J.Serb.Chem.Soc. *65*(9)611-618(2000) UDC 546.289 87/.548.55-54-31:535.56
JSCS-2783 *Original scientific paper*

The optical properties of bismuth germanium oxide single crystals

ALEKSANDAR GOLUBOVIĆ,[*] RADOŠ GAJIĆ,[*] CHANGKANG CHEN[**]
and ANDREJA VALČIĆ[***]

[*]*Institute of Physics, Pregrevica 118, P. O. Box 57, YU-11001 Belgrade,* [**]*Clarendon Laboratory, Parks Road, Oxford OXI 3PU, United Kingdom, and* [***]*Faculty of Technology and Metallurgy, Karnegijeva 4, YU-11000 Belgrade, Yugoslavia*

(Received 1 February, revised 5 June 2000)

$Bi_{12}GeO_{20}$ single crystals were grown by the Czochralski technique. Suitable polishing and etching solutions were determined. Reflection spectra were recorded in the wave numbers range 20–5000 cm^{-1}, and compared with the spectra of $Bi_{12}SiO_{20}$ single crystals to study the position of the phonon modes. The optical constants of the $Bi_{12}GeO_{20}$ single crystals were obtained using Kramers-Kronig analysis. The obtained results are dicussed and compared with published data.

Keywords: Czochralski technique, bismuth germanium oxide, single crystals, optical properties, optical phonons.

INTRODUCTION

Bismuth germanium oxide is one of perhaps ten compounds which make up the sillenite family of piezoelectric bismuth oxides which crystallise in a body centred cubic structure and possess 23 symmetry.[1] These oxide compounds have a congruent melting point and parameters of about 1.0 nm. They have the structure $Bi_{12}MO_{20}$, where M is Si, Ti, Ge, Mn or some other four-valence ion, or a combination of two-ions.[2] All members of the sillenite family, commonly called the $Bi_{12}MO_{20}$ group, have space group I23.[3]

Bismuth germanium oxide (BGO) finds application for long delay lines because it possesses a very slow surface wave velocity. Due to its cubic structure, it is nearly isotropic to surface wave propagation, making it feasible to propagate the surface at an angle to the crystal axis as well as around curved surfaces of a plate. This enables the construction of a delay line where the surface wave follows a spiral path around the plate, making the effective length of the delay line many times longer than the physical length of the plate. Using this technique, it is possible to store a complete video frame of information from a TV broadcast. Coupling this long delay line with the appropriate circuitry to form a shift register, the information could then be circulated and stored indefinitely. Only the information, which has changed in the television picture, need be transmitted in order to update the information stored in the BGO shift register.[4] Besides its memory effect, bismuth germanium oxide finds many applications in the field of optics, such as holographic storage[4] and two-dimensional commutation.[5] These applications place the most stringent requirements on the optical quality of material. The aim of this study was the study of optical properties of the obtained $Bi_{12}GeO_{20}$ single crystals.

EXPERIMENTAL

$Bi_{12}GeO_{20}$ single crystals were grown by the Czochralski technique using a MSR 2 crystal puller controlled by an Eurotherm. This system keeps the crucible temperature constant to within 0.2 ºC. The crystal diameter was predetermined and automatically kept constant by an additional weighing assembly continuously monitoring the crucible weight. The absolute value of the deviation from the given diameter was below 0.1 mm. The atmosphere used was air. An iridium wire was used as the crystal seed.

All crystals were grown from synthesised Bi_2O_3 and GeO_2. The starting materials were mixed together in the stoichiometric ratio (6:1). The melt was contained in a platinum crucible (∅ 4 cm, 4 cm depth), which was placed in an alumina vessel on the zircon-oxide wool. The whole system represents a kind of protection against excessive radiate 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.[6] The crucible was not rotated during the growth. The conditions for the growth of $Bi_{12}GeO_{20}$ single crystals by the Czochralski technique were optimised as these depend 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 about 50 ºC/h down to room temperature.

The obtained crystals were cut, polished and etched. For chemical polishing a solution of HCl + HNO_3 + H_2O in the ratio 1:1:5 was found to be suitable for polishing the crystals of bismuth germanium oxide. The etching solution was HCl + H_2O in the ratio 1:5.

