

Spectroscopy study of $\text{Bi}_{12}\text{GeO}_{20}$ single crystals

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In this work single crystals of bismuth germanium oxide ($\text{Bi}_{12}\text{GeO}_{20}$) have been grown by the Czochralski method. Growth conditions were studied. The critical diameter and the critical rate of rotation were calculated. Suitable polishing and etching solutions were determined. The structure of the $\text{Bi}_{12}\text{GeO}_{20}$ has been investigated by X-ray diffraction, Raman and FTIR spectroscopy. The obtained results are discussed and compared with published data. On the basis of the measurements by Raman spectroscopy, we observed 15 modes.

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1. Introduction

Sillenit crystals $\text{Bi}_{12}\text{MO}_{20}$ ($M = \text{Ge}, \text{Si}, \text{Ti}$) have a number of properties important for practical applications, such as piezoelectric sensors, filters and delay lines of electromagnetic signals, electro-optical and magneto-optical field strength meters, space-time modulators, etc. It is known [1] that these devices require crystals with a low dislocation density and high optical homogeneity. Owing to the great diversity of physical effects in sillenite-type crystals and the possibility of employing them in electronic and optoelectronic devices for various technological applications, a wide variety of techniques have been used to grow both bulk single crystals and epitaxial layers (films) of sillenites. Most research effort has been concentrated on $\text{Bi}_{12}\text{GeO}_{20}$ (BGO), $\text{Bi}_{12}\text{SiO}_{20}$ (BSO), and $\text{Bi}_{12}\text{TiO}_{20}$ (BTO) crystals. The approaches most frequently used to prepare BGO, BSO, and BTO crystals are melt growth (Czochralski(CZ)), Bridgman, Stepanov, and edge-defined film-fedgrowth (EFG) processes) and hydrothermal crystallization. Films of these compounds can be produced by liquid phase epitaxy (LPE), physical sputtering, chemical vapor transport, and solution growth [2].

Most BGO single crystals for acoustic and optical applications are grown by CZ pulling. Using this technique, BGO single crystals 50–70 mm in diameter and up to 400 mm in length have been grown [2].

Bismuth germanium oxide ($\text{Bi}_{12}\text{GeO}_{20}$) is usually abbreviated as BGO in common usage. The $\text{Bi}_{12}\text{GeO}_{20}$ crystal structure is described by the cubic space group $I23$. The unit cell of $\text{Bi}_{12}\text{GeO}_{20}$ contains two formula units, the Ge atoms residing in the centre and in the vertices of the cube. Each one of the Ge atoms is tetrahedral, coordinated by oxygen atoms. The framework of the $\text{Bi}_{12}\text{GeO}_{20}$ structure is formed by the $[\text{BiO}_5\text{E}]$ polyhedra ($E = 6s^2$ is the non-shared electron pair of Bi) which form dimmers

by means of a common edge [3]. The $\text{Bi}_{12}\text{GeO}_{20}$ has considerable applications due to its photoconduction, photochromism, photorefractive and other properties [4–7].

In this paper we have studied the growth of a $\text{Bi}_{12}\text{GeO}_{20}$ single crystal and characterized it by XRD, Raman and FTIR spectroscopy. In this paper, we have studied a $\text{Bi}_{12}\text{GeO}_{20}$ single crystal, which produced growth by the Czochralski technique. The $\text{Bi}_{12}\text{GeO}_{20}$ single crystal was characterized using different methods of characterizations.

2. Experimental procedures

The $\text{Bi}_{12}\text{GeO}_{20}$ single crystals were grown by the Czochralski technique using an 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 monitored the crucible weight continuously. The absolute value of the deviation from the given diameter was below 0.1 mm. The melt was contained in a platinum crucible (ϕ 40 mm, 40 mm 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 after heater was installed around the system with the crucible [8]. The crystals were grown in an air atmosphere. The BGO seed was oriented in the $\langle 111 \rangle$ direction.

The charge was a stoichiometric mixture of Bi_2O_3 (99.9999 wt. %) and GeO_2 (99.9999 wt. %). 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 2.8–3 mm h⁻¹. 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 bole was cooled at a rate of about 50 °C h⁻¹ down to room temperature.

Attempts were made to find the optimal solution for the chemical polishing and etching of Bi₁₂GeO₂₀ single crystals. The combination for the etching solution were: HF + HNO₃ in the ratio 2:1, HCl + H₂O in the ratio 1:2, and HCl + H₂O in the ratio 1:5. For the chemical polishing of the bismuth germanium oxide crystals a solution of HCl + HNO₃ + H₂O we tried the ratio 1:1:5.

