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New nonlinear optical $LiKB_4O_7$ single crystals: Dispersion of refractive indices

V.T. Adamiv [a], Ya.V. Burak [a,*], M.M. Romanyuk [b], G.M. Romanyuk [a], I.M. Teslyuk [a]

[a] *Institute of Physical Optics, 23 Dragomanov Street, Lviv 79005, Ukraine*
[b] *National University "Lviv Polytechnika", 12 Bandera Street, Lviv 79013, Ukraine*

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Abstract

The dispersion of refractive indices has been studied for $LiKB_4O_7$ single crystals growth with Czochralsky technique. In spectral range 420–675 nm the refractive indices $n_a > n_c > n_b$ and dependencies $n_i(\lambda)$ can be described by monomial Zellmeier formulas. At the room temperature (293 K) $n_b = 1.521$, $n_c = 1.554$, $n_a = 1.562$ at $\lambda = 1064$ nm, and $n_b = 1.542$, $n_c = 1.582$, $n_a = 1.593$ at $\lambda = 532$ nm. Estimation of the phase matching conditions for second-harmonic generation (SHG) for radiation of the YAG:Nd laser ($\lambda = 1064$ nm) has been performed. We show that SHG in $LiKB_4O_7$ crystal can be realized by the phase matching of type I. The bisector of acute angle between optical axes ($\varphi \approx 56°$) coincides with crystallographic axis [0 1 0].

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Keywords: Nonlinear optical materials; Borate single crystal; Refractive indices

1. Introduction

Single crystals of anhydrous borates (LiB_3O_5, β-BaB_2O_4 and $Li_2B_4O_7$) demonstrate unique physical properties. In particular, high nonlinear optical parameters, as well as transparency up to long-range ultraviolet and high threshold of the optical damage, permit to use some of these crystals, for example LiB_3O_5 and β-BaB_2O_4, in the laser systems for generation of higher harmonics [1,2]. Nevertheless, the growth of these single crystals can be performed only by the melt-solution technique increasing their cost significantly. The second-harmonic generation (SHG) for radiation of the YAG:Nd laser and in $Li_2B_4O_7$ single crystals, which are grown by the Czochralsky technique from stoichiometric melt had been observed [3]. But because of absence of the phase matching in these crystals the last cannot be applied for SHG. Because, the band structure, playing crucial role in the dispersion of the refractive indices have shown substantial anisotropy, which favours more preferable phase matching conditions for the SHG [4].

Nevertheless, the progress in domain of practical application of the anhydrous borates single crystals is seriously inhibited by the problem of superposition of necessary set of parameters for concrete device and processibility of growth of the single crystals with necessary quality and sizes. That is why the problem of transition to methods for obtaining of the anhydrous borates single crystals by more available method, among which one can name the direct Czochralsky technique of the single crystals growth from stoichiometric melt, under conservation of the necessary physical properties, remains topical.

Investigation of influence of isoelectronic substitution on processibility and physical parameters of the anhydrous borates single crystals is one of directions for solving this problem. In presented paper some optical characteristics have been investigated, and principal refractive indices have been determined for novel nonlinear optical crystal

* Corresponding author. Tel.: +380 322 723853; fax: +380 322 637088.
E-mail address: burak@ifo.lviv.ua (Ya.V. Burak).

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of anhydrous borate $LiKB_4O_7$ obtained in result of isoelectronic substitution of half of Li atoms by K atoms in the $Li_2B_4O_7$ compound.

2. Experimental

The first attempts of substitution of Li atoms by K atoms in the $Li_2B_4O_7$ single crystals had been performed by us previously [5], but their concentration did not exceed 1% molar. The authors of publications [6,7] had observed that under substitution of half of Li by K in $Li_2B_4O_7$ compound, in other words on the constitution diagram of the $Li_2B_4O_7$–$K_2B_4O_7$ system in point of 50% molar, there appears a new chemical compound $LiKB_4O_7$, which belongs to the space group $P2_12_12_1$ [6] and melts congruently at temperature $T_{melt} \approx 680$ °C [7]. That is why for growth of the $LiKB_4O_7$ single crystals we used the direct Czochralsky technique.

The $LiKB_4O_7$ compound for the single crystals growth was synthesized by multi-graded solid-phase method from carbonates Li_2CO_3, K_2CO_3 and boric acid $H_3BO_3$of high purity, which was previously well approved for synthesis of other anhydrous borates. Analogous method for the growth mixture synthesis is used frequently for the single crystals growth of all anhydrous borate compounds. In general, the process of the $LiKB_4O_7$ synthesis can be described by the following chemical equation:

$$Li_2CO_3 + K_2CO_3 + 8H_3BO_3 \rightarrow 2LiKB_4O_7 + 12H_2O + 2CO_2$$

The whole process of the solid-phase synthesis of the $LiKB_4O_7$ growth mixture had been finished at temperature 650 °C which is 30 °C lower from the melting temperature of compound, and the final synthesis took place just in the process of melting and homogenization of the melt in the growth Pt-crucible with size $\varnothing 40 \times 40$ mm. The grown $LiKB_4O_7$ single crystals were of diameter ~20 mm and length 8–12 mm.

