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Electro-optical Pockels effect in $HoAl_3(BO_3)_4$

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The electro-optical Pockels effect has been found in the $HoAl_3(BO_3)_4$ single crystal. The electric field-induced linear optical birefringence was investigated for light with a wavelength of 632.8 nm. The Brewster angles were measured, which allowed determining the main refractive indices of the crystal. The general electro-optical coefficient r_g of the crystal was found to be $\approx 5.9 \cdot 10^{-12}$ m/V at room temperature. The electro-optical properties of holmium and thulium aluminoborates were compared.

Keywords: non-centrosymmetric crystal, rare-earth aluminoborates, electro-optics, Pockels effect, linear birefringence of light, refractive index.

Електрооптичний ефект Поккельса у $HoAl_3(BO_3)_4$. *В.А. Бедарев, Д.М. Меренков, С.М. Поперeжай*

Електрооптичний ефект Поккельса виявлено у монокристалі $HoAl_3(BO_3)_4$. Досліджено індуковане електричним полем лінійне оптичне двозаломлення світла із довжиною хвилі 632.8 нм. Виміряно величини кутів Брюстера, що дозволило визначити основні показники заломлення кристала. Встановлено значення повного електрооптичного коефіцієнта кристала rg ≈ 5.9·10-12 м/В при кімнатній температурі. Проведено порівняння електрооптичних властивостей алюмоборатів гольмію та тулію.

1. Introduction

Non-centrosymmetric crystals of rare earth (RE) aluminoborates $REAl_3(BO_3)_4$ belong to the trigonal system of the space group *R*32. These dielectric materials are sufficiently transparent in the visible region of the spectrum and have pronounced luminescent and nonlinear optical properties. In addition, due to the recent discovery of giant magnetocaloric [1] and magnetoelectric [2, 3] effects in RE aluminoborates, new prospects for the practical application of these materials are opening up.

If a crystal does not have a center of symmetry, then the linear electro-optical Pockels effect (PE) is allowed in it. This effect consists in the fact that an external electric field applied to the crystal induces linear optical birefringence, which is directly proportional to the magnitude of this field. It is known that crystals with PE can be used in various optical radiation control devices, such as light modulators, deflectors and switches. Previously, we discovered and measured PE in the $TmAl_3(BO_3)_4$ crystal at room temperature [4]. Subsequently, the contributions of the primary effect associated with electron polarization and the secondary effect associated with crystal deformation to the total PE in thulium aluminoborate were determined [5]. The study of the nature of PE in these compounds and the search for objects with high PE continues.

It is known that the magnetoelectric effect in aluminoborates depends on the RE ion type. At liquid helium temperature, the magnitude of the effect in the $HoAl_3(BO_3)_4$ crystal (the largest in this family) is an order of magnitude greater than the corresponding value in $TmAl_3(BO_3)_4$ [2,3]. It can be expected that the magnitude of PE will also depend on the RE ion. Therefore, the study of PE in the $HoAl_3(BO_3)_4$ crystal would be of scientific interest. The main goal of this work was to determine the value of the electro-optic coefficient as the main characteristic of the PE in the $HoAl_3(BO_3)_4$ crystal.

2. Experimental

The electric field-induced birefringence of light propagating along the third-order axis *c* of the crystal with the space group *R*32 is determined by the expression [5]:

$$\Delta n_E = n_a{}^3 r_g E_x \quad (1)$$

where E_x is the value of electric field directed along the second-order axis *a*; n_a is the refractive index measured along the *a* axis of the crystal; r_g is the general electro-optical coefficient, taking into account both the primary and secondary mechanisms of PE. Thus, to determine the electro-optic coefficient of the crystal, it was necessary to: 1) measure the induced birefringence of light as a function of the applied electric field and 2) determine the refractive index.

A single crystal of holmium aluminoborate was prepared by solution-melt crystallization. The orientation of the crystal axes was determined using X-ray diffraction. All experiments within this research were carried out at room temperature using laser radiation with a wavelength λ = 632.8 nm.

Electro-optics

For electro-optical studies of $HoAl_3(BO_3)_4$ crystal, a sample was prepared in the form of a plane-parallel plate measuring 4 mm × 4 mm and with a thickness of t = 230 μm. The plane of the plate was perpendicular to the trigonal axis *c* of the crystal. After mechanical polishing, the sample was annealed in air for 10 hours at temperatures close to 950°C. The sample was annealed to remove elastic stresses causing parasitic optical birefringence.

