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# Crystal optical studies of lithium tetraborate

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**Abstract.** Using the HAUP-type universal polarimeter and the Senarmont technique, detailed crystal optical studies of $Li_2B_4O_7$, lithium tetraborate, are carried out. It is shown that the optical indicatrix rotation and the optical activity are absent from the crystal, in accordance with symmetry considerations. Measurements of optical birefringence reveal the existence of a regular staircase-like temperature behaviour in the whole range under investigation (290–480 K), a hysteresis character of the birefringence under cycling temperature and a pronounced thermooptical memory effect. The origins of the above phenomena are analysed, in particular the possible influence of the pyroelectric effect and systematic errors of the optical equipment. A conclusion is drawn that the main features of the birefringence are well explained by an incommensurately modulated superstructure which is at present a matter of debate. The peculiarities of the optical properties of lithium tetraborate are compared with those of incommensurate crystals known from the literature.

## 1. Introduction

Lithium tetraborate ($Li_2B_4O_7$), abbreviated hereafter as LBO, belongs to the polar point symmetry group $4mm$ of the tetragonal class. In spite of the fact that its crystal structure was established as early as the 1960s, LBO has only recently attracted much attention from researchers owing to its good piezoelectric properties and a promising possibility of applications in acoustoelectronics [1]. In the last decade an increasing number of studies has appeared in the literature, devoted to elucidation of different physical properties of LBO, in particular elasticity, pyroelectric and piezoelectric effects [2, 3], heat capacity [4] and conductivity [5], as well as the optical characteristics [6–8].

Nevertheless, there still remain some controversial problems associated with LBO crystals which need further exploration. So, the x-ray diffraction experiments by Zaretski and Burak [9] have revealed a surprising cascade of phase transitions in the temperature dependences of the lattice parameters $a$ and $c$. Those transitions consist in numerous discontinuous changes in $a$ and $c$ taking place in the region between 80 and 260 K, the number of jumps increasing with increasing temperature cycle number. Zaretski and Burak have also found incommensurate (IC) satellites in the whole temperature range under study (80–400 K) and concluded that the wave vector $\boldsymbol{q}$ of the IC modulation is parallel to the $c$ axis ($\boldsymbol{q} = \delta \boldsymbol{c}^*$, where $\boldsymbol{c}^*$ is the reciprocal lattice vector, $q = 0.035$ at $T = 300$ K). However the studies by Ivanov *et al* [10] of the NMR spectra of $^7$Li and $^{11}$B nuclei have not substantiated the existence of the IC superstructure in LBO. A clear staircase-like behaviour in the region of 85–300 K has been observed by Borman and Burak [11] in the temperature variations of the LBO sample dimensions. The authors have referred this

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effect to pyroelectric properties. The latter may in fact lead to the above phenomena via the inverse piezoelectric effect, since the changes in the sample temperature induce electric discharges and abrupt changes in the internal electric fields. The explanation correlates with the results by Antonyak *et al* [8] who have detected numerous thermoscintillations due to the so-called pyroelectroluminescence effect [12]. On the other hand, Bodnar [13] has found a jumplike variation of the refractive indices in LBO at high temperatures and regarded it as a combined result of both the pyroelectric effect and IC modulation. Finally, we should mention the experimental findings by Furusawa *et al* [14] who have observed temperature oscillations in the second harmonic intensity, accompanied by a global decrease of this intensity with temperature increasing from room temperature up to 800 K.

In the present work we undertake combined polarimetric studies of crystal optical characteristics of LBO in order to elucidate further the character of the temperature evolution of its structure and properties.

## 2. Experimental methods

### *2.1. General*

LBO single crystals were grown from the appropriate stoichiometric melt with the aid of the Czochralski technique. We obtained crystals of sufficiently large size and high optical quality. The sample with reflecting surfaces for optical studies was cut in the form of a parallelepiped with the thickness of $d = 3.76$ mm along the [100] direction and the cross section $6 \times 7$ mm$^2$.

