Optical, Ultrasonic and Thermal Expansion Properties of $LiKB_4O_7$ Crystals. Structural Phase Transition

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Abstract

The results for the refractive indices dispersion, optical activity, electro- and piezooptic effects, thermal expansion and the ultrasonic wave velocities for $LiKB_4O_7$ crystals are presented. A structural phase transition is revealed at the temperature T=223K.

Key words: $KLiB_4O_7$ crystals, refractive index, electrooptic and piezooptic effects, thermal expansion, ultrasonic wave velocities.

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Introduction

Non-centrosymmetric borate crystals, in particular, β-BaB_2O_4 (point group of symmetry *3m*), $Li_2B_4O_7$ (*4mm*) and LiB_3O_5 (*mm2*) are widely used for optical harmonics generation and parametric oscillation (see, e.g., [1,2]). The advantages of application of these crystals for controlling laser radiation follows from their wide range of transparency [3], high optical damage threshold [4], high values of nonlinear optical figure of merit [1] and good acoustooptic properties [5]. Consequently, searching for new borate crystals with improved characteristics is promising from the viewpoint of optical material science. As an example, our recent studies have revealed better optical resistance of mixed α-$Sr_{0.1}Ba_{0.9}B_2O_4$ crystals, when compare with pure α-BaB_2O_4 crystals [6]. It has been also revealed that the mixed $CsLiB_3O_5$ borate crystals are new representatives of the borate family [7], which seem to have prospects as a material for nonlinear optical applications. Recently the authors of the work [8] have reported about a successful growth of new mixed tetraborate crystals, $LiKB_4O_7$ and $LiRbB_4O_7$. They belong to acentric point symmetry group 222 and, as supposed [8], can manifest good enough nonlinear optical characteristics. The present paper is therefore devoted to the growth and study of $LiKB_4O_7$ crystal.

Experimental

The dispersion of refractive indices was studied with the index-matching method. Alpha-monobromine naphthalene with kerosene or iodine methane were used as index-matching liquids. Crystal plates that had their surfaces perpendicular to the principal crystallographic planes and the average thickness of some millimetres were prepared from a bulk single crystal. The optical activity characteristics were obtained after measuring rotation angle for the polarization plane of light (the wavelength λ=632.8nm) propagated along one of the optic axis. The electrooptic effect in $LiKB_4O_7$ crystals was measured while determining rotation of the optical indicatrix at the same wavelength λ=632.8nm under applied electric field. The piezooptic effects were characterized using the standard Senarmont and interferometric techniques. The latter was performed under the action of mechanical stress by means of Mach-Zender interferometer.

The measurements of the velocity of longitudinal and transverse ultrasonic waves were performed on single crystals with the pulse-echo overlap method. The accuracy for determination of the absolute velocity was about 0.5%. The acoustic waves in samples were excited using $LiNbO_3$ transducers with the resonance frequency f=10MHz, the bandwidth Δf=0.1MHz and the acoustic power P_a=1–2W. The thermal expansion was determined with the capacity dilatometer that had the sensitivity of 2nm. Those studies were carried out in the cooling and heating temperature runs, the corresponding rate being $\partial T/\partial t$=1K/min.

Results and discussion

Dispersion curves of the refractive indices for $LiKB_4O_7$ crystals is presented in Fig. 1. $LiKB_4O_7$ crystals are optically biaxial, with the *ab* plane containing the optic axis, where *a* axis represents the bisector of the acute angle between the optic axes. These crystals are "optically negative", i.e. $n_g - n_m < n_m - n_p$ (n_g, n_m and n_p being "large", "intermediate" and "small" refractive index values, respectively). The acute angle between the optic axes measured directly turns out to be equal to $2V^m = 111.6°$ at the working wavelength of 632.8nm, while the calculations based on the measured refractive indices and the relation

$$tgV = \sqrt{\frac{n_p^{-2} - n_m^{-2}}{n_m^{-2} - n_g^{-2}}} \qquad (1)$$

give the value $2V^c = 114.48°$. Some mismatch of these values is associated with inaccuracies of the refractive index measurements.

Let us note that the point group of symmetry of $LiKB_4O_7$ crystals permits the existence of optical activity. It has been ascertained that the specific angle of rotation of the polarization plane is equal to $\rho = 6.5\deg/mm$, when the light propagates along one of the optic axes. The crystals are right-handed for the mentioned direction of light propagation.