The specimens for measurements had been prepared from the optically qualitative $LiKB_4O_7$ single crystal and oriented along the basic crystallographic axes. The measurement of refractive indices for $LiKB_4O_7$ had been performed by the Obreimov immersion method with precision better 10^{-3} [8]. Besides, it is necessary to note that the $LiKB_4O_7$ crystals in some way interact with the immersion liquid (mixture of α-monobromnaphthalene and kerosene), in result of which there optical perfection weakens. This circumstance must be taken into account in the process of exploitation of appropriate products.

NLO coefficients were determined using the Marker fringe technique [9,10]. A sample $LiKB_4O_7$ with an aperture of 8 mm (a) ×10 mm (c) and a thickness of 0.9 mm (b) was available for this purpose.

3. Experimental results and discussion

According to $P2_12_12_1$ symmetry, the $LiKB_4O_7$ single crystals are optically biaxial and, as it was shown by experiments, the plane, in which the optical axes are located, passes through the crystallographic axes *a* and *b*, i.e., lies in crystallographic plane (0 0 1), besides axis *b* is bisector of acute angle between the optical axes (56°).

As it was established in publication [6], the frame structure of the $LiKB_4O_7$ crystal lattice is formed simultaneously by two types of anionic boron-oxygen groups $(B_3O_8)^{7-}$ and $(B_5O_{10})^{5-}$, both possessing large values of hyperpolarizability [11]. That is why the investigation of refractive indices in first turn gives the possibility to estimate the perspective of the $LiKB_4O_7$ single crystals for application in nonlinear optics.

Dispersion of refractive indices in the investigated spectral range 420–675 nm is normal, i.e., in all spectral range $n_a > n_c > n_b$ (Fig. 1), and, as it is seen from the figure, the $LiKB_4O_7$ single crystal belongs to the optically negative ones. The following designations $n^z \equiv n_a$, $n^y \equiv n_c$ and $n^x \equiv n_b$ had been introduced for transition to the physical coordinate system; we established that in this case the following conditions $n_2^z > n_2^y > n_1^z > n_1^y > n_2^x > n_1^x$ and $n_2^x > \frac{1}{2}(n_1^x + n_1^z)$ have been fulfilled (the suffices 1 or 2 refer to the fundamental and harmonic frequences).

Spectral dependencies $n_i(\lambda)$ of the $LiKB_4O_7$ crystal in the first approximation can be described by monomial Zellmeier formulas of the following type

$$n_i^2 = 1 + \frac{A\lambda^2\lambda_{0i}^2}{\lambda^2 - \lambda_{0i}^2}, \tag{1}$$

where λ is wavelength, on which the measurement has been performed; $i = a, b, c$; λ_{0i} is wavelength of the absorption maximum of effective *i*-oscillator, *A* is constant.

For investigated spectral range the experimental data lie satisfactorily on straight line:

$$\frac{1}{n_i^2 - 1} = \frac{\pi mc^2}{Ne^2 f_i}\left(\frac{1}{\lambda_{0i}^2} - \frac{1}{\lambda^2}\right) \tag{2}$$

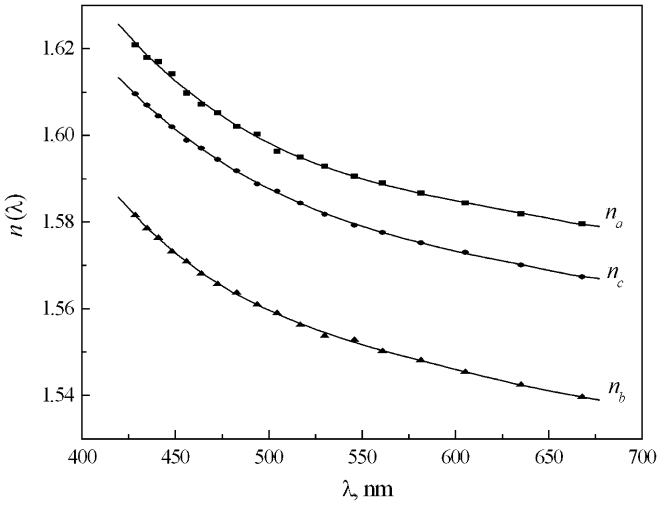

Fig. 1. Dispersion of the refractive indices in $LiKB_4O_7$ single crystal.