When preparing the sample, especial care was taken of the flatness of its surfaces. The reason was the demand for a well defined optical phase retardation $\Delta = 2\pi d\Delta n/\lambda$ ($\Delta n = n_e - n_o$ being the linear birefringence (LB), $n_o$ and $n_e$ the ordinary and extraordinary refractive indices, respectively, and $\lambda$ the wavelength in vacuum) in polarimetric experiments. The resulting plane-parallelity of the surfaces was estimated as $\sim 10^{-4}$ rad, using visual observations of spatial divergence of the laser beams reflected by the surfaces and taking into account the optical parallax effect. According to the raw data [13], LBO exhibits a relatively large LB ($\Delta n \approx 5 \times 10^{-2}$). Therefore even such a high plane-parallelity as reported above can evoke thickness variations $\delta d = 0.1$ $\mu$m over a typical laser beam cross section ($\sim$1 mm). As a consequence, the $\Delta$ value would be 'smeared' out in the region of $\delta\Delta \sim 5 \times 10^{-2}$ rad. We also checked that the sample surfaces were normal to the light beam with accuracy not worse than $5 \times 10^{-4}$ rad.

The sample was placed into the thermostat which allowed us, in the case of measurement following the Senarmont technique, to control and measure the temperature from room temperature to 500 K with an accuracy of 0.01 K. The temperature might be changed evenly, with a rate $\mathrm{d}T/\mathrm{d}t = 0.5$–$50$ K h$^{-1}$. When performing the measurements with the universal null-polarimeter (see the next subsection), we had a worse temperature stabilization ($\sim$0.05 K). This was caused by the absence of any optical windows in the thermostat, a general condition that had to be met in all high-accuracy polarimetric experiments (see e.g. [15–17]). This time the temperature evolution included a series of comparatively fast heatings ($\mathrm{d}T/\mathrm{d}t \sim 20$ K h$^{-1}$), with subsequent stabilization ($\sim$30 min) of the temperature points at which the measurements were to be performed.

A low-noise He–Ne laser with a wavelength of $\lambda = 632.8$ nm was used as a light source in our experiments.

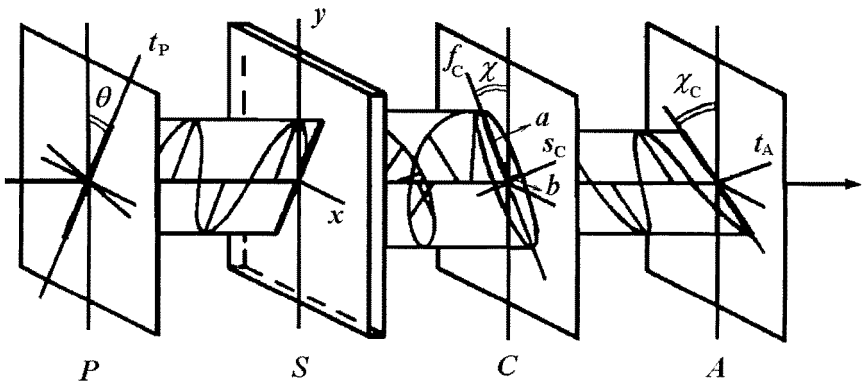


**Figure 1.** An illustration of working principles of the universal null-polarimetric technique (see the text). $t_P$ and $t_A$ are the transmission axes of polarizer and analyser, respectively, $x$ and $y$ the principal axes of the optical indicatrix ellipsoid of the crystal, $f_C$ and $s_C$ the fast and the slow axes of the compensator and $a$ and $b$ the semiaxes of the emergent polarization ellipse. The azimuths $\theta$, $\chi$ and $\chi_C$ are strongly enlarged.

### *2.2. Universal null-polarimetric technique*

We have chosen the universal null-polarimetric technique for preliminary evaluations of the LB value and measurements of the orientation angle of the optical indicatrix and optical activity, while the detailed temperature behaviour of the LB has been examined with the Senarmont technique. Principles and construction of the universal null-polarimeter, similar to a certain extent to the HAUP (see e.g. Kobayashi and Uesu [15]), are described elsewhere [16, 17]. In frame of the method, one measures, at fixed temperature, the linear dependences of the azimuth ($\chi$) and the ellipticity ($\varepsilon$) of the light transmitted through the sample, upon the azimuth $\theta$ of the input light (see figure 1). The input azimuths $\theta$ should lie in the near vicinity of one of the principal directions in the crystal. The corresponding experiments are accomplished in polarimetric systems PSA and PSCA (the compensator C being the quarter-wave plate), after preliminary procedures for co-ordinating the scales of polarizer, compensator and analyser have been done in the PA and PCA systems. On this basis it is easy to derive the cosine and sine of the phase retardation of sample, together with the symmetry azimuth $\theta_0$ and the characteristic ellipticity $\varepsilon_0$ [16]. In the case of transparent crystals those quantities are as follows:

$$\cos\Delta = \frac{\mathrm{d}\chi}{\mathrm{d}\theta} \qquad \sin\Delta = \frac{\mathrm{d}\varepsilon}{\mathrm{d}\theta} \tag{1}$$

$$\theta_0 = (k - p)\cot(\Delta/2) + \delta\chi/(1 - \cos\Delta) + \Delta\theta \tag{2}$$

$$\varepsilon_0 = 2k - p_0 + \delta\chi\cot(\Delta/2) \tag{3}$$

where

$$k = \frac{g_{11}}{2\bar{n}\Delta n} \tag{4}$$

is the ellipticity of the normal waves in crystal related to the circular birefringence $g_{11}/\bar{n}$, $g_{11}$ the optical activity tensor component for the [100] direction, $\Delta\theta$ the rotation angle of the optical indicatrix and $\bar{n} = (n_e + n_o)/2$ the mean refractive index. According to formula (1), the retardation $\Delta$ at each temperature is determined from the slopes of linear dependences $\chi(\theta)$ or $\varepsilon(\theta)$. Beside the crystal optical characteristics $\Delta$, $k$ and $\Delta\theta$, formulae (2) and (3) contain also the contributions from the imperfection parameters of the optical equipment, namely the

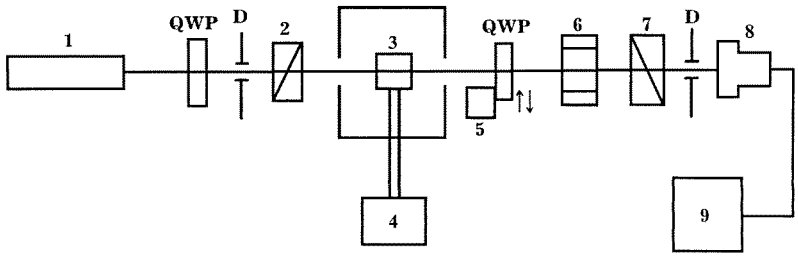


**Figure 2.** A schematic representation of the null-polarimetric set-up. QWP is quarter-wave plate, D a diaphragm, 1 a laser, 2 a polarizer, 3 the sample in a thermostat, 4 a temperature controller, 5 a mechanical device of the QWP, 6 a Faraday cell, 7 an analyser, 8 a photoreceiver and 9 a synchronous detector with a null-indicator.

polarizer ellipticity $p$, the effective parasitic ellipticity $p_0$ and the angular polarimetric error $\delta\chi$ (see [16]). Once those parameters are found it is possible to gain simultaneously the information on all of the optical properties of the crystal.

Though our polarimetric apparatus (see figure 2) enabled us to measure azimuth angles with an accuracy of $10^{-5}$ rad, the real accuracy of determination of the optical characteristics was somewhat lower. It could be evaluated on the basis of the mean square deviations characterizing the fits of the experimental data $\chi$ against $\theta$, $\varepsilon_0$ against $\cot(\Delta/2)$ etc by the corresponding linear dependences (see next section). So, the accuracy of determining the parameter $\cos\Delta$ near the temperature points where $\Delta = \pi/2 + \pi m$ ($m$ being an integer) was better than $5 \times 10^{-3}$, providing an accuracy of the order of $10^{-7}$ for the LB. However, the LB was measured much less accurately in the vicinity of the points $\Delta = \pi m$.

### *2.3. The Senarmont technique*

The method is well described in the open literature, so we shall consider in brief only some essential points. The polarimetric apparatus is the same as that of the universal null-polarimeter (figure 2), but with different orientations of the optical components. The measurements are accomplished in the PSCA system in such a manner that the (relative) phase retardation is derived after determining the azimuth $\chi_C$ of the light emergent from the quarter-wave plate. The fast axis of the sample should be inclined at 45° to the transmission axis of polarizer, and all the components of the optical system are usually regarded as ideal. We have calculated the influence of polarizers' imperfections, deviation of the phase retardation of compensator from its nominal value and different crystal optical effects that accompany the LB of the sample on the final results obtained with the Senarmont technique.

