OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 5, No. 2, February 2011, p. 150 - 152

Study of $Bi_{12}SiO_{20}$ single crystals obtained by Czochralski method

Z. Ž. LAZAREVIĆ*, S. KOSTIĆ, M. J. ROMČEVIĆ, J. TRAJIĆ, B. HADŽIĆ, D. STOJANOVIĆ, N. Ž. ROMČEVIĆ
Institute of Physics, P.O. Box 68, Belgrade, Serbia

Bismuth silicon oxide (BSO), $Bi_{12}SiO_{20}$ has found application in various optoelectronic devices. $Bi_{12}SiO_{20}$ single crystals were grown by Czocharlski method. The conditions for growing this single crystal were calculated. The absence of a core was confirmed. The formation of phase and crystal structure of $Bi_{12}SiO_{20}$ was carried out by XRD analysis and Raman spectroscopy. It can be observed 18 active Raman modes. The three modes are new and not found in the available literature.

(Received June, 23, 2010; accepted February 17, 2011)

Keywords: $Bi_{12}SiO_{20}$ single crystals, Czochralski method, Raman spectroscopy

1. Introduction

$Bi_{12}SiO_{20}$ is attractive material for different optical applications and optical data processing [1]. The most methods used to prepare $Bi_{12}SiO_{20}$ single crys are melt growth Czochralski [2], Bridgman [3], Stepanov [4] processes and hydrothermal crystallization [5].

The two most typical “optical” defects in sillenite-type crystals are second-phase inclusions and regions differing in optical absorption. Increased-absorption regions in bismuth silicate crystals may appear as striations and a so-called central core, which is seen as a dark area in the central part of cross sections (Fig. 1) [6].

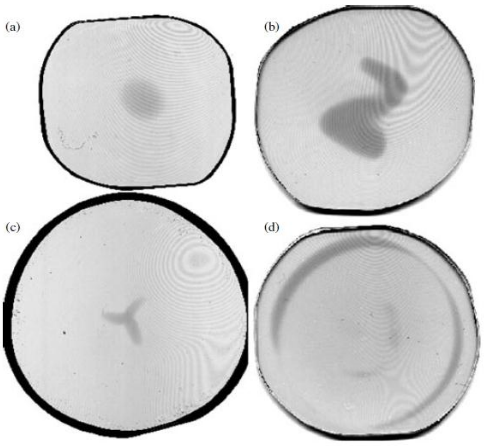


Fig. 1. Central core in cross sections of $Bi_{12}SiO_{20}$ crystals grown in the (a) <001>, (b, d) <110> and (c) <111> directions [6].

It is commonly believed [7, 8] that the central core and selective decoration in the shape of a Maltese Cross for the <100> and <110> growth directions or in the shape of a three-bladed propeller for the <111> growth direction (Fig. 2) are associated with growth rate anisotropy and the difference in the distribution coefficient of “photochromic” impurities between the polar and nonpolar facets of the growth interface. If the interface has the form of a flat (100) facet (usually in faceted growth at fast crystal rotation rates), there is no central core [9]. This is the main reason, why it is very necessary to find optimal conditions for growth, that this does not happen [10].

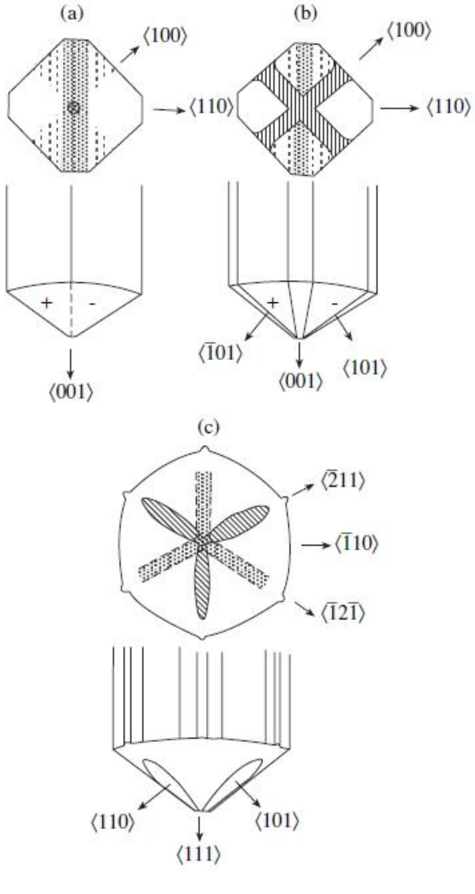


Fig. 2. Morphology of the interface in the crystal growth of $Bi_{12}SiO_{20}$ along (a, b) <001> and (c) <111> directions.

The objective of this work is to study the $Bi_{12}SiO_{20}$ single crystal prepared by Czochralski technique. In the present work, our aim was to obtain a Raman spectrum of $Bi_{12}SiO_{20}$ single crystal, which color was pale yellow.

