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DIELECTRICS

Linear Optical Properties of γ-Modification of Bismuth Borate BiB_3O_6

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Abstract—The refractive index dispersion of the γ-BiB_3O_6 crystal in the wavelength range 0.43–0.81 μm has been measured. It has been shown that the principal refractive indices n_1, n_2, and n_3 are on average higher than those of α-BiB_3O_6, but are slightly lower than those of δ-BiB_3O_6. The temperature dependences of the rotation angle $\varphi(T)$ of the optical indicatrix and birefringence $\Delta n_2(T) = (n_1 - n_3)(T)$ have been studied in the temperature range 100–963 K. It has been shown that the γ-BiB_3O_6 crystal is stable in this temperature region.

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1. INTRODUCTION

Borate compounds are objects of particular attention due to their exclusive optical properties and a variety of formed structures. Currently, at least four structural modifications of bismuth borate are known: monoclinic α-BiB_3O_6 ($C2$), $\rho = 5.033$ g/cm^3 [1, 2]; β-BiB_3O_6 ($P2_1/n$), $\rho = 5.411$ g/cm^3; γ-BiB_3O_6 ($P2_1/n$), $\rho = 6.177$ g/cm^3 [3]; and orthorhombic δ-BiB_3O_6 ($Pca2_1$), $\rho = 6.378$ g/cm^3 [4]. Interest in these substances is explained by their unique properties, i.e., a wide transparency window (50%), from 290 to 2500 nm and more for α-BiB_3O_6 and from 315 to 3500 nm and more for δ-BiB_3O_6, and large refractive indices [5, 6]. Furthermore, the first and last among these modifications have no inversion center and are actively studied as nonlinear-optical materials for optoelectronics. The BiB_3O_6 density gradually increases from α- to δ-modification [1–4]; therefore, a similar tendency for the refractive index should be assumed.

Optical constants, their dispersion, and transmission band were studied in detail only for α- and δ-modifications of BiB_3O_6 [4–6], since only they were obtained in the form of bulk single crystals. The studies of β- and γ-modifications of BiB_3O_6 were restricted to the structure and p–T diagrams of powder samples [3, 7]. The growth technology of bulk γ-BiB_3O_6 single crystals of high optical quality was developed not long ago in [8]. In that work, the habit is described and polarization transmission spectra of this substance are presented. It was shown that the transmission band of the crystal of this modification lies in the range from 315 to 3150 nm (50%) [8].

In this study, we measured the refractive indices and their dispersions in the wavelength range of 430–810 nm, the temperature dependences of the birefringence $\Delta n_2(T) = (n_1 - n_3)(T)$ and the rotation angle $\varphi(T)$ of the optical indicatrix of the γ-BiB_3O_6 crystal were determined in the temperature range of 100–963 K. The principal refractive indices n_1, n_2, and n_3 were measured by the prism method. The temperature dependences of the extinction angle $\varphi(T)$ and birefringence $\Delta n_2(T)$ were measured using an Axioskop-40 polarization microscope with a Berek compensator (Leica) and low- and high-temperature Linkam cameras. The single crystal growth technique for the studies is described in [8].

2. OPTICAL INVESTIGATIONS

The γ-BiB_3O_6 crystal has monoclinic symmetry $P2_1/n$ and unit cell parameters $a = 8.4992$ Å, $b = 11.7092$ Å, $c = 4.2596$ Å, $\beta = 121.141°$ [3]. Such a large monoclinic angle leads to difficulties in sample preparation for measuring physical constants. Figure 1 shows the relative positions of axes of the crystallographic (a, b, c), orthogonal crystal physical (X, Y, Z), and crystal optical (n_1, n_2, n_3) coordinate systems in the γ-BiB_3O_6 crystal. The angle φ describes the optical indicatrix rotation around the [010] direction and can depend on the wavelength and temperature.