The piezooptic coefficients determined with the interferometric method are as follows:

$\pi_{11} = (3.2 \pm 0.3) \times 10^{-11} m^2/N$,

$\pi_{12} = (1.3 \pm 0.1) \times 10^{-11} m^2/N$,

$\pi_{32} = (1.3 \pm 0.1) \times 10^{-11} m^2/N$,

$\pi_{22} = (1.7 \pm 0.2) \times 10^{-11} m^2/N$,

$\pi_{23} = (2.5 \pm 0.2) \times 10^{-11} m^2/N$,

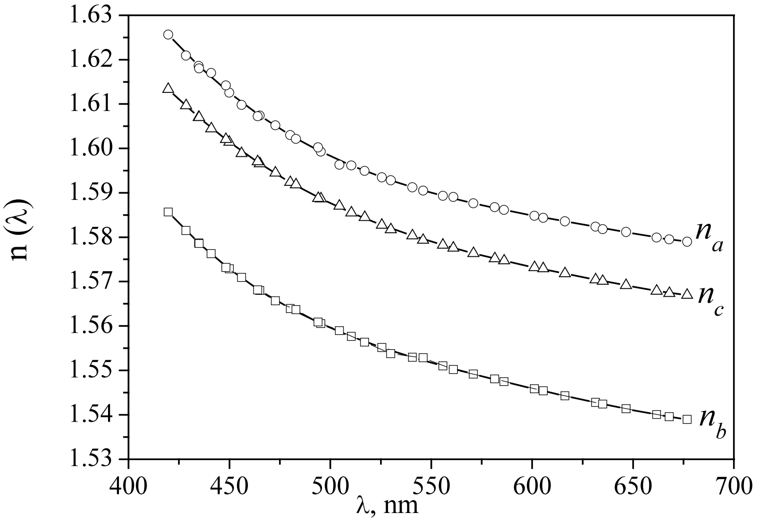
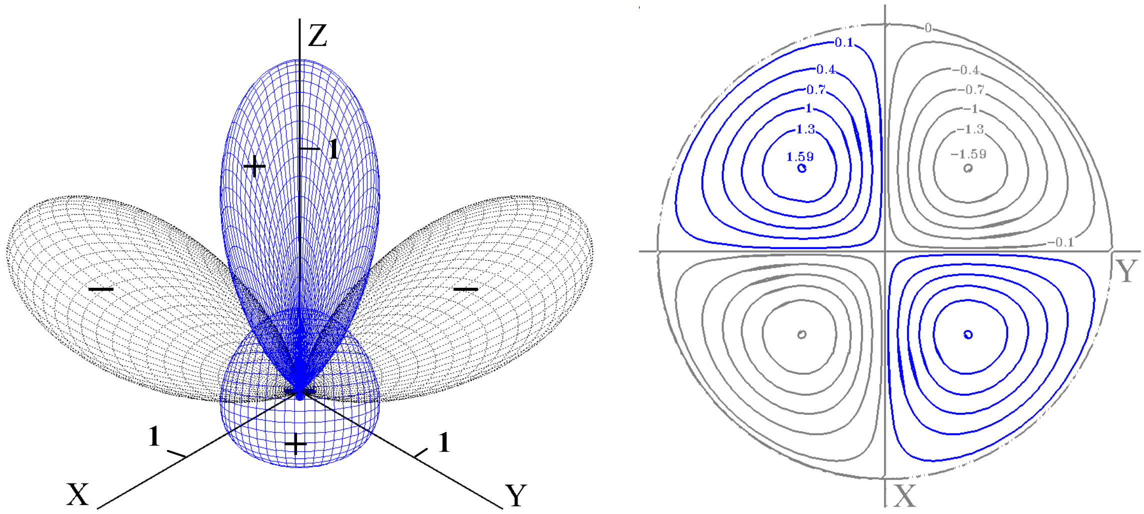


Fig. 1. Dispersion of refractive indices for $LiKB_4O_7$ crystals



a b

Fig. 2. Half indicative surface of electrooptic tensor for $KLiB_4O_7$ crystals (a) and its stereographic projection (b) (in the units of pm/V).

