

PHYSICAL METHODS  
OF INVESTIGATION

Optical Nonlinearity and Dielectric Properties  
of Noncentrosymmetric Crystals  
of RE Borotungstate Family  $\text{Ln}_3\text{BWO}_9$

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**Abstract**—The second harmonic generation method was used to prove the noncentrosymmetric structure of  $\text{Ln}_3\text{BWO}_9$  borotungstates for elements of the RE series from lanthanum through gadolinium. The crystals exhibit moderate optical nonlinearity in the absence of phase matching between the radiation of the neodymium laser and its second harmonic. An increase in the optical nonlinearity in the middle of the RE series is caused by a more severe distortion of the  $\text{WO}_6$  polyhedra in crystals. In the range 500–800 K,  $\text{Tb}_3\text{BWO}_9$  crystals exhibit dielectric relaxation, while at higher temperature, they are conductors of the Arrhenius type. Both phenomena were analyzed for the *a*- and *c*-cuts of  $\text{Tb}_3\text{BWO}_9$  single crystals using the model of oxygen ion transfer over vacancies.

At present, noncentrosymmetric complex boron oxide compounds attract considerable attention because of their nonlinear optical, piezoelectric, and other practically useful properties. In particular, along with the  $\text{LiB}_3\text{O}_5$  and  $\text{Li}_2\text{B}_4\text{O}$  crystals, which have already found technical use, more complex borates of the hantite  $\{\text{NdSc}_3(\text{BO}_3)_4$  and others [1] and stillwellite  $\text{LnBXO}_5$  ( $X = \text{Si}$  and  $\text{Ge}$ ) [2] families, the latter being ferroelectrics with high Curie temperatures, have been extensively studied in the last years.

It was the purpose of this work to establish the structure–property correlations for RE borotungstates  $\text{Ln}_3\text{BWO}_9$  ( $\text{Ln} = \text{La}–\text{Dy}$ ) possessing, according to [3], the noncentrosymmetric crystal structure of two types corresponding to space groups  $P6_3$  (for  $\text{Ln} = \text{La}$ ) and  $P3$  (for  $\text{Ln} = \text{Eu}$ ). The incomplete isomorphism of the members of this family raises the question of the stability of their polymorphs and the possibility of their reciprocal transformations.

The temperature dependences of physical properties of the  $\text{Ln}_3\text{BWO}_9$  compounds are of interest because of their structural proximity to related centrosymmetric (space group  $P6_3/m$ ) RE halide molybdates (tungstates) of the general composition  $\text{Ln}_3\text{MO}_6\text{X}_3$  with  $M = \text{Mo}, \text{W}$  and  $X = \text{Cl}, \text{Br}$  [4]. The structural distinctions between  $\text{Ln}_3\text{MO}_6\text{X}_3$  and  $\text{Ln}_3\text{BWO}_9$  are insignificant and amount to the positioning of boron cations on the threefold axis at a distance of 0.4–0.5 Å from the symmetry plane *m* in the latter compounds. Although this displacement is slightly larger than that ordinarily observed in ferroelectrics (0.1–0.3 Å [5]), it, nevertheless, can occur in

the course of high-temperature phase transformation. In such a situation, the structural changes of borotungstates correspond to the “ferroelectric–centrosymmetric paraelectric” phase transformation and should be accompanied by the peaking of the dielectric constant and the disappearance of second harmonic generation (SHG). At the same time, the above-mentioned acentric arrangement of the boron cations should give rise to a proportionally high optical nonlinearity.

## EXPERIMENTAL

Neodymium and terbium borotungstate single crystals [3], their powders, and the compositionally similar lanthanum, praseodymium, and gadolinium borotungstates prepared by high-temperature solid-phase synthesis were used as subjects for the investigation.

