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# Optical and nonlinear optical properties of orthorhombic $BiB_3O_6$

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ABSTRACT

Dispersion of refraction coefficients of orthorhombic $BiB_3O_6$ in the wavelength range between 435.8 and 1060 nm is studied, nonlinear optical coefficients are determined, and phase matching angles, angular and spectral bandwidths for second harmonic generation processes are calculated. δ-BiBO may be suitable for doubling of lasers with a wavelength in the 1.3 μm region as well as the matrix for self-doubling lasing media.



## 1. Introduction

Studies of new materials for frequency conversion of mostly widespread laser sources like those operating at the different generation lines of $Nd^{3+}$ ion is of great importance. Among these materials, borates are often investigated. Despite lower values of individual nonlinear coefficients than those in potassium titanyl phosphate family or lithium niobate, effective nonlinearity for a certain conversion process in borates may be comparable or better than in other nonlinear media. Borates also offer better stability and absence of photorefractive effect.

As an example, the problem of 1.3 μm doubling was addressed in [1], and good results were obtained using critical phase matching in lithium triborate (LBO). Another promising nonlinear material is the monoclinic crystal $BiB_3O_6$ (α-BiBO) [2,3] that is transparent in the spectral range between 290 nm and more than 2.5 μm. Its NLO coefficients are larger than in other borates widely used in present, such as β-barium borate (BBO), or lithium triborate (LBO) [4]. Monoclonic BiBO is proved to demonstrate superior effective nonlinearity in various conversion schemes with femtosecond pulses from Ti:S laser systems [5,6]. Attempts to create self-doubling laser crystal based on α-BiBO were done via doping it with rare-earth ions, but they were unsuccessful due low doping content level that was found to be characteristic for this crystal [7,8].

In recent years several new polymorphs of BiBO were discovered, including orthorhombic bismuth triborate δ-BiBO with non-centrosymmetric structure [9,10]. It was shown that this polymorph is a stable one at the temperatures close to the melting point, while α-BiBO is a metastable one [11]. Relatively large single crystals of are obtainable at atmospheric pressure, and possibility of doping δ-$BiB_3O_6$ with large amounts of rare earths is demonstrated.

In this paper, we report on the dispersion of the refractive indices in the wavelength range from 435.8 to 1060 nm, Sellmeier coefficients for this crystal, transmission of the crystal, its nonlinear optical coefficients, and calculations of phase-matched second harmonic generation (SHG).

## 2. δ-BiBO crystal structure

The space symmetry group of δ-BiBO is $Pbc2_1$, the relationship between the crystallographic, crystallophysical, and principal optical axes being: $a$–$X$–$n_y$, $b$–$Y$–$n_x$, $c$–$Z$–$n_z$. The lattice parameters of the crystal are $a$ = 4.451 Å, $b$ = 18.4557 Å, and $c$ = 4.2806 Å, the density being $\rho$ = 6.38 g/cm$^3$ [9,10]. The crystal structure of δ-BiBO is featured by the exclusive presence of boron–oxygen tetrahedra forming continuous boron–oxygen network. Such structure enables more dense packing and explains larger density of δ-BiBO with respect to α-BiBO. δ-BiBO single crystals demonstrate high resistance against humidity in comparison with, e.g., LBO, that is evidenced by the fact that our samples of δ-BiBO kept for 2 years in natural ambience show no signs of deterioration by atmospheric water.

In the chosen coordinate system, $\theta$ is the internal polar angle relatively to the $Z$ axis, and $\varphi$ is internal azimuthal angle in $X$–$Y$ plane relative to the $X$ axis. The second order nonlinear coefficients

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tensor for mm2 symmetry class contains five nonzero components $d_{31}$, $d_{32}$, $d_{33}$, $d_{15}$ and $d_{24}$.

## 3. Transmission spectra and Sellmeier equation of δ-BiBO

Transmission measurements are done using Shimadzu UV-3600 and Bruker VERTEX70 spectrometers. An unpolarized transmission spectrum of 420 μm thick (0 1 0) oriented sample is shown in Fig. 1. The transmission range (50% transmission level) is from 315 nm to more than 3500 nm. The maximum transmittance is limited to 80% and is fully due to Fresnel losses, in accordance with refraction indices reported below.