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

Infrared spectra were recorded using a Fourier-transform spectrometer Bomem DA8. For the far infrared region, a beamsplitter was used (the hypersplitter for the spectral range 20–700 cm^{-1}) and for the infrared standard KBr (400–5000 cm^{-1}). All spectra were obtained using a near normal incidence configuration at room temperature. For both spectral regions, Globar (SiC) was used as the source and in addition, for the far infrared region, a Hg lamp. The spectra of $Bi_{12}GeO_{20}$ were recorded with a resolution of 1 cm^{-1} while the resolution of the $Bi_{12}SiO_{20}$ spectra was 2 cm^{-1}. This influenced the signal-to-noise ratio of the obtained spectra.

RESULTS AND DISCUSSION

$Bi_{12}GeO_{20}$ single crystals are obtained using the Czochralski technique. The growth conditions were calculated using the hydrodynamics of the melt. It was found[7] experimentally that the flatter the interface is, the better the quality of the grown crystal. This is a theoretical and practical target for every grown crystal. Inappropriate growth conditions could be responsible for different defects, such as stresses in the crystal, cracks, non-homogenous impurity concentrations, core phenomena, gas-bubble entrapment, *etc.*[8–11] These crystals have anisotropy in the optical density and they are practically unacceptable for most optical devices. There are many theories about dark core formation, but all authors agree that the dark core is absent when the interface is flat.

The conditions for growing single crystals of $Bi_{12}GeO_{20}$ were calculated by using the hydrodynamics of the melt.[12] The values of the critical diameter of the crystal and critical rotation rate were theoretically obtained using a combination of Reynolds and Grashof numbers, and found to be 1.2 cm and 20 rpm, respectively. The crystal pulling rate was determined experimentally to be 5 mm/h. In our experiments, pale yellow crystals about 12 mm in diameter were produced with a length of about 40 mm. The colour of the crystals was in accordance with published data.[13] The absence of a core was confirmed by observing the polished crystal plates under polarised light.

A solution of $HCl + HNO_3 + H_2O$ in the ratio 1:1:5 was found to be suitable for the chemical polishing of the bismuth germanium oxide crystals. Many experiments were performed to find a suitable etching solution. Etching solutions of $HF + HNO_3$ in the ratio of 2:1 and $HCl + H_2O$ in the ratio of 1:2 were found to be unsuitable, but $HCl + H_2O$ in the ratio 1:5 was satisfactory. Observations of the etched pits revealed that the crystals were grown in the [111] direction. Many dislocations could be seen and their investigation, together with the other crystal defects, will be published in the next article about $Bi_{12}GeO_{20}$ single crystals.

The structure properties were obtained using X-ray analysis of powdered samples.[12] The unit cell of $Bi_{12}GeO_{20}$ was calculated by the least square method using 37 reflections. Many of the reflections correspond to $Bi_{12}GeO_{20}$ crystal with the unit cell parameter $a = 1.014558$ nm.[14] Some divergence from the compared results can be explained by the fact that X-ray powder diffraction analysis gives statistical result. Our calculated results for the lattice parameter is $a = 1.014$ nm, which is in good agreement with published data.[2,14] It has been reported[15] 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 excellent quality of the produced crystals.

The $Bi_{12}GeO_{20}$ single crystal reflectance spectrum was recorded at room temperature (298 K) and is shown in Fig. 1.

In order to see any differences between the spectra of bismuth silicon oxide and bismuth germanium oxide, both spectra are presented one over another in Fig. 1. The spectra are almost identical except for the strong 679 cm^{-1} mode in the spectrum of $Bi_{12}GeO_{20}$, which is missing in that of $Bi_{12}SiO_{20}$, and the mode at 169^{-1} in the $Bi_{12}SiO_{20}$ spectrum that is absent in the $Bi_{12}GeO_{20}$ spectrum. Also, the mode at 820 cm^{-1} in the $Bi_{12}SiO_{20}$ spectrum is nearly absent in the $Bi_{12}GeO_{20}$ spectrum. Both modes (at 679 cm^{-1} and 820 cm^{-1}) certainly represent pure oxygen vibrations.

Regarding the other infrared-active modes, the main difference concenrns just three modes at about 170, 200 and 280 cm^{-1}. The mode at 173 cm^{-1} in bismuth silicon oxide almost disappears in bismuth germanium oxide. Also a mode at 203 cm^{-1} is very sharp in bismuth germanium oxide, but at the same position. The mode that certainly comprises the germanium (silicon) atom vibration appears just as a knee at 283 cm^{-1} in bismuth silicon oxide, whereas it is shifted to lower frequencies (271 cm^{-1}) in bismuth germanium oxide. To a first approximation, assuming that this mode consists of pure Ge–O of Si–O vibrations and taking into account the mass diferences between Ge and Si atoms,[16] a frequency shift of about 25 cm^{-1} can