$\pi_{33} = (3.4 \pm 0.2) \times 10^{-11} m^2/N$,

$\pi_{21} = (2.8 \pm 0.3) \times 10^{-11} m^2/N$,

$\pi_{31} = (3.1 \pm 0.3) \times 10^{-11} m^2/N$,

$\pi_{13} = (2.6 \pm 0.5) \times 10^{-11} m^2/N$.

The values of these coefficients are in a quite good agreement with those obtained using the Senarmont method: $n_1^3\pi_{13} - n_3^3\pi_{33} = (1.2 \pm 0.2) \times 10^{-11} m^2/N$, $n_1^3(\pi_{12} - \pi_{11}) = (1.6 \pm 0.3) \times 10^{-11} m^2/N$ and $n_3^3\pi_{31} - n_1^3\pi_{11} = (1.0 \pm 0.2) \times 10^{-11} m^2/N$. The electrooptic tensor for $KLiB_4O_7$ crystals at the working wavelength 632.8nm may be schematically represented as follows:

	E_1	E_2	E_3	
ΔB_1	0	0	0	
ΔB_2	0	0	0	
ΔB_3	0	0	0	$\times 10^{-12} m/V$.
ΔB_4	$-(2.5 \pm 0.5)$	0	0	
ΔB_5	0	4.5 ± 1.0	0	
ΔB_6	0	0	2.1 ± 0.7	

Having the complete matrix of electrooptic coefficients known, one can construct the indicative surfaces of electrooptic effect. We emphasize here that the above surface has just illustrative meaning and it could be applied only while calculating electrooptic figure of merit in certain application geometries. Using the formula

$$r = \frac{1}{2}(r_{52} + r_{63} - r_{41}) \sin 2\Theta \sin 2\varphi \sin\Theta , \qquad (2)$$

which follows from the basic relation $r = r_{ijk} l_i l_j l_k$ ($l_1 = \sin\Theta\cos\varphi$, $l_2 = \sin\Theta\sin\varphi$ and $l_3 = \cos\Theta$, with r, Θ, φ being the coordinates of spherical coordinate system), we have constructed the indicative surface along with its stereographic projection (see Fig. 2). It is found that the extreme values of the function represented by Eq. (2) satisfy the conditions $\Theta = 55^\circ$, $\varphi = m\pi/2 + 45^\circ$; $\Theta = 125^\circ$, $\varphi = m\frac{\pi}{2} + 45^\circ$ ($m = 0, 1, 2, 3$).

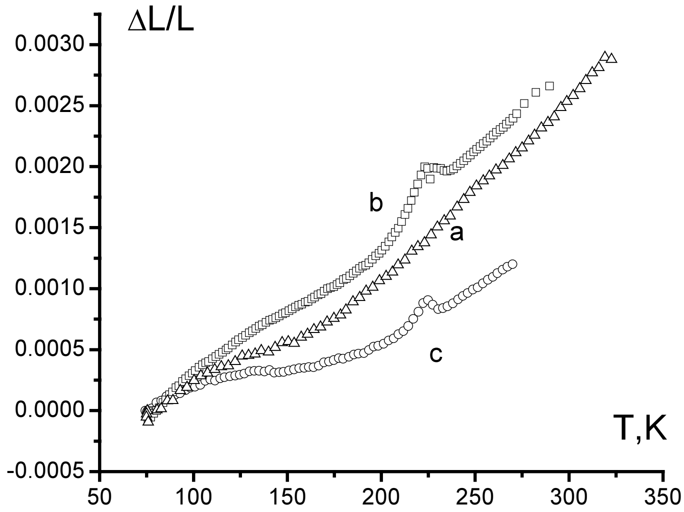


Fig. 3. Temperature dependences of relative elongations for $LiKB_4O_7$ crystals.

Let us notice that we have taken all the components of electrooptic tensor into account, when constructing the mentioned indicative surface. This means that the electrooptic effect is induced by the all possible components of electric field (i.e., $E_1 = E_2 = E_3$). In such a case, the indicative surface depicted in Fig. 2 reflects also the distribution of the change of refractive indices Δn in $LiKB_4O_7$ crystals induced by the electric field components $E_1 = E_2 = E_3$, because $r \sim \frac{\Delta n}{E}$ (change of refractive indices. Thus, the directions defined by the mentioned conditions correspond to maximum values of the induced.