The indices of refraction were measured in the wavelength range between 435.8 and 1060 nm by prism method, and least square fitted to a Sellmeier equation of type

$$n^2 = A + \frac{B}{1 + C \cdot \lambda^2} + D \cdot \lambda^2$$

Since δ-BiBO is a biaxial crystal with point group symmetry mm2, a combined prism was manufactured with output facets skewed by 17° to the (1 0 0) direction and by 11° to the (0 1 0) direction. Overall height of the prism was 7 mm in (0 0 1) direction, and the dimensions in (1 0 0) and (0 1 0) directions were 2.5 mm. This prism allowed the measurement of all three indices of refraction. Values of $n_x$ and $n_z$, the indices of refraction for the electric field vector along Y and Z, were determined using a prism with an angle of 17° with the (1 0 0) face as the incident surface, whereas values of $n_y$ and $n_z$, were determined by using the (0 1 0) face as the incident surface. Therefore, $n_z$ was measured twice, with the absolute deviation between these measurements no more than 0.0007.

Table 1 lists the parameters of the Sellmeier equation for the three indices of refraction of δ-BiBO. The measured and fitted values of the indices of refraction are given in Table 2 and plotted in Fig. 2. According to these results, δ-BiBO is positive biaxial crystal ($2V_z$ = 62.5° at 0.5321 μm).

## 4. Nonlinear optical properties of δ-BiBO

Nonlinear optical coefficients of δ-BiBO were measured using the 1.064 μm Q-switched Nd:YAG laser (pulse width 15 ns). We used wedge technique [12] for this measurement, since this technique offers certain advantages in case of samples with large refraction index and simplifies the analysis in case of low-symmetry crystals. Two crystal samples were oriented according to the Table 3 and polished to a wedge with an apex angle of roughly 1 mrad, so that thickness variation is expected to exceed one coherence length along input facet for all conversion processes. As a reference crystal, we used wedge-cut $KTiOPO_4$ (KTP) crystal that belongs to the same symmetry class. Nonlinear coefficients of KTP were taken from [13]. Difference in Fresnel reflections between KTP and δ-BiBO was taken into account. The values of nonlinear optical coefficients $d_{33}$, $d_{15}$, and $d_{24}$, crystal orientation and polarization of the beams are presented in Table 3. The uncertainty in $d_{33}$ and $d_{24}$ measurement was 15% while for $d_{15}$ it was 20%, being determined mostly by the uncertainty of coherence lengths for the corresponding nonlinear process. The uncertainty for $d_{31}$ and $d_{32}$ was found to be too large, and these values are not presented in the table. The sign of nonlinear coefficients was not determined

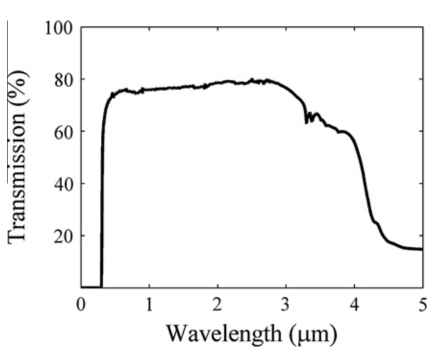


**Fig. 1.** Unpolarized transmission spectrum of δ-BiBO.

**Table 1**
Sellmeier equation coefficients.

| | *A* | *B* | *C* | *D* |
|---|---|---|---|---|
| $n_x$ | 3.98083 | 0.07199 | 0.01282 | 0.01144 |
| $n_y$ | 4.06092 | 0.07166 | 0.01464 | 0.01291 |
| $n_z$ | 4.26631 | 0.09194 | 0.02789 | 0.00726 |