The observations relating to the dislocation were recorded by observing an etched surface of Bi₁₂GeO₂₀ crystal, using a Metaval of Carl Zeiss Java metallographic microscope with magnification of 240x.

The X-ray diffraction (XRD) data for Bi₁₂GeO₂₀ was determined using a CuK α radiation and a monochromator (Model Philips PW 1710 diffractometer) under the following experimental conditions: 40 kV and 20 mA, 20° < 2 θ < 90°, 2 θ = 0,02° for 0.5 s.

Raman spectroscopy measurement was performed at room temperature in the spectral range from 100 to 1000 cm⁻¹, in back scattering geometry, using a Jobin Yvon T64000 spectrometer, equipped with nitrogen cooled charge-coupled device detector. As an excitation source we used the 514 nm line of an Ar-ion laser. The measurements were performed at 20 mW.

The Infrared (IR) spectrum of the powder was obtained with a Fourier transform infrared (FTIR) transmission-KBr disk spectroscopy (Hartmann & Braun, MB-series). The scanning range of FTIR was between 2000 and 400 cm⁻¹.

3. Results and discussion

Part of a polished slice of a Bi₁₂GeO₂₀ single crystal with etched pits of dislocations is shown in Fig. 1. To examination of the dislocations in crystal was used Metaval of Carl Zeiss Java metallographic microscope with magnification from 240x. The absence of a core was confirmed by viewing polished crystal slices in both normal and polarized light. The observations related to the dislocation were recorded by observing an etched surface of Bi₁₂GeO₂₀ crystal, using a metallographic microscope. Grain boundaries can be seen in the image well. The whole area looks like as a wave. From the wavy surface as the sticking black triangles. Also, in Fig. 1 can be observed the appearance of regular pyramid, approximate orientation <111> with distinctive peaks.

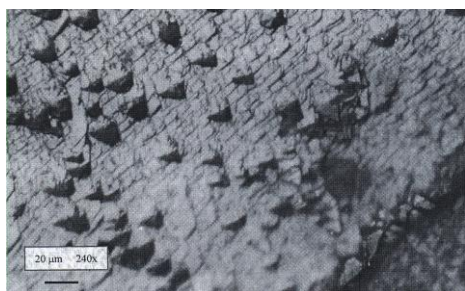


Fig. 1. A view of an etched plate of Bi₁₂GeO₂₀ crystal with triangles of dislocations. Magnification 240x.

Fig. 2 presents the XRD pattern of Bi₁₂GeO₂₀. The diffractometer was used in the 2 θ range from 3° to 95°. XRD indicates that all peaks belong to the Bi₁₂GeO₂₀ phase, which is in good agreement with the JCPDS Card No. 34-0096. The unit cell of Bi₁₂GeO₂₀ was calculated by the least square method using all 24 reflections, including more K α ₂ for 5 reflections. The XRD spectrum of BGO shows a typically crystal structure with the strongest peak centered at 2 θ = 27.8°, as shown in Fig. 1.

Many of the reflections correspond to Bi₁₂GeO₂₀ crystals with the parameter of cubic *I*-centered cell a = 10.1462 Å, and x = 12. Our calculated results for the lattice parameter are in good agreement with published data. It should also be mentioned that a value of x = 12 for crystals Bi _{x} GeO_{1.5 x +2} where the diameters are 10 to 12 mm for a crucible diameter of about 40 mm, have been reported in the literature [9]. This is in accordance with the dimensions of the crystals obtained in this work.

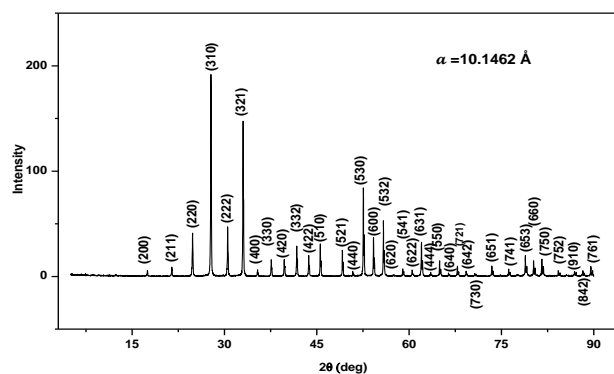


Fig. 2. X-ray diffraction pattern of a Bi₁₂GeO₂₀ single crystal.