The calculation has been performed using the Jones matrix calculus as described in [17]. We conclude that the imperfections of polarizers and compensator hardly contribute any systematic errors (cf the conclusions of [15]). The same may be said about the optical activity and the linear dichroism in the crystal under study. If the indicatrix orientation of the crystal changes by $\Delta\theta$ in the course of an experiment, the azimuth $\chi_C$ and the ellipticity $\varepsilon_C$ of the light emergent from the quarter-wave plate may be written as

$$\tan 2\chi_C = -\frac{2\tan(\Delta/2)}{1 + (4\Delta\theta^2 - 1)\tan^2(\Delta/2)} \tag{5a}$$

$$\sin 2\varepsilon_C = \frac{4\Delta\theta\tan^2(\Delta/2)}{1 + (4\Delta\theta^2 + 1)\tan^2(\Delta/2)}. \tag{5b}$$

It follows from (5*b*) that the polarization of light becomes elliptical, diminishing the accuracy of determination of $\chi_C$, while the simple relation $\chi_C = -\Delta/2$ no longer holds true (formula (5*a*)). The latter introduces a systematic error into the measured retardation $\Delta$. The effect is weak and the temperature-induced rotation $\Delta\theta \sim 2 \times 10^{-2}$ rad leads only to the small error $\delta\Delta \sim 10^{-3}$ rad or, with our sample thickness, an error in the LB† of the order of $\delta(\Delta n) \sim 2.4 \times 10^{-8}$. It seems to be reasonable to neglect the effect of $\Delta\theta$ in most experiments (see e.g. [18]), except those dealing with very fine optical phenomena in the IC phases [19].

Optical parameters of thin transparent crystal samples with perfect surfaces and highly uniform bulk can be influenced by the effect of multiple reflections of light between the surfaces of the sample [20]. To take account of this effect, we have used the results derived by Melle [21] with the modified Jones matrix technique. The working formulae for the Senarmont method then become as follows:

$$\tan 2\chi_C = -\frac{2(1 + 2r^2 \cos 2\varphi) \tan(\Delta/2)}{1 - (1 + 4r^2 \cos 2\varphi) \tan^2(\Delta/2)} \tag{6a}$$

$$\sin 2\varepsilon_C = \frac{4r^2 \sin 2\varphi \tan(\Delta/2)}{1 + (1 + 4r^2 \cos 2\varphi) \tan^2(\Delta/2)} \tag{6b}$$

where

$$r = \frac{\bar{n} - 1}{\bar{n} + 1} \qquad \varphi = \frac{2\pi d}{\lambda}\bar{n}. \tag{7}$$

Formulae (6) are obtained in the approximation of weak anisotropy, commonly used when analysing the multiple reflection in crystals (see e.g. [21] and [22]). As seen from (6*a*), the corrections to the measured phase retardation from the multiple reflections depend on the factor $r^2 \cos 2\varphi$, while the ellipticity $\varepsilon_C$ deviates from zero (formula (6*b*)). Then the measured temperature dependence of the retardation would oscillate about the curve $\Delta(T)$ with the amplitude $r^2$ and the phase $2\varphi$ determined by the $\bar{n}(T)$ dependence. Accounting for inevitable effects of light scattering and absorption, we have in practice to replace the amplitude coefficient $r$ by $ar$, where always $a < 1$.

The resolution of our Senarmont apparatus is determined mainly by the instability of sample temperature ($\delta(\Delta n)_{\min} \sim 2 \times 10^{-8}$ with the thermal coefficient of the LB taken from the data of next section) and the variation of the phase retardation over the cross section of the sample ($\delta(\Delta n)_{\min} \sim 2 \times 10^{-8}$, see subsection 2.1) but not the inaccuracies in the rotation stages of optical components ($\delta(\Delta n)_{\min} \sim 5 \times 10^{-10}$). Thus we have the resulting sensitivity of the setup better than $\delta(\Delta n)_{\min} \sim 10^{-7}$. It is sometimes reported (see e.g. [19]), without sufficient grounds, that the accuracy of Senarmont polarimeters is of the same order of magnitude ($10^{-8}$–$10^{-7}$), although this is rather difficult to achieve, as seen from the above analysis. In the quoted work [19] the value $5 \times 10^{-8}$ represents merely the accuracy of the angular scale of the analyser. Of course, the universal null-polarimeter has a worse sensitivity, since it measures directly the value cos $\Delta$ but not the retardation $\Delta$ itself. Eventually, the same refers to the HAUP technique [15].

## 3. Results

As a first step in our studies with the universal polarimetric technique, we measured, in the PSA system, the cosine of the phase retardation in the heating regime (figure 3, curve 1). These data were well correlated with the results for sin $\Delta$ obtained in the PSCA (see [16]), testifying that

† It is in general difficult to make thermal expansion corrections to the retardation, so that the term LB in this paper means in fact the quantity $\delta(\Delta n) = \lambda\Delta/(2\pi d)$ defined up to a constant additive at constant thickness.