Single crystals of size up to 3 mm were hexagonal prisms with acute vertices. For the microscopic dielectric and optical studies, plates with normals along the prism edge (*c*-cut) or in the perpendicular direction (*a*-cut) were prepared from the  $\text{Ln}_3\text{BWO}_9$  ( $\text{Ln} = \text{Nd}, \text{Tb}$ ) single crystals. Crystal color was standard for neodymium (lilac) and terbium (grayish yellow) oxides, but the transparency of  $\text{Tb}_3\text{BWO}_9$  was worse than that of  $\text{Nd}_3\text{BWO}_9$ , likely, because of a slight oxygen nonstoichiometry, which is typical of many oxides of multivalent terbium. The optical uniaxiality of the crystals was proved by the examination of conoscopic figures on the *c*-cut plates using a polarizing micro-

scope; it was found that the crystals were optically negative; i.e.,  $N_e < N_0$ .

Highly conducting electrodes were applied to the crystals by a burning-in platinum-containing paste. A value of 1200 K chosen for the burning-in temperature coincided with the highest temperature of dielectric measurements and precluded a change in the metal–insulator properties. The dielectric constant  $\epsilon$  and the dielectric loss tangent  $\tan\delta$  were measured in the frequency range 1–1000 kHz on an automated setup built at the Karpov Research Institute of Physical Chemistry. The sample temperature was varied at a rate of 3–5 K/min in the heating and cooling modes. The data obtained in the cooling mode were subjected to quantitative analysis because they corresponded to a more equilibrium state of the samples. The accuracy in determining the absolute value of the dielectric constant was not high ( $\pm 10\%$ ) at room temperature because of the low capacitance of the samples with a small surface area (1–2 mm<sup>2</sup>) and the relative accuracy of measurements no worse than  $\pm 1\%$ .

The SHG studies were carried out in the reflection mode using fine powders with a crystallite size of 3–5  $\mu\text{m}$ . A pulsed Nd:YAG laser with a pulse duration of 10 ns, an output of  $\sim 0.1$  J, and a repetition rate of 3 Hz was used as a radiation source at a wavelength of 1.064  $\mu\text{m}$ . According to [6, 7], the use of fine powders enables one to eliminate the influence of the so-called coherent interaction length on the SHG and to quantitatively relate the second harmonic signal  $I_{2\omega}$  to the optical nonlinearity  $\langle d \rangle$  averaged over the crystallographic directions of the material [8]. Measurements were made using a reference  $\alpha$ -quartz sample with the same dispersivity as the sample under study.

## RESULTS AND DISCUSSION

### Optical Nonlinearity

The fact that the SHG effect for all five members of the  $\text{Ln}_3\text{BWO}_9$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Gd}, \text{Tb}$ ) family studied was much stronger than the same effect for the quartz reference sample provided strong evidence of their nonsymmetric structure. This result, in conjunction with the available structural data confirming the absence of the center of symmetry in the compounds with  $\text{Ln} = \text{La}$  and  $\text{Eu}$ , is evidence of the existence of a family of single-type nonlinear materials. One can see from Fig. 1 that the temperature dependences of the SHG signal, although qualitatively similar to each other, can be divided into two groups displaying either a relatively low ( $\text{Ln} = \text{La}, \text{Pr}$ ) or a considerably higher ( $\text{Ln} = \text{Gd}, \text{Tb}$ ) magnitude  $I_{2\omega}$  of the effect. This division correlates with a change in the symmetry of the compounds, from high at the beginning of the RE series (space group  $P6_3$ ) to low in the middle of the series (space group  $P3$ ) [3]. Although the  $\text{Nd}_3\text{BWO}_9$  compound should belong, according to [3], to the second

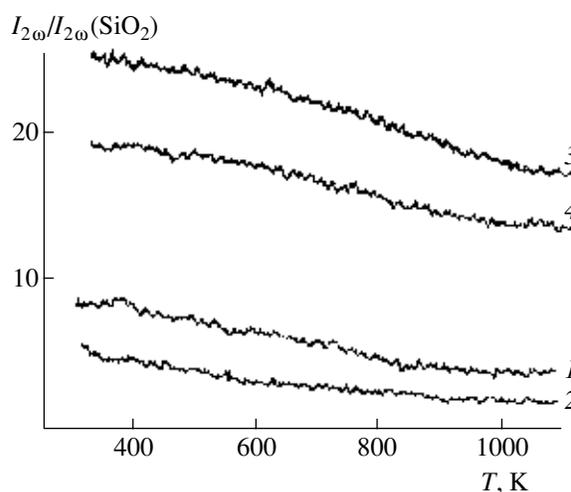


Fig. 1. Temperature dependences of SHG efficiency for the  $\text{Ln}_3\text{BWO}_9$  powders with  $\text{Ln} = (1) \text{La}, (2) \text{Pr}, (3) \text{Gd},$  and  $(4) \text{Tb}$ .