The linearly polarized laser light beam was directed along the trigonal axis of the crystal. The plane of polarization of light passing through the sample was rotated by a certain angle corresponding to the natural optical activity of the studied non-centrosymmetric crystal. An applied external electric field can reduce the optical class of the crystal from uniaxial to biaxial. In this case, the cross-section of the optical indicatrix by the plane perpendicular to the c-axis will be an ellipse. When linearly polarized light passes through the crystal, right- and left-elliptically polarized modes will propagate. There is a phase shift between these modes: $\Delta = \sqrt{\delta^2 + (2\rho)^2}$, where δ is the phase shift in the absence of spontaneous rotation, 2ρ is the phase shift in the absence of linear birefringence. In general, linearly polarized light passing through a crystal becomes elliptically polarized. If the plane of polarization of light is directed at an angle of 45° to the main axis of the cross-sectional ellipse, and the value of Δ is small enough, then the magnitude of ellipticity will be determined only by linear birefringence, and will be practically independent of spontaneous rotation. Then, the magnitude of ellipticity *e* will be determined using the following expression [6]:

$$e \approx \delta/2 \quad (2)$$

and the linear birefringence ΔnE will be related to the phase shift δ as follows:

$$\Delta n_E = \delta\lambda/2\pi t \quad (3)$$

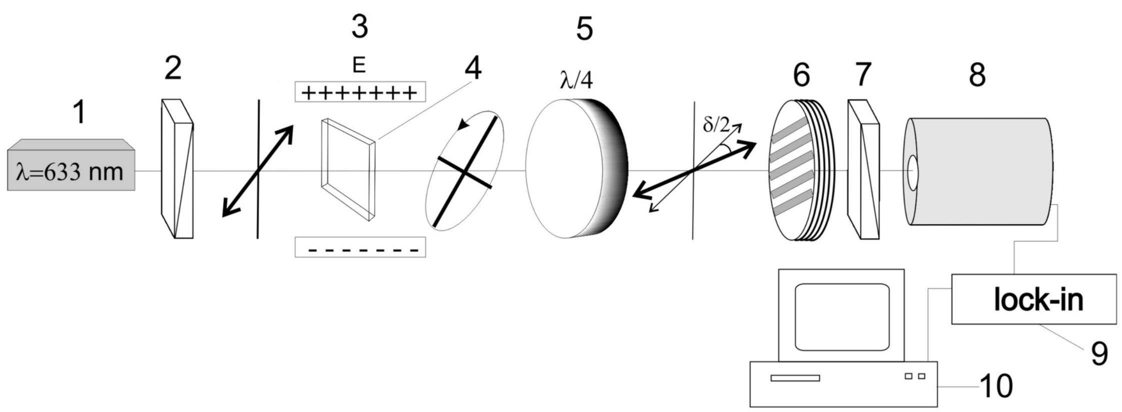

Fig. 1. Schematic diagram of the setup for electro-optical measurements: (1) He-Ne laser with λ = 632.8 nm, (2) polarizer, (3) capacitor, (4) sample, (5) λ/4-plate, (6) modulator, (7) analyzer, (8) photomultiplier tube, (9) modulator, (10) computer.