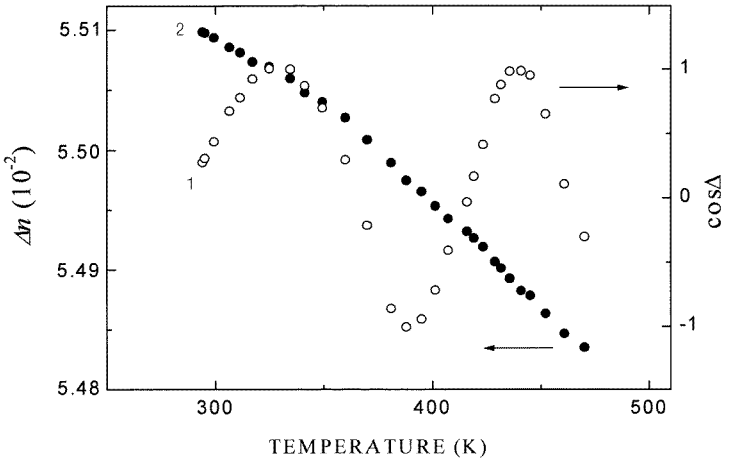


**Figure 3.** Temperature dependences of cosine of the phase retardation, $\cos\Delta$ (curve 1, ○), and the absolute value of the LB, $\Delta n$ (curve 2, ●), for LBO.

the linear dichroism in LBO is absent (the difference absorption coefficient related to linear dichroism was at most less than $2.5 \times 10^{-7}$). The relative LB values $\delta(\Delta n)$ were derived from the temperature dependence of $\cos\Delta$. Additionally, we determined the absolute magnitude of the LB at 293 K ($\Delta n = 5.51 \times 10^{-2}$, accuracy better than 0.5%), when analysing quantitatively the interference spectrum obtained for white light after passing through the PSA system, in which the optical axis of the sample was inclined by 45° with respect to the principal axes of the crossed polarizers. On this basis, we obtained the temperature dependence of the LB displayed in figure 3 (curve 2). The dependence turns out to be almost linear and no clear phase transitions are visible in the temperature range under test.

Since only relative readings $\theta'$ are experimentally accessible instead of true azimuths $\theta$ [15–17], figure 4 displays the data for the $\theta'_0$ readings. The values $\theta'_0$ are related to the symmetry azimuths $\theta_0$ in the following manner [16]:

$$\theta_0 = \theta'_0 - \theta'_{orig} \tag{8}$$

where $\theta'_{orig}$ is the reading value referred to the zero symmetry azimuth ($\theta_0 = 0$). According to figure 3 and formula (2), sharp divergences in the $\theta'_0(T)$ dependence in the vicinities of 330 and 441 K are caused by the retardation approaching the values $2\pi m$. Taking into account that the optical activity and the indicatrix rotation should be absent for the symmetry group of LBO ($k = \Delta\theta = 0$), formulae (2) and (8) yield

$$\theta'_0(1 - \cos\Delta) = -p \sin\Delta + \delta\chi + \theta'_{orig}(1 - \cos\Delta). \tag{9}$$

A quite good fit of the data $\theta'_0(1 - \cos\Delta)$ against $\Delta$ with formula (9) (see figure 5) confirms the validity of these symmetry considerations. The corresponding mean square deviation of the fit ($2 \times 10^{-4}$ rad, or $10^{-2}$°) gives the estimation of the upper limit for the indicatrix rotation value. Comparatively small values of the parasitic parameters ($p = -1.9 \times 10^{-4}$ rad and $\delta\chi = 3.8 \times 10^{-5}$ rad) demonstrate the satisfactory quality of our optical equipment.

We performed the additional experiment in the PSCA system in which the characteristic ellipticity $\varepsilon_0$ was measured in the temperature region of 330–400 K. An even better fit of $\varepsilon_0$ against $\cot(\Delta/2)$ (see figure 5, inset, and formula (3)), with the mean square deviation $\sim 10^{-5}$ rad, also shows the absence of observable optical activity in LBO crystals (the corresponding gyration component $g_{11}$ is less than $8 \times 10^{-7}$).