group, its SHG magnitude is not too high ( $I_{2\omega}/I_{2\omega}(\text{SiO}_2) = 3$ ), likely, because of the low transparency of neodymium oxides to the second harmonic of a neodymium laser ( $\lambda_{2\omega} = 0.532 \mu\text{m}$ ).

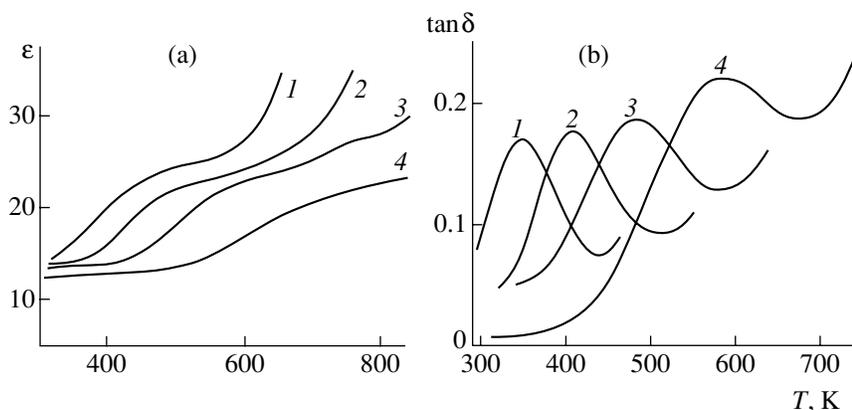
To determine the optical nonlinearity, we used the palest colored La and Gd compounds. The relative SHG magnitudes for their fine powders are quantitatively described by the simple expression [6]

$$\langle d \rangle = Ad_{11}(q)[(n+1)/(n_q+1)]^3 [I_{2\omega}/I_{2\omega}(q)]^{1/2}. \quad (1)$$

Here,  $d_{11}(q) = 0.364 \text{ pm/V}$  is the nonlinear susceptibility of  $\alpha$ -quartz;  $n$  and  $n_q$  are the refractive indices of the substance under study and quartz, respectively;  $I_{2\omega}$  and  $I_{2\omega}(q)$  are the corresponding SHG magnitudes; and  $A$  is a geometric factor of order unity. Ignoring the difference in the refractive indices of the compounds and quartz ( $n \approx n_q$ ), we obtain the values of 1.1 and 1.9 pm/V for the optical nonlinearities of lanthanum and gadolinium borotungstates, respectively.

Because of a weak optical birefringence of RE borotungstates, phase matching between the radiation of the neodymium laser and its second harmonic is impossible in these crystals. With regard to their larger, compared to quartz, optical nonlinearity, this fact allows one to relate them to the nonlinear substances of class C [8].

The measured nonlinearities are typical of many noncentrosymmetric complex borates [1, 2]. At the same time, these nonlinearities are too small to be assigned to the displacement of boron cations from the symmetry planes ( $\Delta z \sim 0.5 \text{ \AA}$ ) in RE borotungstates, because this displacement is comparable with the acentricity of strongly nonlinear materials such as  $\text{LiNbO}_3$  ( $\Delta z \sim 0.27 \text{ \AA}$ ) [5] or  $\text{KTiOPO}_4$  ( $\Delta z \sim 0.65 \text{ \AA}$ ) [9]. For this reason, the optical nonlinearity of the  $\text{Ln}_3\text{BWO}_9$  compounds should be attributed not to the positioning



**Fig. 2.** Temperature dependences of (a) dielectric constant and (b) dielectric loss tangent at frequencies (1) 1, (2) 10, (3) 100, and (4) 1000 kHz for the *c*-cut of Tb<sub>3</sub>BWO<sub>9</sub> crystal.