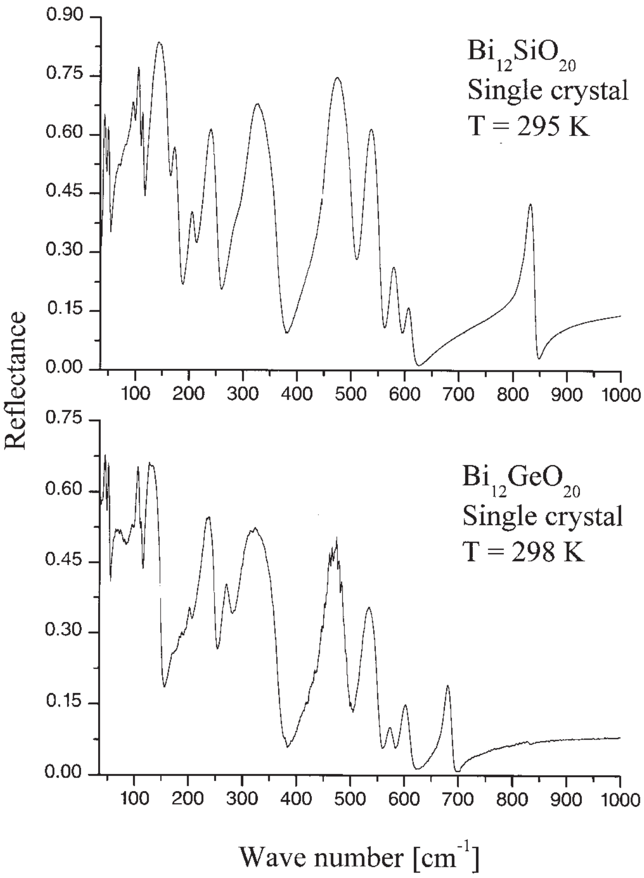

Fig. 1. The infrared reflectance spectra of $Bi_{12}GeO_{20}$ and $Bi_{12}SiO_{20}$ in the range 35–1000 cm^{-1} at 298 K and 295 K, respectively.

be estimated. The simple calculation below, based on a crystal with two different atoms is in fairly good agreement with our experimental finding for the normal mode at 283 cm^{-1} (Si). Namely, in this case one should take a phonon frequency as:

$$\omega^2 = \frac{const.}{\overline{m}} \tag{1}$$

where $\overline{m} = \dfrac{m_{\text{Ge(Si)}} \cdot m_{\text{O}}}{m_{\text{Ge(Si)}} + m_{\text{O}}}$

Hence, one obtains $\dfrac{\omega_{\text{Ge-O}}}{\omega_{\text{Si-O}}} = \sqrt{\dfrac{\overline{m}_{\text{Si-O}}}{\overline{m}_{\text{Ge-O}}}} = 0.9$ (2)

To the best of our knowledge, the parameters of the TO and LO modes of a $Bi_{12}GeO_{20}$ single crystal have not been published in the literature. Using Kramers-Kroning analysis, the TO and LO functions presented in Figs. 2 and 3 were obtained. The positions of the TO and LO modes are presented in Tables I and II.

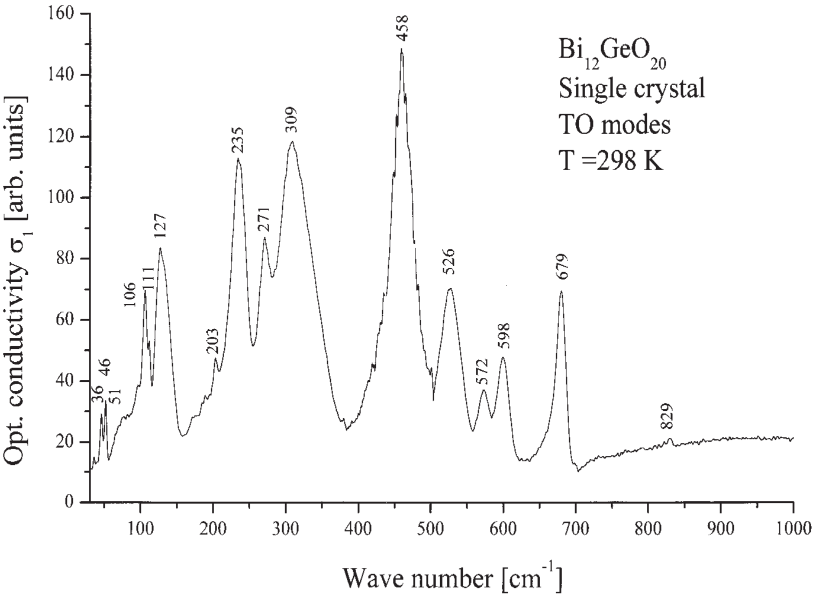

Fig. 2. TO modes (ω_{TO}) of a $Bi_{12}GeO_{20}$ single crystal at 298 K.

