Concentration dependence of refractive index of the glassy $Li_2B_4O_7$ on the Er^{3+}, Tb^{3+}, Eu^{3+} activators

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Introduction

The structure, optical and luminescent properties of lithium tetraborate ($Li_2B_4O_7$) in different phase states have been intensively studied in recent years. Such materials are of particular interest providing optical media for the creation of optical quantum generators and act as frequency converters for laser radiation, being important for the use as superionic conductors in manufacturing solid electrolytes and, consequently, solid power sources. In addition, lithium tetraborate (LTB) is a promising material for the use as a dosimetric tissue-equivalent material, and has nonlinear optical, acousto-optical and piezoelectric properties [1-5].

The refractive index n is one of the main LTB optical characteristics, and studying its dispersion and temperature dependence in the region of high and low temperatures (down to the liquid nitrogen temperature) was performed by the authors of Refs. [6-8]. Thus, in [8], a weak dependence of $n(T)$ in the 77–294 K temperature range was obtained for single-crystal LTB samples, and a change (break) in the behavior of this dependence was revealed at T=235 K. According to the results of complex studies, the authors relate this anomaly to some rearrangement of the electronic subsystem of the crystal mainly in the XY plane.

Determination of the refractive index of vitreous LTB and the influence on it of any dopants, especially the rare-earth (RE) oxides, which are included in the matrix of solids in the form of three-charged ions, has not been realized at all. This work is the beginning of such studies. It should be noted that, in such materials, excitation and radiation occur due to the transitions between the 4*f*-electronic states of trivalent lanthanide ions, which are very sensitive to the symmetry and structure of the local environment. As shown in [9-12], introduction of Er^{3+}, Tb^{3+} or Eu^{3+} causes activation of absorption bands and the X-ray luminescence. When interpreting the spectra of thermo-, X-ray, photoluminescence and absorption spectra, a knowledge of the refractive index and its change with introduction of different activators (in this case, vitreous $Li_2B_4O_7$ activation by triple-charge RE ions) is necessary to calculate the probabilities of optical (both radiative and excitative) transitions and the factor of splitting the optically active activator energy levels [12]. It should be taken into account that when introducing such activators into the vitreous LTB matrix a significant change in the coordination environment occurs, which causes a change in the refractive index as well.

Experimental results

To determine n we used an ellipsometric technique that, operating a complex refractive index $N=n-ik$, allowed us to determine simultaneously the absorption index k (attenuation of light, which is related to the absorption coefficient by the formula $\alpha=4\pi k/\lambda$). It was used to study the refractive index $n_{x,y,z}$ of ferroelectrics and their solid solutions [13] and the change of N in the glassy As_2S_3 as a result of doping with manganese (1 at.%), samarium (0.1 at.%) and tin (1 at.%) [14]. These measurements were carried out using an LEF-3M ellipsometer with a helium-neon laser (λ=632.8 nm wavelength). In the course of measurements, the change in the polarization state of the elliptically polarized beam reflected from the sample surface was determined.

At the interface between two (1 and 2) media with refractive indices N_1 and N_2, the incident beam (I) splits into the reflected (R) and transmitted (refracted) ones. The electric vectors **E** of these rays are represented by two mutually perpendicular components: $\mathbf{E_p}$ is parallel to the plane of incidence and $\mathbf{E_s}$ is perpendicular to it. The relationship between the amplitudes A of these components when light passes through the interface of two media is determined by the following relations (φ_1, φ_2 being the incidence and refraction angles) [15, 16]:

$$r_p = \frac{A_p^R}{A_p^I} = \frac{N_2\cos\varphi_1 - N_1\cos\varphi_2}{N_2\cos\varphi_1 + N_1\cos\varphi_2}; \quad r_s = \frac{A_s^R}{A_s^I} = \frac{N_1\cos\varphi_1 - N_2\cos\varphi_2}{N_1\cos\varphi_1 + N_2\cos\varphi_2}. \qquad (1)$$

In the case of reflection from the surface (a semi-infinite medium), using formulae (1), we obtain the following expression:

$$\mathrm{tg}\,\Psi = \frac{r_p}{r_s} = \frac{N_1N_2(\cos^2\varphi_1 - \cos^2\varphi_2) + (N_2 - N_1)\cos\varphi_1\cos\varphi_2}{N_1N_2(\cos^2\varphi_1 - \cos^2\varphi_2) - (N_2 - N_1)\cos\varphi_1\cos\varphi_2}. \qquad (2)$$