**Table 2**
Experimental and fitted values for the indices of refraction.

| λ (μm) | $n_x$ | | $n_y$ | | $n_z$ | |
|---|---|---|---|---|---|---|
| | Exp. | Fit | Exp. | Fit | Exp. | Fit |
| 0.4358 | 2.0931 | 2.0941 | 2.1127 | 2.1136 | 2.1972 | 2.1983 |
| 0.4584 | 2.0849 | 2.0841 | 2.1043 | 2.1035 | 2.1849 | 2.1839 |
| 0.4654 | 2.0819 | 2.0813 | 2.1013 | 2.1007 | 2.1806 | 2.1799 |
| 0.4728 | 2.0791 | 2.0784 | 2.0985 | 2.0979 | 2.1765 | 2.1759 |
| 0.4807 | 2.0758 | 2.0756 | 2.0952 | 2.0950 | 2.1723 | 2.1719 |
| 0.4889 | 2.0728 | 2.0728 | 2.0922 | 2.0922 | 2.1680 | 2.1680 |
| 0.4978 | 2.0697 | 2.0699 | 2.0891 | 2.0893 | 2.1637 | 2.1639 |
| 0.5073 | 2.0667 | 2.0670 | 2.0861 | 2.0863 | 2.1595 | 2.1599 |
| 0.5175 | 2.0636 | 2.0640 | 2.0830 | 2.0834 | 2.1555 | 2.1558 |
| 0.5284 | 2.0606 | 2.0610 | 2.0800 | 2.0804 | 2.1511 | 2.1518 |
| 0.5402 | 2.0576 | 2.0580 | 2.0770 | 2.0774 | 2.1472 | 2.1477 |
| 0.5531 | 2.0547 | 2.0550 | 2.0741 | 2.0744 | 2.1431 | 2.1435 |
| 0.5672 | 2.0516 | 2.0519 | 2.0710 | 2.0713 | 2.1391 | 2.1394 |
| 0.5828 | 2.0484 | 2.0487 | 2.0678 | 2.0681 | 2.1348 | 2.1351 |
| 0.6002 | 2.0453 | 2.0455 | 2.0647 | 2.0649 | 2.1308 | 2.1308 |
| 0.6195 | 2.0424 | 2.0422 | 2.0618 | 2.0616 | 2.1269 | 2.1265 |
| 0.6410 | 2.0393 | 2.0389 | 2.0587 | 2.0583 | 2.1228 | 2.1221 |
| 0.6649 | 2.0363 | 2.0356 | 2.0557 | 2.0550 | 2.1185 | 2.1178 |
| 0.6912 | 2.0330 | 2.0323 | 2.0524 | 2.0517 | 2.1141 | 2.1136 |
| 0.8070 | 2.0205 | 2.0214 | 2.0399 | 2.0409 | 2.0988 | 2.0998 |
| 1.0600 | 2.0083 | 2.0082 | 2.0277 | 2.0276 | 2.0839 | 2.0838 |

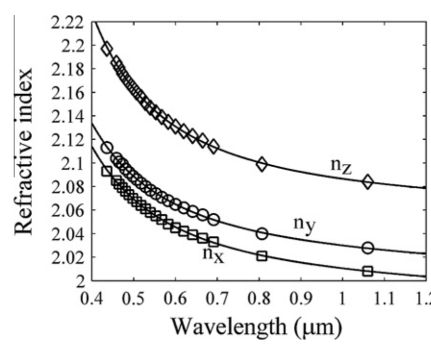


**Fig. 2.** Measured (points: $n_x$(□), $n_y$(○), $n_z$(◇)) and fitted (lines) refractive indices of δ-BiBO.

**Table 3**
Second-order nonlinear optical coefficients of δ-BiBO.

| NLOC | Plate orientation | Polarization | | Value (pm/V) |
|---|---|---|---|---|
| | | Pump | Harmonic | |
| $d_{33}$ | Y | Z | Z | 2.4 ± 0.4 |
| $d_{15}$ | Y | XZ | X | 0.9 ± 0.2 |
| $d_{24}$ | X | YZ | Y | 1.6 ± 0.3 |

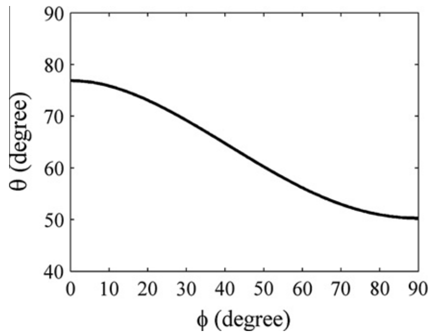


**Fig. 3.** Angle of propagation relative to $Z$ axis $\theta$ as the function of angle of propagation relative to the azimuthal angle $\varphi$ for Type I phase-matched SHG at 1.064 μm.