of boron cations but to the acentric distortion of the metal–oxygen polyhedra, primarily, of the WO<sub>6</sub> polyhedra. With this approach, an almost twofold increase in the optical nonlinearity of gadolinium borotungstate, compared to its lanthanum analogue, is explained in a quite natural way. Indeed, the tungsten cations in the borotungstates of early members of the RE series are situated almost at the center of a trigonal prism, whose shortest and longest W–O bonds differ only slightly from each other (1.93 and 1.95 Å; i.e.,  $\Delta l = 0.02$  Å). For the middle (Eu) of the series, the tungsten cation has an octahedral environment. The difference  $\Delta l$  is as large as 0.06 Å in one of the structurally inequivalent octahedra and 0.10 Å in another. Since, according to the Boyd's model of polarizable bonds [10], the macroscopic nonlinearity is determined by the sum of all bonds, with regard to their directions, the above-mentioned increase in the inequivalency of the W–O bonds correlates with the increase in the nonlinearity of Ln<sub>3</sub>BWO<sub>9</sub> in the middle of the RE series.

A decrease in the SHG effect with a rise in temperature is observed for all Ln<sub>3</sub>BWO<sub>9</sub> compounds and can be explained, within the framework of the above structural model, by a partial symmetrization of the WO<sub>6</sub> polyhedra. It follows from the SHG data that the symmetrization of the WO<sub>6</sub> polyhedra is incomplete and is even impossible from structural considerations because of the noncentrosymmetric position of the boron atoms. The latter play the stabilizing role in the crystal, because their rigid positioning in the trigonal configuration with oxygen atoms, likely, prevents distortional phase transitions and the appearance of a center of symmetry in these compounds.

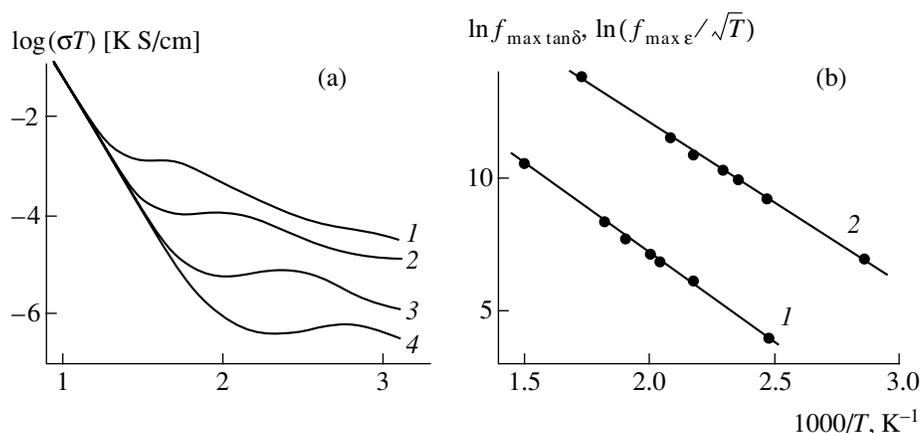
#### Dielectric Properties

The Ln<sub>3</sub>BWO<sub>9</sub> crystals are insulators with a small anisotropy of dielectric constant  $\epsilon$ . For Nd and Tb borotungstates,  $\epsilon$  at 295 K equals 15–20, both along the trigonal axis and in the perpendicular direction. It is seen