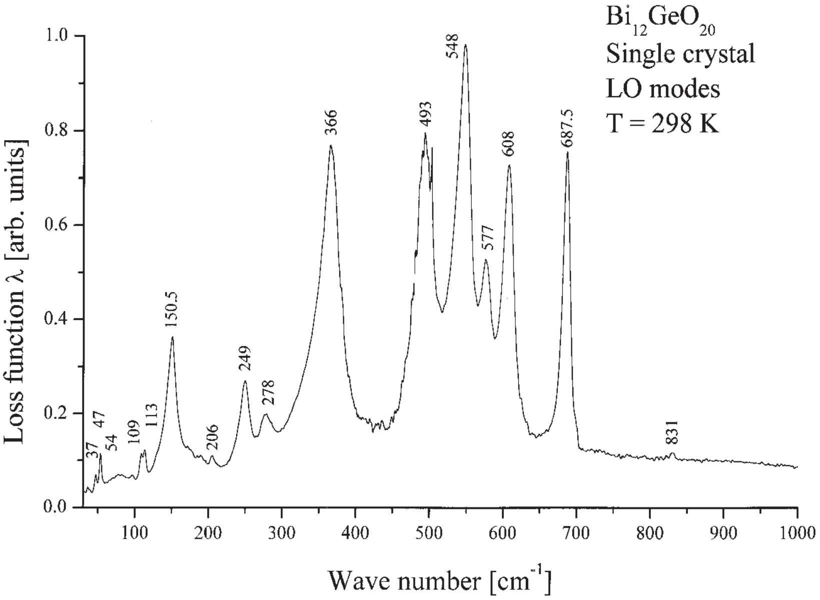

Fig. 3. LO modes (ω_{LO}) of a $Bi_{12}GeO_{20}$ single crystal at 298 K.

From Figs. 2 and 3, and Tables I and II can be seen that there are 16 active infrared modes of $Bi_{12}GeO_{20}$ single crystal at room tepmerature (298 K). This is in accordance with our results for the $Bi_{12}SiO_{20}$ single crystal[17] where 16 active infrared modes were also found. In the litarature[18] 10 active modes for the $Bi_{12}SiO_{20}$

TABLE I. The transverse (TO) frequencies of the optical phonons for $Bi_{12}GeO_{20}$ in the range 30–1000 cm^{-1} at 298 K.

Number of phonon mode	Position of phonon mode/cm^{-1}
1	36
2	46
3	51
4	106
5	111
6	127
7	203
8	235
9	271
10	309
11	458
12	526
13	572
14	598
15	679
16	829

TABLE II. The longitudinal (LO) frequencies of the optical phonons for $Bi_{12}GeO_{20}$ in the range 30–1000 cm^{-1} at 298 K.

Number of phonon mode	Position of phonon mode/cm^{-1}
1	37
2	47
3	54
4	109
5	113
6	150.5
7	206
8	249
9	278
10	366
11	493
12	548
13	577
14	608
15	687.5
16	831

single crystal were reported and our results for both $Bi_{12}GeO_{20}$ and $Bi_{12}SiO_{20}$ single crystals could be very useful for understanding an assignment of the normal modes and overall characterization of these crystals.

The quality of the results obtained by Kramers-Kronig analysis were tested using the Lyddane-Sachs-Teller relation:

$$\frac{\varepsilon_0}{\varepsilon_\infty} = \prod_{j=1}^{n} \frac{\omega^2_{\mathrm{LO},j}}{\omega^2_{\mathrm{TO},j}} \tag{3}$$

The obtained values of the ratio $\varepsilon_0/\varepsilon_\infty$ are about 9.2 and 4.4 for $Bi_{12}SiO_{20}$ and $Bi_{12}GeO_{20}$, respectively. The static relative permittivities ε_0, ε_∞ were determined from the measured reflectance at low (R_0) and high wave numbers (R_∞) according to the following relation:

$$\varepsilon = \left(\frac{1+\sqrt{R}}{1-\sqrt{R}} \right)^2 \tag{4}$$

The obtained values for $Bi_{12}GeO_{20}$ were ε_0 about 20, and $\varepsilon_\infty = 4.5$, which are in a good agreement with the ratio $\varepsilon_0/\varepsilon_\infty$ οβταινεδ υσινγ ρελατιον (3).