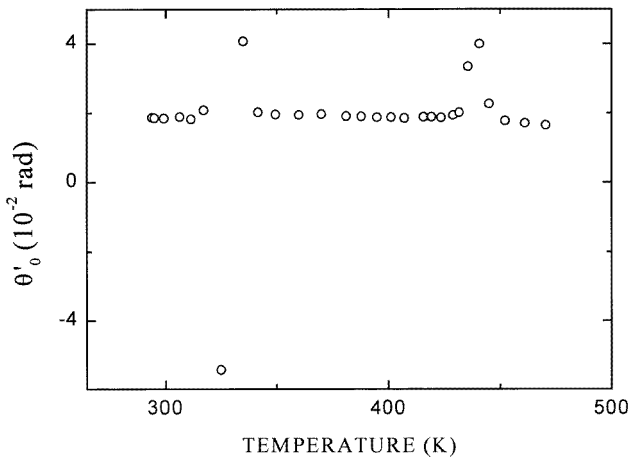


**Figure 4.** Temperature dependence of polarizer scale readings $\theta_0'$ related to the symmetry azimuths $\theta_0$ for LBO.

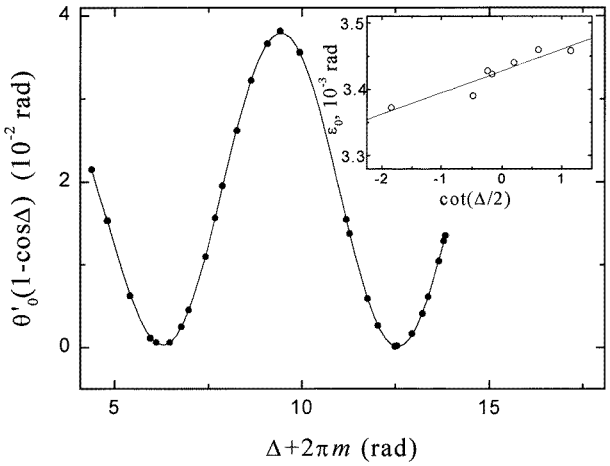


**Figure 5.** Dependence of the experimental values $\theta_0'$ $(1 - \cos\Delta)$ on the relative phase retardation $\Delta + 2\pi m$ of LBO. The solid line is the best fit with formula (9) ($p = -1.9 \times 10^{-4}$ rad, $\delta\chi = 3.8 \times 10^{-5}$ rad, $\theta'_{orig} = 1.86 \times 10^{-2}$ rad). The inset represents the linear fit of the characteristic ellipticity $\varepsilon_0$ against $\cot(\Delta/2)$ ($p_0 = -3.4 \times 10^{-3}$ rad, $\delta\chi = 3.3 \times 10^{-5}$ rad).

Using the scale coordination data obtained in the PA, PCA and PSA systems, we have modified the PSCA system according to the Senarmont geometry and measured the LB of LBO in more detail (figure 6). The $\delta(\Delta n)(T)$ dependence obtained in the heating regime consists of regions of almost invariable (or, at least, very sloping) LB which are alternated with the regions of its fast changes, revealing a staircase-like behaviour (figure 6, inset). Although the behaviour becomes less pronounced in some temperature regions and cannot be clearly seen on the scale of figure 6 (the slopes of the steep and sluggish $\delta(\Delta n)(T)$ changes are less different there), it still remains characteristic of the whole investigated temperature range. As seen from figure 6, inset, the height of the LB steps in the regions with a more pronounced

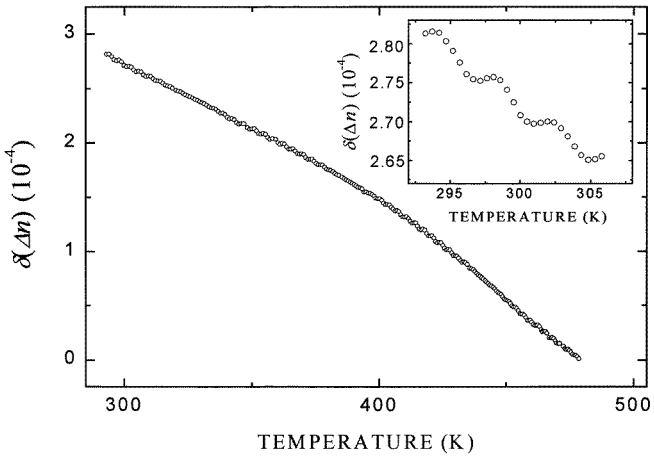


**Figure 6.** Temperature dependence of the LB $\delta(\Delta n)$ of LBO crystals with an arbitrarily taken origin (heating run, temperature variation rate $\mathrm{d}T/\mathrm{d}t = 50$ K h$^{-1}$). The inset represents a greatly enlarged part of the curve in the vicinity of room temperature.

staircase behaviour is approximately equal to $6 \times 10^{-6}$. Furthermore, this value is practically unchanged in the whole temperature range.

