which belongs to the stretching mode of OH groups as the Bi<sub>12</sub>GeO<sub>20</sub> single crystals were grown in an air atmosphere. The position of OH group at 3451 cm<sup>-1</sup> is in accordance from this found in the literature [14].

The Bi<sub>12</sub>GeO<sub>20</sub> crystal has a cubic unit cell with parameters  $a = 1.014558$  nm,  $Z = 2$  (two identical motives in the unit cell), and the space group  $I23 (T^3)$ . The factor group analysis yields [15]:

$$\Gamma = 8A + 8E + 25F \quad (4)$$

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

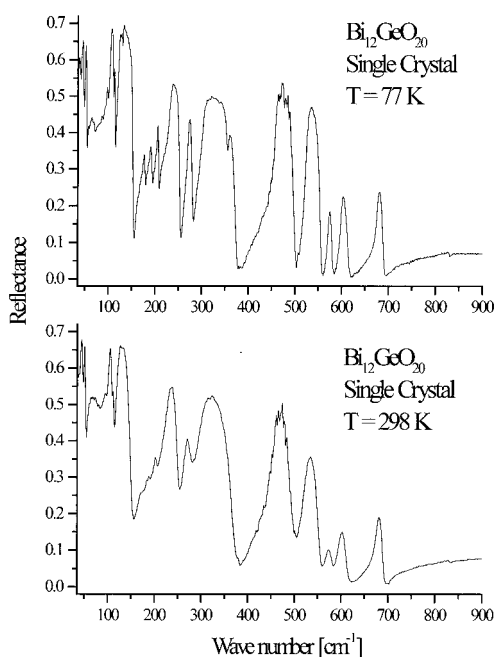


Figure 1. Reflectance spectra of Bi<sub>12</sub>GeO<sub>20</sub> single crystals at 77 K and 298 K

To the best of our knowledge, the parameters of the TO and LO modes of a Bi<sub>12</sub>GeO<sub>20</sub> single crystal have not been published in the literature. By the Kramers–Kronig analysis of the spectrum of a Bi<sub>12</sub>GeO<sub>20</sub> single crystal at 77 K (Figure 2), the positions of the TO modes were obtained. This analysis gave all 25 infrared active modes, which were predicted by the mentioned symmetry relation (4). The Kramers–Kronig analysis of the Bi<sub>12</sub>SiO<sub>20</sub> spectrum gave results [8, 16] which were in accordance with published data where also KKA was used [17].

The values of the TO and LO modes at 77 K and 298 K are presented in Tables 1 and 2, respectively.

The positions of the TO modes at 69, 87 and 131 cm<sup>-1</sup> are not entirely reliable. In comparison with the TO modes from a Bi<sub>12</sub>SiO<sub>20</sub> single crystal [16], the TO mode at 131 cm<sup>-1</sup> has its corresponding well-defined mode at 134 cm<sup>-1</sup>, but the modes at 69, 87 cm<sup>-1</sup> have not. It is worth emphasizing that only 20 TO modes from the Bi<sub>12</sub>SiO<sub>20</sub> single crystal [16] were revealed in the infrared spectra at 75 K, and 5 TO modes are absence.

Compared with previous results [12] on the infrared spectra of Bi<sub>12</sub>SiO<sub>20</sub>, the main difference was found to concern the modes at 680 cm<sup>-1</sup> (Bi<sub>12</sub>GeO<sub>20</sub>) and 821 cm<sup>-1</sup> (Bi<sub>12</sub>SiO<sub>20</sub>). These vibrations consist entirely of Ge–O (Si–O) vibrations according to [15]. This assumption can be confirmed using the simple formula for a diatomic molecule:

$$\frac{\omega_{\text{Ge-O}}}{\omega_{\text{Si-O}}} = \sqrt{\frac{m_{\text{Si-O}}}{m_{\text{Ge-O}}}} = 0.88 \quad (5)$$

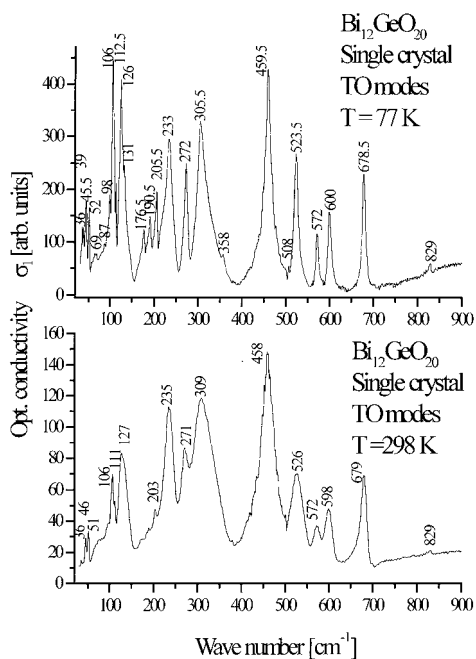


Figure 2. TO modes ( $\omega_{\text{TO}}$ ) of Bi<sub>12</sub>GeO<sub>20</sub> single crystals at 77 K and 298 K

Table 1. The transverse (TO) frequencies of the optical phonons of Bi<sub>12</sub>GeO<sub>20</sub> single crystals in the range 35–900 cm<sup>-1</sup> at T = 77 K and T = 298 K