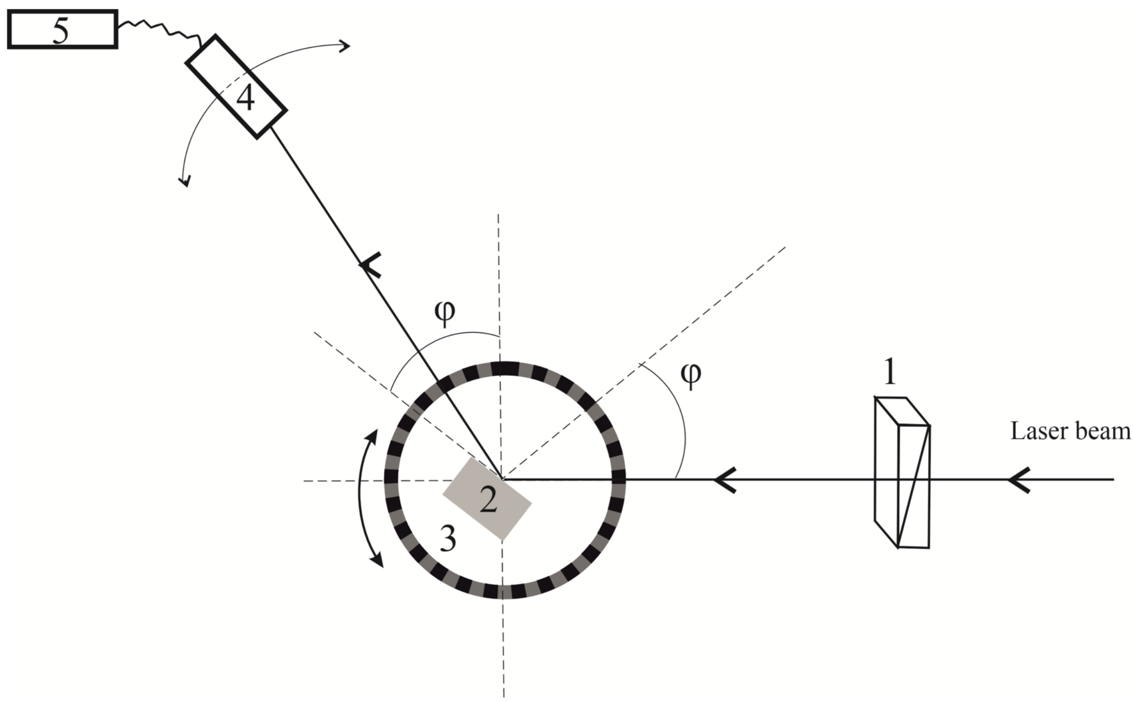

Fig. 2. Schematic diagram for determining the Brewster angle: (1) polarizer, (2) sample, (3) table with limb, (4) detector, (5) voltmeter.

The schematic diagram of the experimental setup for measuring the value of linear optical birefringence by the Senarmon method is shown in Fig. 1.

In the experiment, a helium-neon laser (1) was used. The light beam passed through a polarizer (2) and propagated along the *c*-axis. The electric field **E** was created between the plates of the capacitor (3). The sample (4) was placed inside the capacitor. The fixation of the sample in the capacitor was not rigid. The **E** direction coincides with the second-order crystal axis a ($\mathbf{E}||a$). With the help of the λ/4 plate (5), elliptically polarized light emerging from the crystal is converted into linearly polarized light. As a consequence of this conversion, the polarization plane of light is rotated by an angle $\delta/2$ relative to the plane of polarization of the light incident on the crystal. To measure the angle $\delta/2$, modulation along the plane of light polarization (modulator (6)) and synchronous detection (amplifier (9)) were used. The modulated light passed through the analyzer (7) and got to the photoelectronic multiplier (8). The output signal of the amplifier (9) was transmitted to a personal computer (10). As noted earlier, the polarizer (2) should be exposed so that the plane of polarization of light incident on the crystal makes an angle of 45° with the principal axis of the cross-sectional ellipse. Therefore, the azimuthal dependence of the ellipticity of the light passing through the crystal in the field of $4\cdot10^5$ V/m was measured before starting the experiment. The desired position of the polarizer corresponded to the maximum of this dependence.

Refractive indices

To determine the electro-optic coefficient r_g, the principal refractive index n_a should be measured. In addition, it is necessary to determine the second principal index n_c for the general description of the crystal material, as well as for establishing the role of the primary and secondary effects in the PE. In this work n_a and *nc* were determined by measuring the angular dependence of the intensity of light. The laser beam is reflected from the crystal surface in the Brewster geometry, i.e., when the polarization vector of the light lies in the incident-reflection plane. For these studies, a sample of $HoAl_3(BO_3)_4$ crystal was prepared with one of the planes (natural face) parallel to the *c*-axis, and the other plane (polished surface) perpendicular to this axis. The principle scheme of measurements is presented in Fig. 2.

The laser beam passed through a polarizer (1) adjusted in accordance with Brewster geometry, and fell on the surface of a crystalline sample (2). The sample was located in the center of a table (3) equipped with a limb. The table could rotate along its axis. The beam

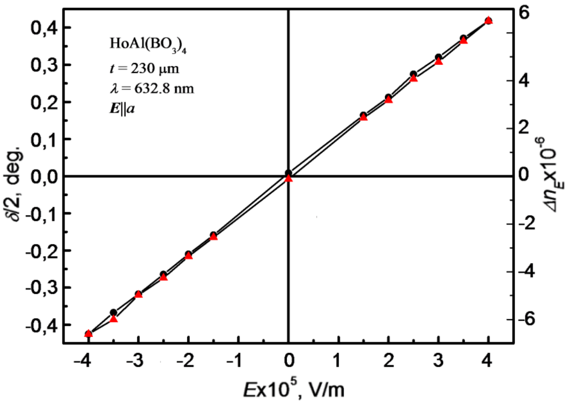

Fig. 3. Dependence of the linear birefringence of light Δn_E in $HoAl_3(BO_3)_4$ crystal on the external constant electric field $E \| a$ at room temperature. The value of birefringence was calculated according to formula (3).

reflected from the surface fell on the photodetector (4), which could move smoothly along the arc of the circle depending on the angle of rotation of the table. The photodetector converted the reflected light into an electrical signal, which was fed to the voltmeter (5). The reading of the limb began from the position at which the measuring beam of light fell perpendicular to the surface of the sample. Thus, the angle of rotation of the crystal from the initial position was equal to the angle φ between the normal to the surface of the crystal and the incident beam. The value φ at which the minimum of the reflected light intensity was observed corresponded to the Brewster angle. The measurement error was no more than 0.3°.