Notice that the 'averaged' curve $\delta(\Delta n)(T)$ is monotonic (the thermal coefficient $\mathrm{d}(\Delta n)/\mathrm{d}T \sim -1.6 \times^{-6}$ K$^{-1}$) and follows in general the corresponding dependence depicted in figure 3. A slight deviation of the two curves obtained with different experimental methods, in particular, the absence of the LB steps in the latter is caused by the too small number of data points derived with the universal null-polarimetric technique and different regimes of temperature variations, as well as lower sensitivity of the mentioned technique. A small (∼3.7%) difference is also found in the total temperature variations of the LB (cf figures 3 and 6). The most likely reason lies in the availability of optical windows in the thermostat when using the Senarmont technique. In this case we deal additionally with a temperature-dependent stress-induced LB in the windows (see [15] and [17]).

It is interesting to compare the characters of the staircase temperature behaviour in LBO observed in the present work and in [9], [11] and [13], despite the different nature of the corresponding physical quantities and, sometimes, even different temperature ranges under study. In [13] the refractive index dependence $n(T)$ at high temperatures (405–900 K, $\mathrm{d}T/\mathrm{d}t = 60$ K h$^{-1}$) represents a series of broad (∼20 K) plateaus, the width of the plateaus increasing with temperature increase. At the same time, our step width is notably less ($\Delta T \sim$ 2–2.3 K, see e.g. figure 6, inset) and does not practically depend on temperature, while the regions of the fast $\delta(\Delta n)(T)$ changes have a finite width (∼1.5 K) which is comparable with that of the sloping regions. It must be said in this relation that our measurements seem to be much more detailed, whereas the sensitivity of our method, being based on interference of the normal waves, is essentially higher than that of the method [13] ($\delta n_{\min} \sim 5 \times 10^{-5}$). For example, the experimental 'resolution' (the ratio of the total variation range to the sensitivity) is, respectively, 3000 and 40 for the parameters measured in the present work and in [13]. This should explain the fact that the author of [13] did not detect the $n(T)$ jumps in the region of 290–450 K. Similarly, broadening the $n(T)$ plateaus at higher temperatures may be the only visible effect caused by the decrease in the $\mathrm{d}n/\mathrm{d}T$ slope and lack of resolution.

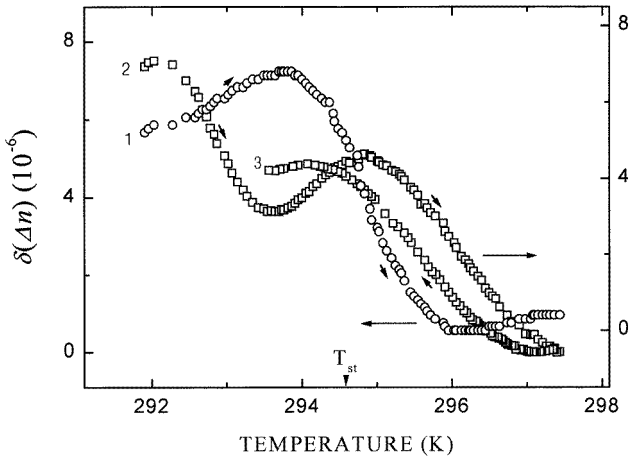


**Figure 7.** Manifestations of the optical memory and hysteresis effects in the LB $\delta(\Delta n)$ of LBO crystals (see text). Curve 1 (○) corresponds to the heating run ($dT/dt = 2.5$ K h$^{-1}$), curves 2 (□) and 3 (□), respectively, the heating and cooling runs ($dT/dt = 1.3$ K h$^{-1}$). The temperature stabilization point is $T_{st} = 294.6$ K.