Number of phonon mode	Position of phonon mode at T = 77 K [cm <sup>-1</sup> ]	Position of phonon mode at T = 298 K [cm <sup>-1</sup> ]
1	36	36
2	39	
3	45.5	46
4	52	51
5	69	
6	87	
7	98	
8	106	106
9	112.5	111
10	126	127
11	131	
12	176.5	
13	190.5	
14	205.5	203
15	233	235
16	272	271
17	305.5	309
18	358	
19	459.5	458
20	508	
21	523.5	526
22	572	572
23	600	598
24	678.5	679
25	829	829

Table 2. The longitudinal (LO) frequencies of the optical phonons of Bi<sub>12</sub>GeO<sub>20</sub> single crystals in the range 35–900 cm<sup>-1</sup> at T = 77 K and T = 298 K

Number of phonon mode	Position of phonon mode at T = 77 K [cm <sup>-1</sup> ]	Position of phonon mode at T = 298 K [cm <sup>-1</sup> ]
1	37	37
2	40.5	
3	48	47
4	54.5	54
5	70.5	
6	88	
7	99.5	
8	111	109
9	115	113
10	153.5	150.5
11	131	
12	179	
13	193.5	
14	208	206
15	253.5	249
16	280	278
17	355	366
18	373	
19	498	493
20	508	
21	553	548
22	580	577
23	613	608
24	689	687.5
25	830	830

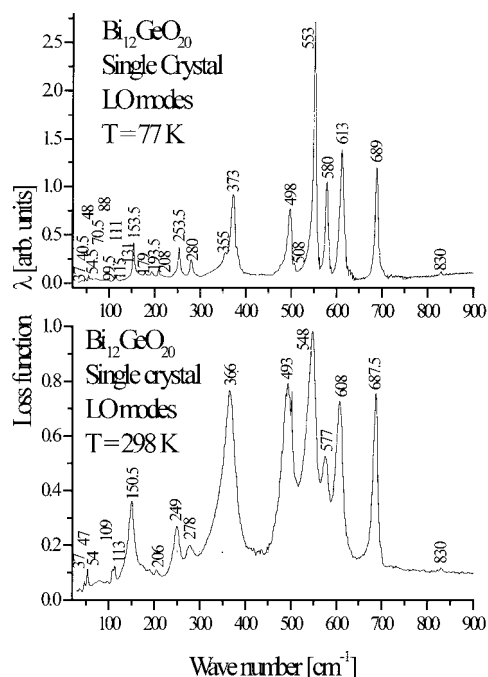


Figure 3. LO modes ( $\omega_{LO}$ ) of  $\text{Bi}_{12}\text{GeO}_{20}$  single crystals at 77 K and 298 K

where  $\bar{m} = \frac{m_{\text{Ge}(\text{Si})} \cdot m_0}{m_{\text{Ge}(\text{Si})} + m_0}$ . Taking  $\omega_{\text{Si-O}} = 821 \text{ cm}^{-1}$ , one obtains  $\omega_{\text{Ge-O}} = 722 \text{ cm}^{-1}$ , which is in fairly good agreement with the experimental value at  $680 \text{ cm}^{-1}$ .

It was found that the TO–LO splitting in  $\text{Bi}_{12}\text{GeO}_{20}$  is not very large, indicating the weak ionic bond in the material (Table II). The values of the LO modes are presented in Figure 3.

## CONCLUSION

The conditions for growing  $\text{Bi}_{12}\text{GeO}_{20}$  single crystals were calculated using a combination of Reynolds and Grashof numbers. It was assumed that the influence of the Marangoni number could be neglected. The pale yellow crystals were obtained as a result of the used hydrodynamics formulae, which were

## IZVOD

### OPTIČKE OSOBINE MONOKRISTALA $\text{Bi}_{12}\text{GeO}_{20}$ U INFRACRVENIM SPEKTRIMA

(Naučni rad)

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Monokristali  $\text{Bi}_{12}\text{GeO}_{20}$  su dobijani iz rastopa metodom rasta kristala po Čochraskom. Vrednosti kritičnog prečnika kristala i kritične brzine rotacije su određeni korišćenjem jednačina iz dinamike fluida. Određena su optimalna sredstva za hemijsko poliranje i hemijsko nagrizanje. Refleksioni spektri su snimani na različitim temperaturama u opsegu talasnih brojeva od 20–5000  $\text{cm}^{-1}$ . Korišćenjem Kramers–Kronig analize (KKA) nađene se vrednosti TO i LO vibracionih modova za sve snimljene refleksione spektre. Dobijeni rezultati su diskutovani i upoređivani sa podacima iz literature.

Ključne reči: Čochraski • monokristal •  $\text{Bi}_{12}\text{GeO}_{20}$  • infracrvena spektroskopija • optičke osobine • optički fononi •

Key words: Czochralski technique • Bismuth germanium oxide • Single crystals • IR spectroscopy • Optical properties • Optical phonons •

in accordance to published data. It was found that a solution of  $\text{HCl} + \text{HNO}_3 + \text{H}_2\text{O}$  in the ratio 1:1:5 is suitable for chemical polishing of  $\text{Bi}_{12}\text{GeO}_{20}$  crystals. A solution of  $\text{HCl} + \text{H}_2\text{O}$  in the ratio 1:5 was shown to be suitable for chemical etching.

The values of all 25 active infrared modes were revealed in the reflectance spectra recorded at 77 K using the Kramers–Kronig analysis. Eighteen active infrared modes were found at room temperature (298 K). There is some dilemma about the lines at 69, 87 and  $131 \text{ cm}^{-1}$  for the TO modes at 77 K, which more precise measurements in the far-infrared region could resolve.

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