For absorbing media, the refractive index is a complex quantity ($N=n-ik$) and expression (2) could be written as:

$$\frac{r_p}{r_s} = \mathrm{tg}\,\Psi \cdot e^{-i\Delta}, \tag{2a}$$

where Ψ i Δ=(Δ_p–Δ_s) are the parameters measured by the ellipsometer (i.e. the change in the angle of rotation of the polarization ellipse and the phase shift angle of the vectors $\boldsymbol{E}_{p,s}$ when the beam is reflected from the test sample surface).

If N_1=1, the optical quantities (n, k) of the second medium are calculated using such formulae [17]:

$$n^2 - k^2 = \sin^2\varphi_1\left[1 + \mathrm{tg}^2\,\varphi_1 \cdot \frac{(1-tg^2\Psi)^2 - 4tg^2\Psi \cdot \sin^2\Delta}{(1+tg^2\Psi + 2tg\Psi \cdot \cos\Delta)^2}\right]; \tag{3a}$$

$$nk = 2\sin^2\varphi_1 \cdot \mathrm{tg}^2\,\varphi_1 \cdot \frac{(1-tg^2\Psi)\cdot tg\Psi \cdot \sin\Delta}{(1+tg^2\Psi + 2tg\Psi \cdot \cos\Delta)^2}\ . \tag{3б}$$

They can be used to calculate (n, k) by measuring Ψ and Δ at only one incidence angle φ_1. To increase the accuracy of determining the indices (n, k), a polygonal ellipsometry was used, when two values (Ψ, Δ) were measured at different incidence angles (Figs. 1, 2). In our measurements, the incidence angle successively varied from 50° to 63°. The samples had the form of the 5 x 8 mm rectangles, 0.4–0.6 mm thick, the upper surface of which was polished and the lower was made matte to prevent the effect of the reflected beam.

Having the experimental dependences Ψ(φ) and Δ(φ), the inverse problem was solved [18, 19]: changing the values n and k with a small step in given intervals, the angles (Ψ,Δ) were calculated by formula (2a), and the values of indices (n, k) were chosen by a least-square method, which gave the smallest standard deviation (σ) of the calculated (theoretical) dependences Ψ(φ) and Δ(φ) from the experimental ones. Some of the graphs of these dependences are given below (Figs. 1 and 2), and other results are presented in Table 1 and Fig. 3. Here, all graphical and tabular results of calculations of the optical parameters of the samples are given as the average values of several measurements on the same sample at different points of its surface, and sometimes at different times. It is seen that the experimental points agree very well with the theoretically calculated dependences, and in terms of the relative error of determining (Ψ,Δ), for example, of pure LTB samples, it averages ≈0,75 %. The relative error for other samples calculated in a similar way lied in the range of (0.5–1.0) %. Assuming the same value for the relative error of the refractive index, the absolute error values are plotted on the concentration dependences n (%) represented by the length of the error bars.

Table 1.

Indices (n, k) of the glassy $Li_2B_4O_7$ samples under study:
a pure LTB and that with activator dopants

Concentration, wt. %	Er_2O_3		Tb_2O_3		Eu_2O_3	
	n	***k***	***n***	***k***	***n***	***k***
0 (LTB)	1.523	0.061	1.523	0.061	1.523	0.061
0.0005	1.586	0.0145				
0.001	1.580	0.015				
0.005	1.588	0.006				
0.05	1.585	0.031				
0.5	1.575	0.034	1.531	0.056	1.543	0.046
1.0	1.545	0.050	1.537	0.047		
1.5	1.535	0.060				
n and k change at 0.5 wt.%	Δn= + 0.052	Δk= - 0.027	Δn= + 0.008	Δk= - 0.005	Δn= + 0.020	Δk= - 0.015

Analyzing the results of studies, we may note as follows.

The values of n determined for all samples studied by us lie within the 1.52–1.59 range, which includes the values for single crystals [7, 8]. However, for vitreous $Li_2B_4O_7$, n_{glass}=1.523 (at the λ=623.8 nm wavelength) that is less than n_{cr}= 1.54–1.55 for crystalline substance. Note that the values of n_c given here relate to the n_z [8] and n_e (an extraordinary beam) [7] geometry, while the values of $n_{x,y}$ and n_o (an ordinary beam), according to these works, are even larger (n≈1.61).