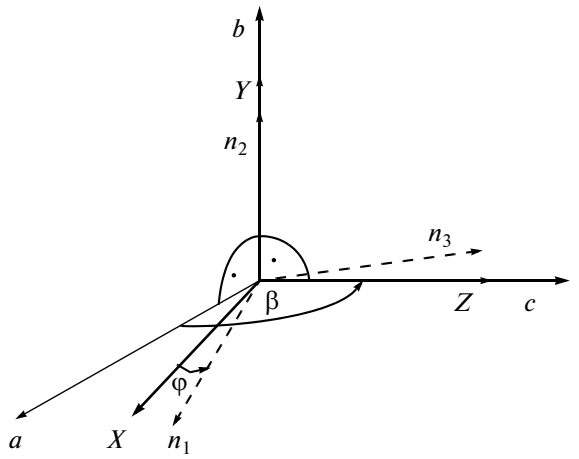

Fig. 1. Relative positions of the crystallographic (*a*, *b*, *c*), crystal physical (*X*, *Y*, *Z*), and crystal optical (n_1, n_2, n_3) coordinate systems in γ-BiB_3O_6. The angles are β = 121.14° and φ = 4.6° at room temperature.

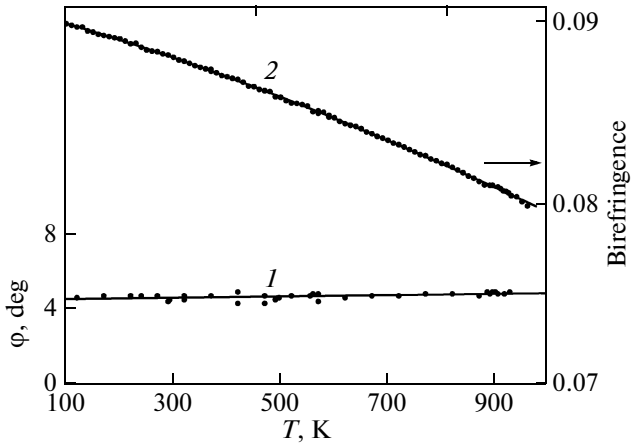

Fig. 2. Temperature dependences of the optical characteristics of the γ-BiB_3O_6 crystal: (*1*) rotation angle φ(*T*) of the optical indicatrix and (*2*) birefringence $\Delta n_2(T)$.

In the experiment, the angle φ was measured relative to the *X* and *Y* axes of the crystal physical system. According to [8], in γ-BiB_3O_6, the (010) growth face is formed by edges arranged along the *c* (*Z*) axis; therefore, the angle φ in the experiment was determined on a (010) plate with natural faceting, which allowed high-accuracy measurements. The extinction of this plate has a dispersion which is manifests itself as sample reddening or blueing upon rightward–leftward rotation from the maximum darkening position. The room-temperature rotation angle of the optical indicatrix is φ = 4.6°; in the temperature range of 100–963 K, it varies insignificantly (Fig. 2, curve *1*). The room-temperature birefringence of the plate is $\Delta n_2 \approx 0.088$ and gradually decreases with increasing temperature (Fig. 2, curve *2*), not exhibiting some anomalies which would indicate structural changes in γ-BiB_3O_6. Small deviations from the smooth dependence near 900 K are associated with melting of a thin surface layer at temperatures above 870 K, which was observed in the microscope field of view during the experiment.

The refractive indices were measured using two prisms with refracting angles θ ≈ 22° and different orientations of input faces, (010) and $(\bar{1}01)$. The first sample was used to determine the refractive indices n_1 and n_3, the index n_2 was measured using the second prism. The results of measurements are listed in Table 1 and Fig. 3. We can see that the values obtained are on average higher than refractive indices of α-BiB_3O_6 [5], but lower than those of δ-BiB_3O_6 [6]. The crystal exhibits the largest optical anisotropy along the [010] direction of light propagation: the birefringence is $\Delta n_2 = (n_1 - n_3) = 0.076$–$0.088$ at various wavelengths from the red to violet region. At the same time, the birefringence $\Delta n_1(T) = (n_2 - n_3)(T)$ is very small and is close to zero in the red spectral region. The obtained experimental refractive indices are fitted into the dispersion curve such as the Sellmeier dependence

$$n^2 = A + \frac{B}{1 + C\lambda^2} + D\lambda^2. \quad (1)$$

The coefficients *A*, *B*, *C*, and *D* of this equation for indices n_1, n_2, and n_3 are given in Table 2.