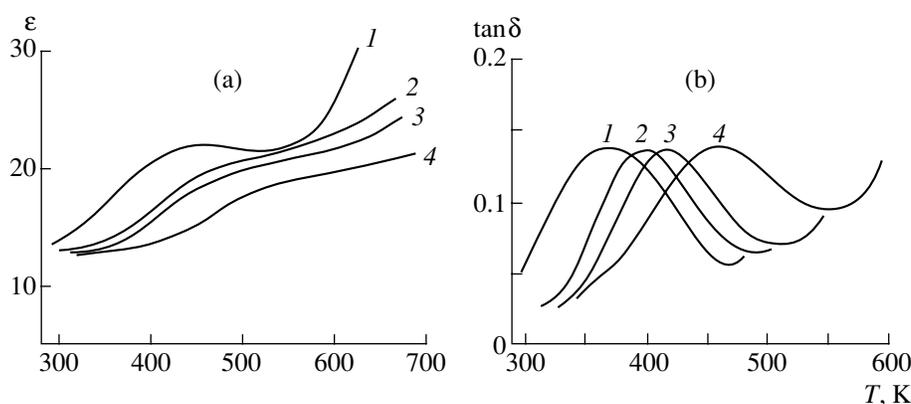
from the temperature dependences of  $\epsilon$  and  $\tan \delta$  (Fig. 2) that the high-frequency dielectric constants of Nd<sub>3</sub>BWO<sub>9</sub> and Tb<sub>3</sub>BWO<sub>9</sub> increase only slightly with temperature, whereas below 100 kHz, the relaxation phenomena are clear for the Tb<sub>3</sub>BWO<sub>9</sub> crystal. This relaxation is even more pronounced in the  $\tan \delta(T)$  curves at 300–700 K. At higher temperatures, the relaxation is suppressed by electrical conductivity of the Arrhenius type (Fig. 3a) with activation energy  $E_a = 1.0$  eV. At  $T = 1000$  K, the conductivity reaches  $10^{-4}$  S/cm. Compared to its terbium analogue, the conductivity of the Nd-containing crystal is lower by an order of magnitude. A characteristic increase in the conductivity with increasing frequency suggests its mostly ionic nature. The structurally and energetically forbidden migration of multiply charged cations in these compounds forces us to assume that the relaxational process and the ensuing conductance are due to oxygen transfer. This also correlates with the fact that the measured activation energy  $E_a$  is typical of the oxygen-mediated conductivity of oxide conductors.

The dielectric relaxation and the ionic conductivity of the Tb<sub>3</sub>BWO<sub>9</sub> crystals can be rationalized in terms of the oxygen ion transfer between interstices. In these crystals, the interstice formation is favored by the variable coordination number of the RE cations, which, according to [3], ranges from nine to eight without noticeable rearrangement of the crystal framework in Ln<sub>3</sub>BWO<sub>9</sub>.

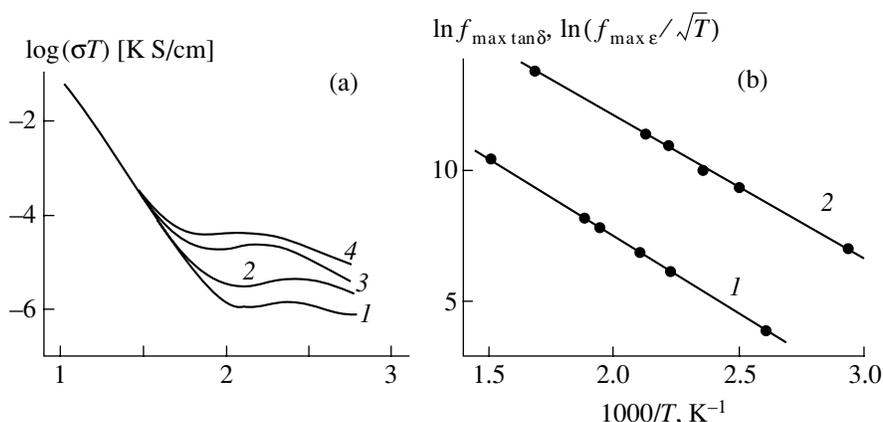
A systematic high-temperature shift of the  $\epsilon$  and  $\tan \delta$  maxima upon an increase in frequency allows one to relate the temperature and frequency of  $\epsilon$  and  $\tan \delta$  maxima to the microscopic characteristics of ion transfer between the crystal vacancies, both for cationic [11, 12] and anionic [13] conductivities. The validity of this model can be judged from the linear correlation between the inverse temperatures of  $\epsilon$  and  $\tan \delta$  maxima, on the one hand, and the logarithm of the corresponding electric field frequency, on the other. In con-



**Fig. 3.** (a) Temperature dependences of electrical conductivity at frequencies (1) 1, (2) 10, (3) 100, and (4) 1000 kHz and (b) frequencies of (1)  $\epsilon$  and (2)  $\tan\delta$  maxima for the *c*-cut of  $\text{Tb}_3\text{BWO}_9$  crystal.