The data of Table 1 and concentration dependences (Fig. 3) indicate that introduction of already very small amount of the Er_2O_3 dopants increases sharply (by Δn≈0.05) the refractive index (i.e. by ≥ 3%, which is 3–4 times higher than the error of determining n) that almost does not vary up to the ≈0.1 wt.% concentration, and then slowly decreases with a tendency to approach that for the pure sample in the range of a few percent. The absorption (extinction) index k shows a symmetrical change (Fig. 3a), however, within the k=(0.01–0.06) range it changes 6 times.

The terbium oxide (Tb_2O_3) introduction into the vitreous LTB matrix of two (0.5 and 1.0) concentrations causes the opposite to erbium change in (*n, k*) and it is smaller (Fig. 3b).

The studies of the effect of the Er^{3+}, Tb^{3+} and Eu^{3+} RE oxide ion dopants at the 0.5 wt.% concentration on the complex refractive index of glassy LTB (Fig. 2) variation show that the largest change in *n* and *k* is peculiar for the samples activated by the erbium ions (Table 1). Here $\Delta n(Er^{3+})=0.052$ or it is ≈34% of the value of *n* for the pure $Li_2B_4O_7$, and the extinction coefficient *k* decreases almost 2 times.

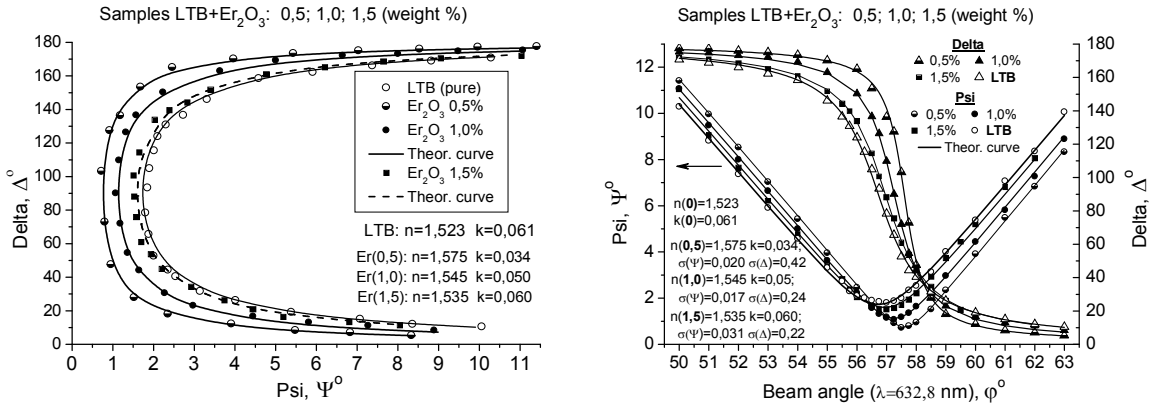

Fig. 1. Comparative dependences of the phase shift (**Δ**) of the vectors $\boldsymbol{E}_{\mathbf{p,s}}$ and the angle of polarization ellipse rotation (**Ψ**) on the angle φ of the laser beam (λ=632.8 nm) incidence onto the pure $Li_2B_4O_7$ and activated erbium sample surface with different weight concentrations (graphs show the determined complex refractive indices of the samples and the corresponding values σ of the ellipsometric parameters **Ψ** and **Δ**); the dots on the dependences Δ(Ψ) correspond to the sequence of experimental angles on the curves Ψ(φ),Δ(φ).