The Raman spectra of Bi₁₂GeO₂₀ single crystals formed by the Czochralski technique, in the spectral range from 50 to 900 cm⁻¹ at room temperature is shown in Fig. 3. Raman spectra are often analysed with the help of a Lorentzian curve. Our interest is quantitative analysis with a partial discussion of trend, and we assume that all lines are of the Lorentzian type (Eq. (1)). Solid lines in Fig. 3, were obtained by adding 15 different profiles:

$$I(\omega) = I_0 + \frac{2A}{\pi} \cdot \frac{W}{4(\omega - \omega_c)^2 + W^2} \quad (1)$$

Here I – is the line intensity, I_0 – the height of the baseline, ω_c – the position of the maximum, W – the half-width of the peak and A – a parameter that depends on W . For BGO, group-theoretical analysis gives:

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

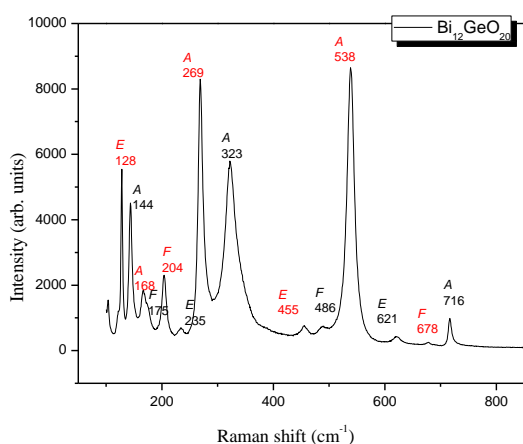


Fig. 3. Raman spectra of $\text{Bi}_{12}\text{GeO}_{20}$ single crystals at room temperature.

The triply degenerated oscillations ($F = TO+LO$, 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. Because all these oscillations are manifested in the Raman spectra, these spectra give the most complete information on the internal crystal oscillations. This spectrum contains 14 Raman modes of different relative intensities, indicated as strong, medium and weak. The spectrum of $\text{Bi}_{12}\text{GeO}_{20}$ exhibits intense modes at about 121, 128, 144, 168, 175, 204, 235, 269, 323, 455, 486, 538, 621, 678 and 716 cm^{-1} (Fig. 3). In the low-frequency region, the Raman spectra of sillenites, together with the spectra of other complex oxide compounds of bismuth, are similar to the Raman spectra of the $\alpha\text{-Bi}_2\text{O}_3$. Among numerous intense lines in the spectra of $\text{Bi}_{12}\text{GeO}_{20}$ narrow lines are observed which coincide with an accuracy of several cm^{-1} with the lines at 121 and 128 cm^{-1} in the Raman spectra of sillenites. The oscillations in the region $\omega < 150\text{ cm}^{-1}$ in the Raman spectrum of $\alpha\text{-Bi}_2\text{O}_3$ are related to the external oscillations of the Bi atom. The oscillations of O lie in the region $\omega > 150\text{ cm}^{-1}$. The internal modes should be sought in the range from 200 to 600 cm^{-1} . This fact confirms once more that the main contribution to the vibration spectrum of sillenites in the region $\omega < 650\text{ cm}^{-1}$ is given by excitations of the bismuth–oxygen sublattice.

At the same time, for a number of oscillations, especially in the high-frequency region ($\omega > 650\text{ cm}^{-1}$), 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 $[\text{MO}_4]$. In accordance with the structural data, the tetrahedron $[\text{MO}_4]$ is surrounded by twelve heavy atoms of bismuth, and its oscillations do not cause notable displacements. Indeed, the calculation of the normal oscillation frequencies for the complex molecule $M[\text{O}_4(\text{Bi})_3]_4$ ($M = \text{Ge}, \text{Si}, \text{Ti}$) shows that the values of these frequencies are in good agreement with the

experimentally measured ones and are close to the values of the corresponding frequencies of the group $[\text{MO}_4]^{4-}$.

Registered Raman modes on Fig. 3 are shown: $5A$, $4E$ and $5F$ ($1TO$, $1LO$ and $3(TO+LO)$). The intensity modes at about 168, 171, 269, 323, 538 and 716 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 [10]. Also, these vibrations are combinations of bending and stretching modes in Bi_3O_4 - Bi-O stretching, O-Bi-O bending, O-Ge bending, and symmetric Ge-O stretching. The modes at about 128, 235, 455 and 621 cm^{-1} belong to the symmetry type E and show Bi and O vibrations elongating the cluster along either $\langle 100 \rangle$ or $\langle 001 \rangle$, $\langle 100 \rangle$ or $\langle 010 \rangle$, respectively. These modes can be present combinations of bending and stretching modes in Bi_3O_4 , Bi-O stretching, O-Bi-O bending, and O-Ge bending. Also, the modes at about 121, 175, 204, 486 and 678 cm^{-1} belong to the symmetry type F , while the symmetry type (TO) have modes at about 175 cm^{-1} . They describe the vibrations in the GeO_4 (MO_4) unit: rocking of GeO_4 , asymmetric stretching mode in GeO_4 . The modes at about 121, 486 and 678 cm^{-1} can be present by symmetry type ($TO+LO$). The mode at about 323 cm^{-1} can be described as rotation of the GeO_4 unit. The mode at 204 cm^{-1} has symmetry type LO . It should be noted that the frequency of the asymmetric stretching mode of the MO_4 tetrahedral is lower than that of the symmetric one. This is due to the strong influence of the Bi-O framework on the vibration behaviour of the MO_4 tetrahedral in sillenites. It is characteristic of the MO_4 structure. This is in agreement with literature data. The subject of our future study of the $\text{Bi}_{12}\text{GeO}_{20}$ single crystal will still be with the help of Raman spectroscopy.