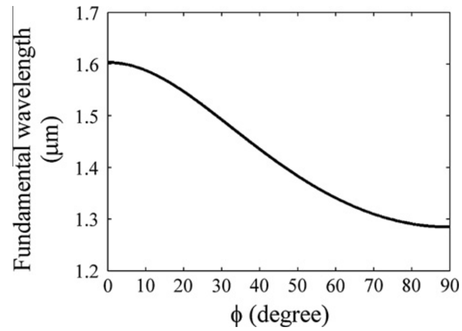


**Fig. 4.** Noncritical ($\theta = 90°$) phase-matchable wavelength as the function of azimuthal angle $\varphi$ for Type II phase-matched SHG.

in our study. As one can see from the table, on the whole, nonlinearity of δ-BiBO is of the same order of magnitude as that of α-BiBO.

## 5. Phase matching

Calculations show that noncritical Type I phase matching in the directions of main axes is impossible for any wavelength, however, critical Type I phase matching can be achieved for the fundamental wavelength range above 0.87 μm. For example, calculated phase matching directions at 1.064 μm fundamental wavelength are illustrated in Fig. 3.

Calculation of second harmonic phase matching in the principal crystal planes of δ-BiBO showed that noncritical Type II phase matching exists for $\theta = 90°$ and $\varphi = 90°$ at the fundamental harmonic wavelength 1.280 μm, the effective nonlinearity for this direction being equal to $d_{24} = 1.6$ pm/V. Experimental observation of this phase matching using optical parametric oscillator Vibrant LD 355 II with 2 mm thick X-cut crystal plate of δ-BiBO revealed the presence of noncritical phase matching of the second type at the 1.285 μm fundamental wavelength. The discrepancy between the results observed with the calculation is due to the fact that the refractive indices in this region of the spectrum were not measured. The calculated value $n_x(\lambda/2) - (n_x(\lambda) + n_z(\lambda))/2$ at 1.285 μm equals to 0.0003 that does not exceed the accuracy of refractive indices measurement. Calculated noncritical phase matching directions as the function of fundamental wavelength are presented in Fig. 4. For $\theta = 90°$ and $\varphi = 0°$ phase-matchable wavelength of the fundamental is estimated to lie at 1.6 μm, the effective nonlinearity for such a direction being $d_{15} = 0.9$ pm/V.

At 1.32°μm nearly noncritical phase matching occurs ($\varphi = 64.35°$ and $\theta = 90°$). The external acceptance angle $\Delta\theta_{ext}$ is large (∼4.8°cm) because of the 90° phase match, while $\Delta\varphi_{ext}$ is still large, too (∼1.1°cm), despite the critical phase matching, because of the relatively small ($X$–$Y$) birefringence. These acceptance angles are much better than those for α-BiBO in this spectral region. The phase matching spectral width for the fundamental radiation is equal to 0.2 nm cm. Effective nonlinear optical coefficient for this case is about 1.2 pm/V, for both cases of relative signs of $d_{15}$ and $d_{24}$.

δ-BiBO may be suitable for a doubling of laser radiation with the wavelength of 1.3°μm generated in the $Nd^{3+}$-containing crystals. Despite denser packing of δ-BiBO crystal structure with respect to that of α-BiBO, the former is much more favorable to rare-earth ions doping, and absorption coefficient of the order of 50 $cm^{-1}$ could be attained at 800 nm for $Nd^{3+}$:δ-BiBO. Generally, this is advantageous for using δ-BiBO as the self-doubling laser crystal in comparison to α-BiBO.

## 6. Conclusion

δ-BiBO is a non-linear optical material characterized by large nonlinearity and favorable phase-matching properties for SHG at 1.3 μm. Although both Type I and Type II phase matching are possible, Type II interactions are much more efficient. δ-BiBO may be suitable for doubling of laser with a wavelength 1.32 μm, especially as the concentrated self-doubling laser crystal for this wavelength.

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