Table 1. Experimental refractive indices of the γ-BiB_3O_6 crystal at 295 K (measurement error is ±0.0002)

λ, μm	n_1	n_2	n_3
0.436	2.1430	2.0622	2.0550
0.462	2.1298	2.0496	2.0436
0.470	2.1262	2.0465	2.0413
0.477	2.1232	2.0430	2.0380
0.485	2.1202	2.0404	2.0357
0.493	2.1168	2.0374	2.0328
0.502	2.1135	2.0344	2.0300
0.512	2.1100	2.0314	2.0272
0.522	2.1069	2.0283	2.0244
0.533	2.1035	2.0250	2.0215
0.545	2.0996	2.0220	2.0181
0.559	2.0969	2.0188	2.0158
0.573	2.0937	2.0156	2.0132
0.590	2.0904	2.0127	2.0103
0.608	2.0868	2.0095	2.0071
0.628	2.0833	2.0064	2.0041
0.651	2.0802	2.0034	2.0012
0.676	2.0768	2.0008	1.9986
0.705		1.9975	
0.807	2.0631	1.9884	1.9868

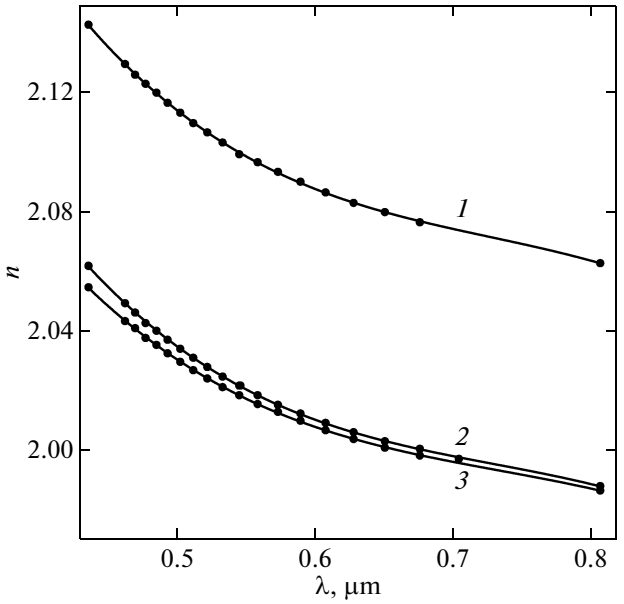

Fig. 3. Room-temperature dispersion of the refractive indices of γ-BiB_3O_6: (*1*) n_1, (*2*) n_2, and (*3*) n_3.

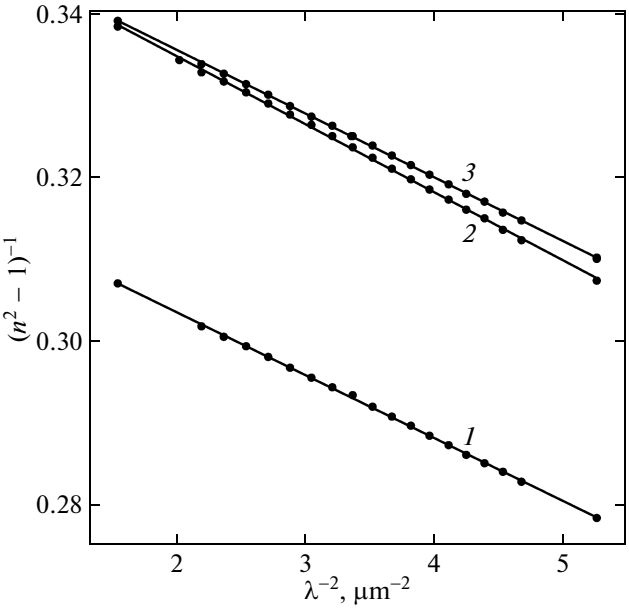

Fig. 4. Dependence of $[n^2(\lambda) - 1]^{-1}$ on λ^{-2} for the refractive indices (*1*) n_1, (*2*) n_2, and (*3*) n_3.