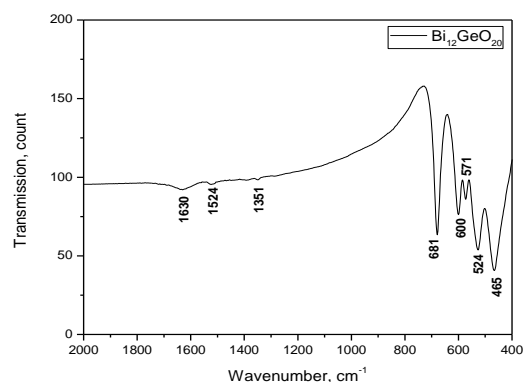


Fig. 4. FTIR transmittance spectra of $\text{Bi}_{12}\text{GeO}_{20}$ single crystals at room temperature.

Fig. 4 has the IR spectra of samples of $\text{Bi}_{12}\text{GeO}_{20}$. The IR absorption spectra of $\text{Bi}_{12}\text{GeO}_{20}$ could be associated directly with the spectra of Bi_2O_3 . We expect to have a good agreement with the Raman and IR spectra of the crystalline BGO. Also, the infrared spectrum is in good agreement with the data reported in the literature. The major line BGO was identified in our $\text{Bi}_{12}\text{GeO}_{20}$ single crystal. Five IR active modes are observed in the range from 400 to 900 cm^{-1} (Fig. 4).

All modes are *TO* symmetry. The FTIR spectrum shows well-defined peaks located at 681, 600, 571, 524 and 465 cm⁻¹. The peak located at 741 cm⁻¹ is due to the stretching vibration mode of Bi–O–Ge bonds. In the present case, in the Bi–O–Ge bonds, when the vibrations of the Bi–O and Ge–O are in phase, the absorption is located at 740 cm⁻¹ and 712 cm⁻¹. The shift observed in the bands' location can be associated with the difference between the atomic masses of germanium and bismuth atoms. There are small peaks at 1351, 1524 and 1630 cm⁻¹. These belong to the stretching mode of OH- groups as the Bi₁₂GeO₂₀ single crystals were grown in an air atmosphere. The positions of the OH- group at this point are in accordance with those found in the literature [11].

The peak at 600 cm⁻¹ is related to the cationic vibrations in the network or Bi–O vibration. The peak located at 571 cm⁻¹ is associated with the bending vibration mode of the distorted tetrahedron formed by the (GeO₄)⁴⁻ groups. The band located at 524 cm⁻¹ is assigned to the deformation vibration of isolated (GeO₄)⁴⁻ groups. The band located at 465 cm⁻¹ is related to Ge–O bond rocking and interaction by the [BiO₆] polyhedron.

The Bi₁₂GeO₂₀ single crystal prepared by the Czochralski technique was pale yellow (Fig. 5). The crystal has no central core.

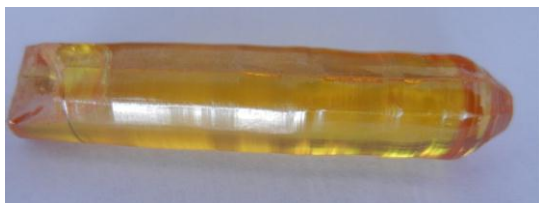


Fig. 5. Photographic image of the studied obtained crystal of Bi₁₂GeO₂₀.

4. Conclusions

In conclusion, the Czochralski technique has been used successfully to produce a Bi₁₂GeO₂₀ single crystal. The obtained crystal was studied by X-ray diffraction, Raman and FTIR spectroscopy. The single crystal structure Bi₁₂GeO₂₀ was confirmed by XRD. The Raman and FTIR spectroscopy results suggest that way synthesis leads to the formation of BGO, as seen by X-ray diffraction analysis. We observed 15 *Raman* and 5 *IR* modes. It can be concluded, that the obtained single crystal of BGO is pale yellow in colour and there is no central core.

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