2. Experimental procedures

$Bi_{12}SiO_{20}$ single crystals were grown by the Czochralski method. All the conditions for acquiring crystals we have shown in previous work [10]. The critical crystal diameter (d_c = 10 mm) and the critical rate rotation ω_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^{-1}. The crystal growth was in the <111> direction. The crystal was grown mixed starting oxides (Bi_2O_3 and SiO_2) in the stoichiometric ratio 6:1.

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 $Bi_{12}SiO_{20}$ crystal. This crystal etched by the solution HCl:H_2O = 1:5.

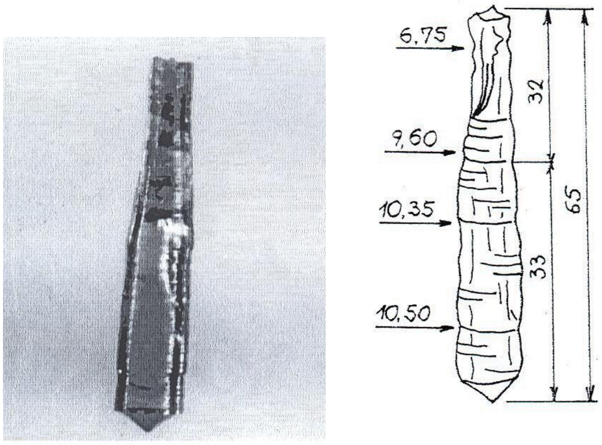
The X-ray diffraction (XRD) data for $Bi_{12}SiO_{20}$ was determined using a CuKα radiation and a monochromator (Model Philips PW 1710 diffractometer) under the following experimental conditions: 40 kV and 20 mA, $20^\circ < 2\theta < 80^\circ$, $2\theta = 0{,}02^\circ$ for 0.5 s.

Raman spectroscopy measurement was performed at room temperature in spectral range from 50 to 900 cm^{-1}, in back scattering geometry, using Jobin Yvon T64000 spectrometer, equipped with nitrogen cooled charge-coupled device detector. As excitation source we used the 514 nm line of an Ar-ion laser. The measurements were performed at 20 mW.

3. Results and discussion

The yellow crystals 10 mm in diameter with a length of about 40 mm can be grown from the melt without inclusions provided that the growth rate is about 5 mm h^{-1}. They should not have inclusions in the centre of the crystal. Also, it was found that rotation rate would be 20 rpm. It can be concluded that color of the crystal is in accordance with the published date [11]. The obtained crystal is shown in Fig. 3.

The structure properties were obtained using X-ray analysis of the sample. The XRD indicates that all peaks belong to the $Bi_{12}SiO_{20}$ phase that is in good agreement with the JCPDF Card No. 37-0485. The unit cell of $Bi_{12}SiO_{20}$ was calculated by the least square method using all 21 reflections including more $K\alpha_2$ for 5 reflections. All reflections correspond to crystal with the parameter of the cubic *I*-centered cell. An XRD diffractogram for $Bi_{12}SiO_{20}$ was given in our other article [12].



(a) (b)

Fig. 3. (a) Photography image and (b) scheme obtained crystal of $Bi_{12}SiO_{20}$.

The Raman scattering spectrum of prepared $Bi_{12}SiO_{20}$ single crystals was measured in spectral range from 50 to 900 cm^{-1} at room temperature (Fig. 4). For BSO, group-theoretical analysis gives:

$$\Gamma = 8A + 8E + 25F$$

The degenerated oscillations ($F \equiv TO+LO$, TO, LO) are manifested in the Raman and IR spectra, and the nondegenerated (A) and doubly degenerated (E) oscillations are manifested in the Raman spectra. The spectrum of $Bi_{12}SiO_{20}$ exhibits intense modes at about 16.9, 69.8, 87.1, 97.1, 105, 130.4, 134.9, 144.8, 170.8, 206.7, 249.7, 279.3, 330.3, 366.9, 461.9, 497.9, 541.5, 624.1 and 829.6 cm^{-1} (Fig. 4). In the low-frequency region, the oscillations in the region from 0 to 150 cm^{-1} in the Raman spectrum of α-Bi_2O_3 are related to the external oscillations of the Bi atom. The oscillations of O lie in the region > 150 cm^{-1}. This fact confirms once more that the main contribution to the vibration spectrum of sillenites in the region < 650 cm^{-1} is given by excitations of the bismuth–oxygen sublattice.