As seen from Fig. 3 and Fig. 4, the relative linear elongation and the thermal expansion coefficients show anomalous temperature behaviour at T_c=223K. Obviously, such the anomalies should correspond to a structural phase transition. It is interesting to note that the anomalies in both the relative linear sample dimension changes and the thermal expansion coefficients are observed just for the two principal crystallophysical directions, *b* and *c*. Moreover, it is slightly seen from Fig. 3 that the increments of the relative elongation for the *b* and *c* directions, taking place at T_c, have opposite signs, while the increment of relative elongation along the *a* axis is equal to zero. The mentioned increments represent in fact spontaneous deformations e_b and e_c. Following from this fact, one can reconstruct the spontaneous deformation tensor $e_s = \begin{vmatrix} 0 & 0 & 0 \\ 0 & e_b & 0 \\ 0 & 0 & e_c \end{vmatrix}$, where $e_b = -e_c$. It is worthwhile that the spontaneous deformation tensor of such a form corresponds to ferroelastic-ferroelectric phase transition with the change of point symmetry group 222F2.

The velocities of the ultrasonic waves in

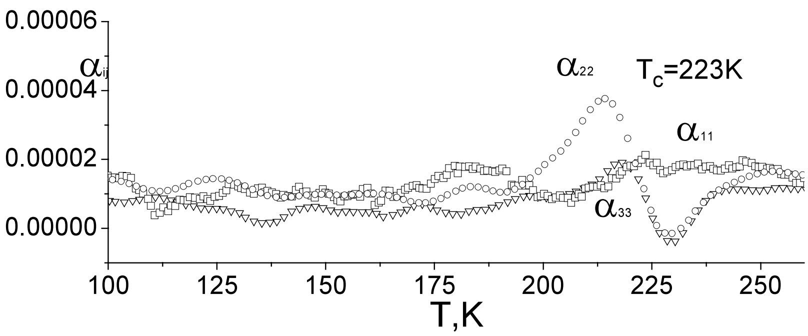


Fig. 4. Temperature dependences of thermal expansion coefficients for $LiKB_4O_7$ crystals.