The dispersion of the refractive indices of the γ-BiB_3O_6 crystal in the visible spectral region can be described within the effective oscillator model by the formula

$$n^2(\lambda) - 1 = \frac{S_0\lambda_0^2}{1 - (\lambda_0/\lambda)^2}, \quad (2)$$

where S_0 and λ_0 are the average values of the oscillator force and wavelength [9]. This assumption is confirmed by the linear dependences of $[n^2(\lambda) - 1]^{-1}$ on λ^{-2} (Fig. 4). The data of this figure can be used to estimate S_0, λ_0, and other model parameters: the oscillator energy $E_0 = (hc/e)\lambda_0^{-1}$, the dispersion energy $E_d = (hc/e)^2 S_0 E_0^{-1}$, and the ionicity f_i or covalence of chemical bonds of the compound under consideration. The results of such estimation are given in Table 3. We can see that the calculated model parameters λ_0, E_0, and E_d are characteristic of oxides [9]. According to this estimate, the ionicity of this crystal is $f_i \approx 70\%$; therewith, covalent bonds play an important role, i.e., γ-BiB_3O_6 is characterized by the polar covalent bond.

Table 2. Coefficients of the Sellmeier equation (1) for the γ-BiB_3O_6 crystal

n	*A*	*B*	*C*	*D*
n_1	4.16423	0.06584	0.03827	0.02216
n_2	3.86328	0.05837	0.04098	0.00608
n_3	3.86215	0.05757	0.03185	0.01092

As is known [9], light absorption in the one-electron oscillator model is related to direct electronic transitions between the valence band and conduction band. In this case, the band gap E_g is approximately equated to the oscillator self-energy E_0, and the transition intensity is described by E_d. It should be noted that for γ-BiB_3O_6 the oscillator self-energy E_0 calculated by formula (2) is two times larger than the band gap $E_g \approx 4$ eV found in the study of transmission–absorption spectra at room temperature [8].

3. CONCLUSIONS

The dispersion of the refractive indices of the γ-modification of bismuth borate BiB_3O_6 was studied in the wavelength range of 430–810 nm. It was shown that, similarly to the density ρ, the principal refractive indices n_1, n_2, and n_3 of this crystal are on average higher than those of α-BiB_3O_6, but are slightly lower than those of δ-BiB_3O_6. The studies conducted allow the conclusion that the γ-BiB_3O_6 crystal is a high-quality optical material. It features a wide transmis-

Table 3. Dispersion parameters of the effective oscillator model for the γ-BiB_3O_6 crystal

n	λ_0, nm	$S_0 \times 10^{-14}$, m^{-2}	E_0, eV	E_d, eV	f_i, %
n_1	155	1.30	8.0	25	
n_2	153	1.21	8.1	23	70
n_3	148	1.28	8.38	23.5	

sion band, 315–3150 nm (50%), high density $\rho = 6.177$ g/cm^3, and high refractive indices $n > 2.0$. In the temperature range of 100–900 K, the crystal is stable, no structural phase transitions are observed. The developed growth technique makes it possible to obtain large (~6 cm^3) single crystals. This substance has low hygroscopicity and high hardness, strength, and workability. In the case of proper doping, the γ-BiB_3O_6 crystal can be used as a matrix for solid-state lasers or as a material for scintillation detectors (γ-radiation, neutrons).

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REFERENCES

1. E. M. Levin and C. L. McDaniel, J. Am. Ceram. Soc. **45**, 355 (1962).
2. R. Fröhlich, L. Bohatý, and J. Liebertz, Acta Crystallogr., Sect. C: Cryst. Struct. Commun. **40**, 343 (1984).
3. L. Li, G. Li, Y. Wang, F. Liao, and J. Lin, Inorg. Chem. **44**, 8243 (2005).
4. A. S. Aleksandrovsky, A. D. Vasiliev, A. I. Zaitsev, and A. V. Zamkov, J. Cryst. Growth. **310**, 4027 (2008).
5. H. Hellwig, J. Liebertz, and L. Bohaty, J. Appl. Phys. **88** (1), 240 (2000).
6. A. V. Cherepakhin, A. I. Zaitsev, A. S. Aleksandrovsky, and A. V. Zamkov, Opt. Mater. **34** (5), 790 (2012).
7. R. Cong, J. Zhu, Y. Wang, T. Yang, F. Liao, C. Jin, and J. Lin, Cryst. Eng. Commun. **11**, 1971 (2009).
8. P. N. Gavryushkin, L. I. Isaenko, A. P. Yelisseyev, V. A. Gets, and O. S. Il'ina, Cryst. Growth. Des. **12**, 75 (2012).
9. S. H. Wemple and M. DiDomenico, Jr., Phys. Rev. B: Solid State **3** (4), 1338 (1971).

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