When light is reflected from the sample plane that is parallel to the c-axis, the Brewster angle φ_{Ba} is related to the principal refraction index n_a through the simple relation

$$n_a = \tan \varphi_{Ba} \qquad (4)$$

In the case of light reflection from a plane perpendicular to the c axis, the Brewster angle φ_{Bc} is determined by both principal refractive indices n_a and n_c:

$$\tan \varphi_{Bc} = n_a \sqrt{\frac{n_c^2 - 1}{n_a^2 - 1}} \qquad (5)$$

3. Results and discussion

Before starting the electro-optical measurements, it was established that the natural optical activity of the sample is quite small (no more than 0.25°), and does not affect the measurement of the electric field-induced optical linear birefringence.

Table 1. Parameters of $HoAl_3(BO_3)_4$ and $TmAl_3(BO_3)_4$ crystals. The measurements were carried out at room temperature for a light wavelength of 632.8 nm. The bottom row shows the ratio of the parameters.

	α	$1/n_a^3$	r_g
Ho	$1.6 \cdot 10^{-11}$ m/V	0.37	$5.9 \cdot 10^{-12}$ m/V
Tm [5]	$2.0 \cdot 10^{-11}$ m/V	0.33	$6.6 \cdot 10^{-12}$ m/V
(Ho)/(Tm)	0.80	1.12	0.89

The field dependence of the birefringence of light, induced by an external electric field in the $HoAl_3(BO_3)_4$ crystal is presented in Fig. 3. The measurement error was about 5%. No appreciable hysteresis on the dependence was observed. In an electric field of $4 \cdot 10^5$ V/m, the value of Δn_E reaches $6.5 \cdot 10^{-6}$. The obtained dependence is linear and can be extrapolated using the following expression

$$\Delta n_E = \alpha E_x \qquad (6)$$

where $\alpha \approx 1.6 \cdot 10^{-11}$ m/V.

The angular dependences of the intensity of light reflected from two different planes of the $HoAl_3(BO_3)_4$ crystal (Figs. 4a, 4b) are described well by cubic functions. The values of minima on these functions allow us to determine the Brewster angles φ_{Ba} = 54.3°±0.15° and φ_{Bc} = 59.3°±0.15°, respectively. Substituting the values of Brewster angles into expressions (4) and (5), it is easy to obtain the values of the principal refractive indices of the $HoAl_3(BO_3)_4$ crystal: $n_a \approx 1.39$ and $n_c \approx 1.54$. Now from expressions (1) and (6) it is easy to determine the value of the electro-optic coefficient $r_g = a/n_a^{\ 3} \approx 5.9 \cdot 10^{-12}$ m/V.

As shown in Table 1, the parameters of holmium and thulium aluminoborates are very close at room temperature. This significantly complicates their comparative analysis. The values of the refractive index n_c (not indicated in the Table 1) of both crystals within the measurement error can generally be considered equal. However, it can be noted that the ratio of the values of the main electro-optical coefficient r_g(Ho)/r_g(Tm) is somewhat larger than the ratio of the coefficients of field-induced birefringence a(Ho)/a(Tm). This is a consequence of the disproportionately large reciprocal of the cube of the fundamental refractive index the n_a for holmium aluminoborate compared to thulium (n_a(Tm) ≈ 1.44 [5]).