**Fig. 4.** Temperature dependences of (a) dielectric constant and (b) dielectric loss tangent at frequencies (1) 1, (2) 10, (3) 20, and (4) 80 kHz for the *a*-cut of  $\text{Tb}_3\text{BWO}_9$  crystal.



**Fig. 5.** (a) Temperature dependences of electrical conductivity at frequencies (1) 1, (2) 10, (3) 50, and (4) 80 kHz and (b) frequencies of (1)  $\epsilon$  and (2)  $\tan\delta$  maxima for the *a*-cut of  $\text{Tb}_3\text{BWO}_9$  crystal.

structuring the respective curves, the frequency of  $\epsilon$  maximum was corrected by introducing the  $1/\sqrt{T_{\max}}$  multiplier. Indeed, linear dependences of these types are fulfilled well by the  $\text{Tb}_3\text{BWO}_9$  crystals (Fig. 3b).

The slope of curve 1 in Fig. 3b reflects the height of the potential barrier [12] between the neighboring positions of the migrating ion. In our case, it equals  $U = 0.58 \pm 0.01$  eV. The value  $U' = 0.52 \pm 0.01$  eV corresponding to the slope of curve 2 has no direct physical

meaning, but the difference  $U - U'$  is related to the density  $n$  of migrating particles as

$$n = \varepsilon_{\infty}(U - U')/2\pi ql^2, \quad (2)$$

where  $\varepsilon_{\infty}$  is the high-frequency dielectric constant,  $l$  is the distance between the neighboring positions of migrating ion, and  $q$  is its charge. Making use of the value  $\varepsilon = 13$  that was obtained for the  $c$ -cut of  $\text{Tb}_3\text{BWO}_9$  at a frequency of 1000 kHz, the charge  $q = 2$  for oxygen ion, a distance  $l = 2.72 \text{ \AA}$ , and a value of  $175 \text{ \AA}^3$  for the volume per one formula unit of the crystal, we arrive at  $n = 0.01$ . Therefore, the ionic transport at relaxational temperatures involves 1% of all oxygen atoms, which seems to be reasonable for the crystal structure of  $\text{Tb}_3\text{BWO}_9$ .

The crystal anisotropy of  $\text{Tb}_3\text{BWO}_9$  allows the determination of  $n$  from an analysis of the relaxation characteristics in the direction perpendicular to the  $c$ -axis. The temperature variations of the dielectric and the conducting properties of crystals in the  $a$ -direction (Figs. 4, 5), on the whole, are analogous to those for the  $c$ -cut, but they correspond to different energy parameters:  $E_a = 0.91 \text{ eV}$ ,  $U = 0.50 \pm 0.01 \text{ eV}$ , and  $U' = 0.46 \pm 0.01 \text{ eV}$ . Since the difference between the two last parameters ( $0.04 \pm 0.02 \text{ eV}$ ) coincides, to within the error of measurements, with the analogous difference for the  $c$ -cut, the substitution of these new values into Eq. (2) with the other parameters unchanged gives a value  $n = 0.008$  close to the oxygen deficiency for the  $c$ -cut.

The discrepancy between the activation energy  $E_a$  for Arrhenius-type conductivity and the potential barrier  $U$  for dielectric relaxation is noteworthy. The relation  $E_a > U$  implies that the maxima in the  $\varepsilon(T)$  and  $\tan\delta(T)$  curves are primarily due to the ion hopping over the lowest potential barriers. As to the ionic conductivity, it necessitates the overcoming of all barriers along the continuous chain of ion transfer through the crystal, including the hopping at distances exceeding the sum of ionic radii. The fact that  $E_a$  in  $\text{Tb}_3\text{BWO}_9$  is close to  $U$  enables one to assert that most of the oxygen ions in the RE borotungstates studied are separated by distances similar to the sum of oxygen ionic radii  $R_O$  and can be efficiently involved in ion transfer. A comparison of the potential barriers  $U$  and the activation

energies  $E_a$  for conductivity in the  $a$ - and  $c$ -cut  $\text{La}_3\text{BWO}_9$  samples suggests that the transfer in the plane perpendicular to the crystal  $c$ -axis is slightly more efficient.

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