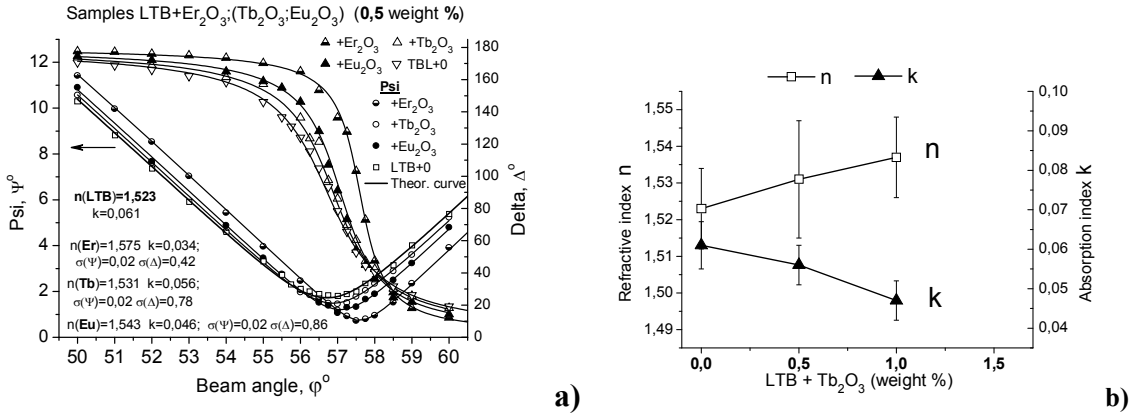

Fig. 2. a) Experimental and theoretical (for determined indices *n, k*) dependences Ψ(φ) and Δ(φ) for the samples of pure glassy $Li_2B_4O_7$ and that activated by introducing the Er_2O_3, Tb_2O_3 or Eu_2O_3 dopants at the 0.5 weight % concentration.

b) Dependence of refractive (*n*) and absorption (*k*) indices for the glassy $Li_2B_4O_7$ on the Tb_2O_3 activator concentration.

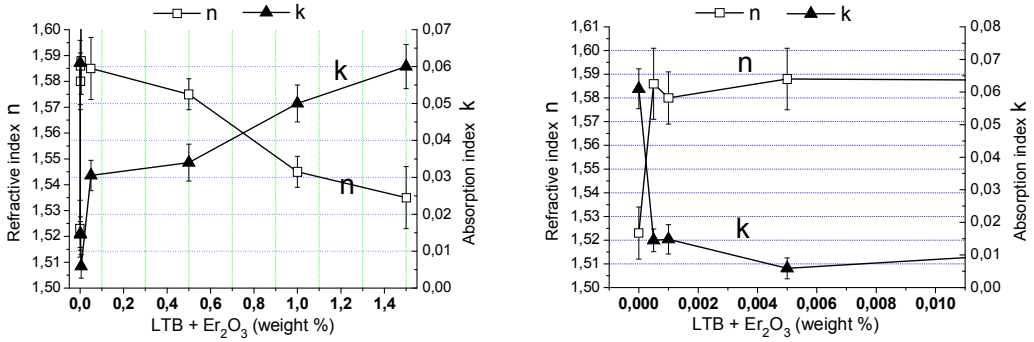

Fig. 3. Dependence of refractive (*n*) and absorption (*k*) indices for the glassy $Li_2B_4O_7$ on the Er_2O_3 activator concentration.

Conclusions

The influence of the rare earth Er^{3+}, Tb^{3+}, Eu^{3+} ions on the complex refractive index ($N=n-ik$) of the vitreous lithium tetraborate was studied by introducing the oxide dopants $(Er,Tb,Eu)_2O_3$. It has been found that their introduction increases *n*, while at 0.5 wt.% concentration the most pronounced effect is exerted by erbium ions.

One may note two characteristic areas of the (*n, k*) dependences on the Er_2O_3 concentration, i.e. those seen up to 0.0005 wt.% and, probably, after 0.5 wt.%. Very small (0.0005–0.05 wt.%) concentrations increase drastically the refractive index *n* and several times reduce the absorption index *k*, and concentration above 0.05 wt.% leads to a decrease in the *n* values, while after 0.5 wt.% this decrease appear to be more fast, approaching the value of the refractive index of the crystalline sample [7,8].

A sharp leap in the (*n, k*) values was recorded at the Er_2O_3 activator introduction. In our opinion, this is due to the rearrangement of the electronic subsystem due to the hybridization of the Er^{3+} ions, which occupy the place of the lithium atoms with a coordination number of 4–6 [20]. The clustering process takes place in a disordered matrix, i.e. due to the hybridization of the Er^{3+} ions an erbium-oxygen cluster is formed in the structure of vitreous LTB [20]. In [10], this was confirmed by detailed studies of the X-ray luminescence spectra transformation depending on the Er_2O_3 activator concentration.

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