A more significant difference in the electro-optical properties of the studied crystals can be

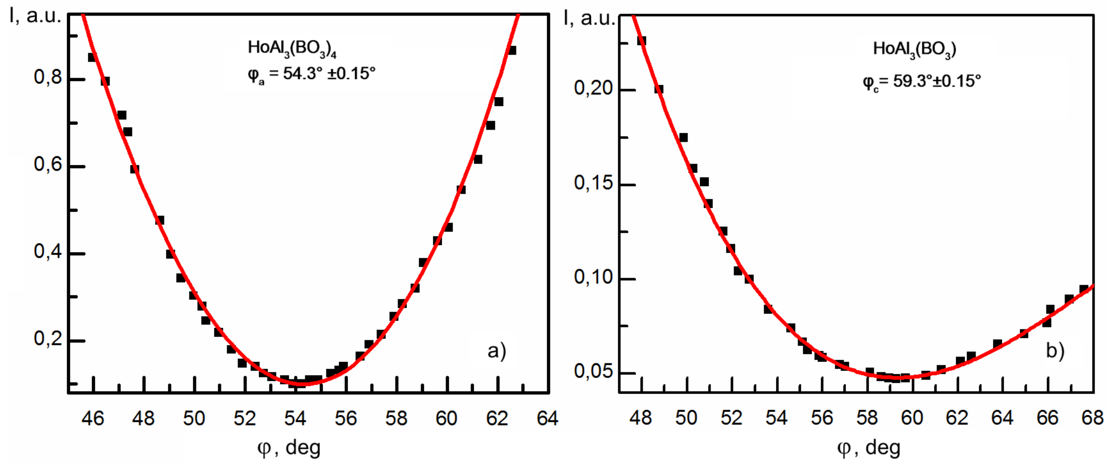

Fig. 4. The intensity of the light reflected by the $HoAl_3(BO_3)_4$ crystal planes parallel (a) and perpendicular (b) to the *c*-axis; φ is the angle between the normal to the crystal surface and the incident beam. Symbols denote the results of measurements. The line represents the approximation of these results by a cubic function. The minima of the functions correspond to the Brewster angles φ_{Ba} and φ_{Bc}

expected at low temperatures. The magnitude of the primary PE associated with the polarization of the RE ion is proportional to n_a^3 [5]. Since $n_a = \sqrt{\varepsilon_{xx}}$ (ε_{xx} is the corresponding component of the dielectric permittivity tensor), the temperature changing of permittivity will affect the magnitude of the PE. It was shown in [7, 8], that the behavior of the temperature dependence of the dielectric permittivity of RE aluminoborates is determined by the ground multiplet of the RE ion. The dependence is determined by expression [8]:

$$\frac{\varepsilon_{xx}(T)-\varepsilon_{xx}(T_0)}{\varepsilon_{xx}(T_0)} = \frac{\sum_i a_i exp\left(-\frac{E_i}{T}\right)}{Z} \qquad (7)$$

Here E_i are the energy levels of the ground multiplet; $Z = \sum_i exp\left(-\frac{E_i}{T}\right)$ is their statistical sum; a_i is the phenomenological constant; T_0 is the room temperature. Thus, temperature dependence of the primary Pockels effect in RE aluminoborates will be determined by the ground multiplet of the RE ion.

The magnitude of the secondary PE is not only proportional to n_a^3, but also depends on the crystal deformation caused by the application of the electric field. Although the external electric field **E** will cause a shift in the levels of the ground multiplet, the temperature dependence of the relative deformation will also be determined by an expression similar to (7). Therefore, the secondary PE will have a more complex temperature dependence than the primary PE. However, it will also be determined by the main multiplet of the RE ion.

The lowest level of the ground multiplet $^5I_8$ of the Ho^{3+} ion in the $HoAl_3(BO_3)_4$ crystal is separated from the first excited multiplet by an interval of about 18 cm^{-1} [9]; the lowest level of the ground multiplet $^3H_6$ of the Tm^{3+} ion in the $TmAl_3(BO_3)_4$ crystal is separated from the first excited multiplet by a much larger interval, which is about 29 cm^{-1} [10]. Therefore, it can be expected that at low temperatures, the electro-optical properties of holmium and thulium aluminoborates will differ most significantly, since they will be determined mainly by these levels. At room temperature, the sums $\sum_i a_i exp\left(-\frac{E_i}{T}\right)$ for holmium and thulium aluminoborates are probably close, and the differences should be small due to the influence of higher-lying levels of the ground multiplet.

4. Conclusions

It has been shown that external electric field induces the linear birefringence of light – the electro-optic Pockels effect – in the crystal $HoAl_3(BO_3)_4$. The Brewster angles φ_{Ba} = 54.3°±0.15° and φ_{Bc} = 59.3°±0.15° were determined by measuring the angular dependence of the intensity of polarized light reflected from the surfaces of the $HoAl_3(BO_3)_4$ crystal. The values of the principal refractive indices $n_a \approx 1.39$ and $n_c \approx 1.54$ were calculated. The value of the general electro-optic coefficient of the $HoAl_3(BO_3)_4$ crystal was determined to be $r_g \approx 5.9 \cdot 10^{-12}$ m/V for the light wavelength of 632.8 nm at room temperature.

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