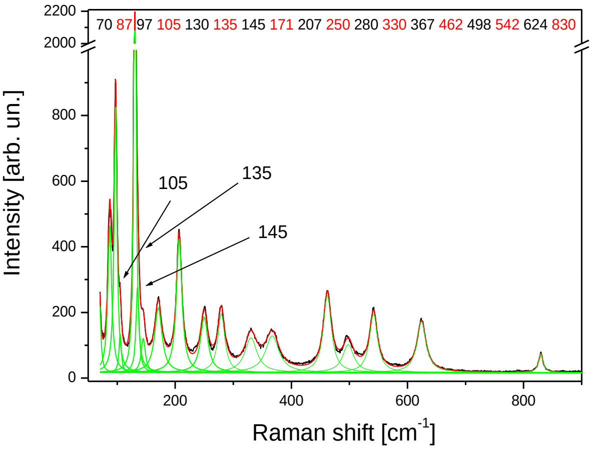


Fig. 4. Raman spectra of $Bi_{12}SiO_{20}$ single crystal at room temperature.

At the same time, for a number of oscillations, especially in the high-frequency region ($\omega > 650$ cm^{-1}), an opposite situation takes place. The frequencies of these oscillations depend substantially on the mass of the atom *M*. The main contribution to these oscillations of the crystal lattice is given by oscillations of the tetrahedral [MO_4].

Registered modes on Fig. 4 are shown: 5*A*, 5*E*, 3*F*, 3*TO* and 2(*TO*+*LO*). The intensity modes at about 87, 145, 280, 330 and 541 cm^{-1} belong to the symmetry type *A*. These modes are characterized by the type of vibration, which shows "breathing" of Bi and O atoms. The modes at about 70, 130, 250, 462 and 624 cm^{-1} belong to the symmetry type *E* and shows Bi and O vibrations. The mode at about 87 cm^{-1} is very interesting because it is not so simple. This mode is the result of duplication or aggregation of two modes, whose intensities are 85 cm^{-1} and 89 cm^{-1}. The modes at about 97, 170 and 207 cm^{-1} belong to the symmetry type *F*. The mode at 498 cm^{-1} can be described Bi-O stretching and deformation of MO_4 tetrahedral (symmetry type *TO*+*LO*). The mode at 789 cm^{-1}, and modes at 830 and 841 cm^{-1} are characteristic of symmetric stretching of MO_4 tetrahedral and anti-symmetric stretching of MO_4 tetrahedral, respectively. These measurements, we come to know about the new modes (105, 134, 145 cm^{-1}) which are not shown in the available literature (Fig. 4).

4. Conclusions

Our paper reports on work carried out on single crystal $Bi_{12}SiO_{20}$ obtained by the Czochralski technique. The critical diameter and critical rate of rotation were calculated. Suitable polishing and etching solutions were determined. Pale yellow crystals were obtained, as a result of our experiments. The single crystal structure $Bi_{12}SiO_{20}$ was confirmed by XRD. The Raman spectroscopy results suggest that way synthesis leads to formation of BSO, as seen by X-ray diffraction analysis. We observed 18 Raman modes. It can be concluded, that the three new modes are not found in the published literature.

Acknowledgements

This research was financially supported by Serbian Ministry of Science through project No.141028B.

References

[1] I. F. Vasconcelos, M. A. Pimenta, A. S. Sombra, J. Mater. Sci., **36**, 587 (2001).

[2] A. R. Tanguay, S. Mroczkowski, R. C. Barker, J. Cryst. Growth, **42**, 431 (1977).

[3] X. W. Xu, J. Y. Liao, B. F. Shen, P. F. Shao, X. Q. Chen, C. F. He, J. Cryst. Growth, **133**, 267 (1993).

[4] S. I. Stepanov, M. P. Petrov, A. A. Kamshilin, Sov. Tech. Phys. Lett., **3**, 345 (1977).

[5] J. Larkin, M. Harris, J. E. Cormier, J. Cryst. Growth, **128**, 871 (1993).

[6] V. M. Skorikov, Y. F. Kargin, A. V. Egorysheva, V. V. Volkov, M. Gospodinov, Inorg. Mater., 41 (1), S24 (2005).

[7] S. A. Kukushkin, A. I. Maksikov, A. A. Petrov, Zh. Tekh. Fiz., **2**, 431 (1980).

[8] P. J. Picone, J. Cryst. Growth, **87**, 421 (1988).

[9] M. D. Aggrawal, W. S. Wang, J. Choi, J. Cryst. Growth, **137**, 132 (1994).

[10] A. Golubovic, S. Nikolic, R. Gajic, S. Djuric, A. Valcic, J. Serb. Chem. Soc., **67** (4), 279 (2002).

[11] P. A. C. Whiffin, T. M. Bruton, J. C. Brice, J. Cryst. Growth, **32**, 205 (1976).

[12] Z. Z. Lazarevic, S. Kostic, V. Radojevic, M. Romcevic, N. Romcevic, B. Hadzic, A. Valcic, J. Alloy. Compd., (2010), article in press.

---

*Corresponding author: lzorica@yahoo.com