CONCLUSION

A solution $HCl + HNO_3 + H_2O$ in the ratio 1:1:5 was found to be suitable for chemical polishing of bismuth germanioum oxide crystals. The etching solution was $HCl + H_2O$ in the ratio 1:5.

The positions of the TO and LO modes of a $Bi_{12}GeO_{20}$ single crystal were determined. A comparison between the $Bi_{12}GeO_{20}$ and $Bi_{12}SiO_{20}$ reflectance spectra showed that new modes appeared in $Bi_{12}GeO_{20}$ around 679 cm^{-1} and the mode at 169 cm^{-1} in $Bi_{12}SiO_{20}$. Also, a significant softening (12 cm^{-1}) of the 283 cm^{-1} mode on substitution of Ge for Si. The magnitude of this shift undoubtably indicates that this band results from germanium-oxygen (silicon-oxygen) vibrations.

ИЗВОД

ОПТИЧКЕ ОСОБИНЕ МОНОКРИСТАЛА БИЗМУТ ГЕРМАНАТА

АЛЕКСАНДАР ГОЛУБОВИЋ*, РАДОШ ГАЈИЋ,* ЧАНГКАНГ ЧЕН** и АНДРЕЈА ВАЛЧИЋ***

**Институт за физику, Прегревица 118, п. пр. 57, 11001 Београд, **Кларендон лабораторија, Паркс Роуд, Оксфорд OX1 3PU, Уједињено Краљевство и ***Технолошко-металуршки факултет, Карнегијева 4, 11000 Београд*

Монокристали бизмут германата су расли техником раста кристала по Чохралском. Одређена су погодна средства за хемијско полирање и нагризање. Рефлексиони спектри су снимани у опсегу таласних бројева од 20-5000 cm^{-1} и поређени су са рефлексионим спектрима монокристала бизмут силиката да би се проучавао положај фононских модова. Оптичке константе монокристала бизмут германата су добијене коришћењем Kramers-Kronig анализе. Добијени резултати су дискутовани и поређени са литературним подацима.

(Примљено 1. фебруара, ревидирано 5. јуна 2000)

REFERENCES

1. A. A. Ballman, *J. Crystal Growth* **1** (1967) 37
2. Lj. Karanović, *Primenjena kristalografija*, Univerzitet u Beogradu, Beograd, 1996, p. 59 (in Serbian)
3. M. T. Santos, C. Marin, E. Dieguez, *J. Crystal Growth* **160** (1996) 283
4. J. P. Huignard, F. Micheron, *Appl. Phys. Lett.* **29** (1976) 591
5. J. P. Herriau, A. Delboulbe, B. Loiseaux, J. P. Huignard, *J. Optica* **15** (1984) 314
6. A. Valčić, S. Nikolić, T. Valčić, *37th Yugoslav Conference ETAN-a*, Beograd, 1993, p. 3
7. J. P. Fontaine, G. P. Extremet, V. Chevrier, J. C. Launay, *J. Crystal Growth* **139** (1994) 67
8. V. Nikolov, K. Iliev, P. Peshev, *J. Crystal Growth* **89** (1988) 313
9. V. Nikolov, K. Iliev, P. Peshev, *J. Crystal Growth* **89** (1988) 324
10. S. Miyazawa, *J. Crystal Growth* **49** (1980) 515
11. M. T. Santos, J. C. Rojo, L. Arizmendi, E. Dieguez, *J. Crystal Growth* **142** (1994) 103
12. A. Golubović, S. Nikolić, R. Gajić, S. Đurić, A. Valčić, *Hemijska industrija* **53** (1999) 227
13. F. Smet, W. J. P. Van Enckevort, *J. Crystal Growth* **100** (1990) 417
14. JCPDS table number 34-0096
15. S. Đurić, *Nauka Tehnika Bezbednost* **1** (1995) 45
16. J. R. Hardy, A. M. Karo, *The Lattice Dynamics and Statics of Alkali Halide Crystals*, Plenum Press, New York, London, 1979, p. 39
17. A. Golubović, R. Gajić, V. Radojević, A. Valčić, *Tehnika: Novi materijali* **9** (2000) 17
18. L. Zengfa, S. Dazhao, S. Sufa, Z. Wanlin, *Infrared Phys.* **31** (1991) 59.