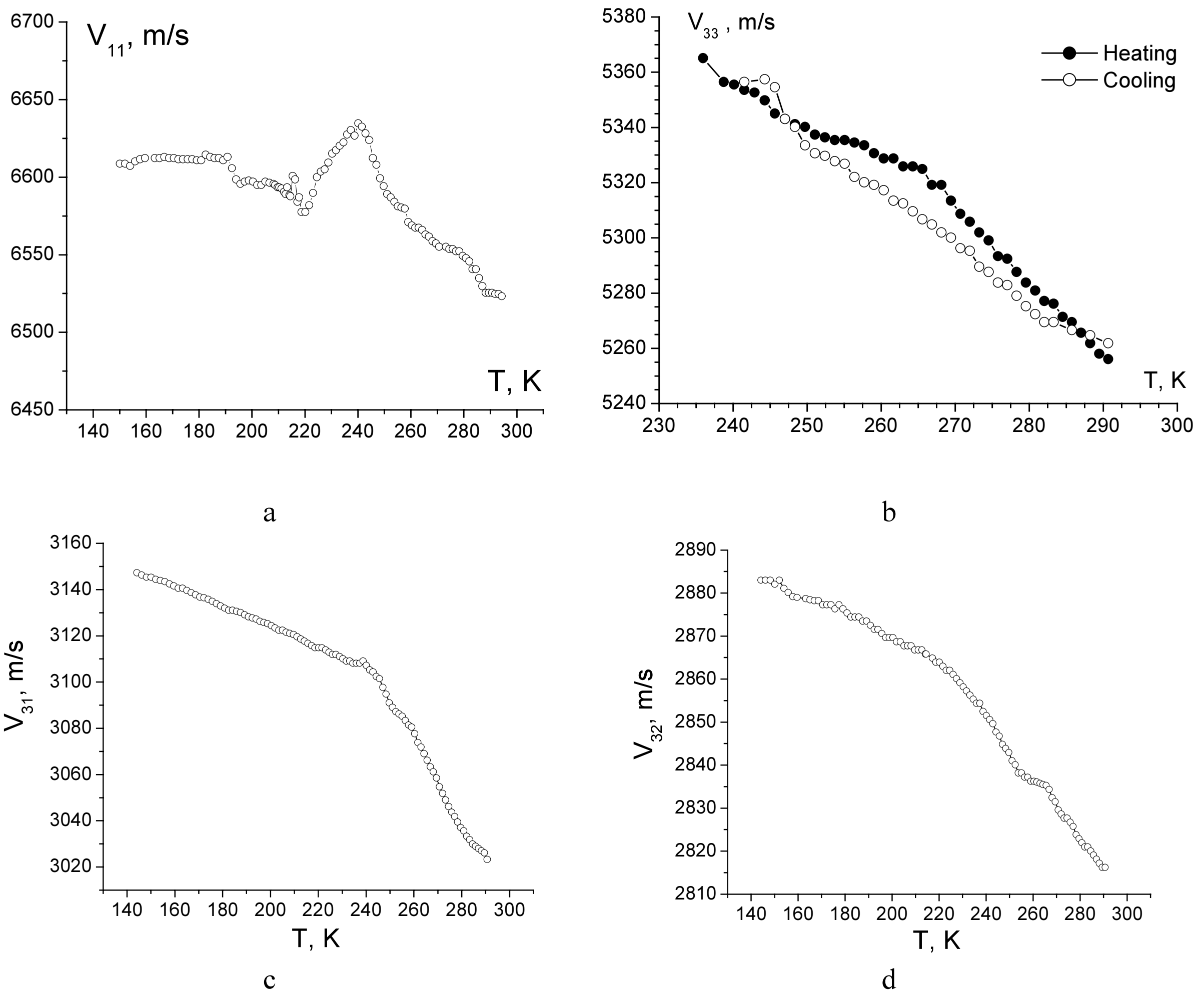


Fig. 5. Temperature dependences of the velocities of longitudinal (a, b) and transverse (c, d) ultrasonic waves in $LiKB_4O_7$ crystals.

$LiKB_4O_7$ crystals also exhibit anomalies at T_c=233K (see Fig. 5). It is interesting that the transverse acoustic waves v_{32} and v_{31} show only a small break-like behaviours at T_c, whereas the anomalies at T_c in the temperature dependences of the longitudinal waves v_{11} and v_{33} are more distinctive, probably, due to a coupling of these velocity components with the order parameter. Moreover, we have observed a scattering of the ultrasonic wave v_{33} in the temperature region $T < T_c$, which could be explained by existence of domain structure below the phase transition temperature.

Conclusions

\Resulting from the results presented above, one can conclude that $LiKB_4O_7$ crystals possess a structural phase transition at T_c=233K which is, most probably, of ferroelastic-ferroelectric type, with the symmetry change 222F2. This phase transition is very close to a second order one. Notice that the availability and information of phase transitions in the crystals under test is revealed for the first time. The electooptic and piezooptic properties of $LiKB_4O_7$ crystals have been also studied by us, as well as the refraction indices, the acoustic wave velocities and the thermal expansion. The complete matrix of Pockels coefficients has been experimentally obtained and the corresponding indicative surface has been constructed.

Acknowledgement

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Errata 2

Vlokh R., Mys O., Romanyuk M., Girnyk I., Martunyuk-Lototska I., Adamiv V. and Burak Ya. Ukr.J.Phys.Opt. (2005) **6** 136-141.

Pages 137-138.
Instead sentence:
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Should be:
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$|\pi_{32}| = (1.3 \pm 0.4) \times 10^{-12} m^2 / N$,
$|\pi_{22}| = (1.7 \pm 0.6) \times 10^{-11} m^2 / N$,
$|\pi_{23}| = (2.5 \pm 0.8) \times 10^{-12} m^2 / N$,
$|\pi_{33}| = (3.4 \pm 1.1) \times 10^{-12} m^2 / N$,
$|\pi_{21}| = (2.8 \pm 0.9) \times 10^{-12} m^2 / N$,
$|\pi_{31}| = (3.1 \pm 1.0) \times 10^{-12} m^2 / N$,
$|\pi_{13}| = (2.6 \pm 0.8) \times 10^{-12} m^2 / N$."