In order to compare qualitatively our results with the data [9, 11], we further investigated the LB at different rates of temperature change ($dT/dt = 0.6$–$50$ K h$^{-1}$). According to Borman and Burak [11], the temperature width and the amplitude of the jumps in the dependence of sample dimension changes $\Delta d(T)$ are influenced by both $dT/dt$ (in the region from 36 to 360 K h$^{-1}$) and thermal prehistory of the sample. The authors of [11] were unable to observe any jumplike changes $\Delta d(T)$ above 300 K and estimated that the relative values of those jumps should be very small ($\Delta d_{jump}/d < 10^{-5}$). We found (see also the results presented below) that the exact location of the $\delta(\Delta n)$ plateaus on the temperature scale in fact depends on the prehistory. In contrast, our width and the height ($(4$–$6) \times 10^{-6}$) of the plateaus turned out to be almost independent of the latter factor, as well as the temperature change rate. Furthermore, the multiplication of the number of jumps observed in [9] at lower temperatures was also absent from the $\delta(\Delta n)(T)$ dependence, despite multiple temperature cycling.

Making use of the data [11], one can estimate the contribution of thermal expansion jumps $\Delta d_{jump}$ to the phase retardation to be equivalent to LB jumps less than $5 \times 10^{-7}$. As seen from figure 6, inset, we do deal with the LB jumps but not the associated influence of specific linear expansion in LBO. Therefore the staircase-like behaviour is to be regarded as a general regularity characteristic of different physical properties of LBO.

It is reasonable to compare the situation with that occurring in incommensurately modulated BCCD where similar, to some extent, behaviour found in the LB and other characteristics has been associated with a peculiar temperature dependence of the modulation wave vector [18, 23]. In order to verify the hypothesis of the IC phase in LBO, we studied the influence of temperature variation regimes, in particular reversing the temperature, on the LB. We chose comparatively low time rates of temperature variation when the sample temperature was more homogeneous and the interaction between the IC structure and defects should be more pronounced (see e.g. [19, 24, 25]). Curve 1 in figure 7 displays the $\delta(\Delta n)(T)$ dependence obtained in the heating run in the vicinity of room temperature. After this experiment, the sample was kept for 42 h at the point $T_{st} = 294.6$ K located in the temperature region of fast LB changes (see curve 1 in figure 7). Passing repeatedly through the point $T_{st}$ in the course

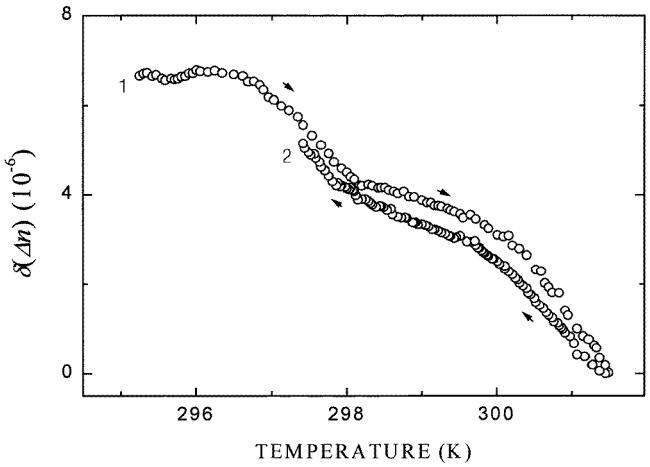


**Figure 8.** Temperature hysteresis of the LB $\delta(\Delta n)$ observed for LBO crystals after annealing at high temperatures (see text). Curves 1 and 2 correspond, respectively, to the heating and cooling runs ($\mathrm{d}T/\mathrm{d}t = 1.9$ K h$^{-1}$).

of the next 'read-out' experiment gives rise to the S-shaped anomaly (figure 7, curve 2) which has to be ascribed to the thermooptical memory effect inherent to the IC systems (see [24] and [26]).

Furthermore, it is obvious from figure 7 (curves 2 and 3) that cycling the temperature produces an irreversible hysteretic behaviour of the LB that may be naturally related to the pinning of the IC structure at frozen-in defects [24]. It is worth noticing that there is another temperature 'stabilization point', room temperature (the first data point which shifts slightly in different experiments). One can see that this point lies always in the small-slope region of $\delta(\Delta n)(T)$ dependences and, moreover, is marked by a fairly expressive anomaly in LB, the feature which is the best visualized in curve 1 of figure 7. It can also be treated as a specific manifestation of the memory effect. It is well known [24, 26] that annealing of an IC crystal at high temperatures within the high-symmetry phase results in weakening the pinning effect and irreversible phenomena. Since we might detect no paraphrase in LBO, the annealing was performed for several days at 480 K. In figure 8 the $\delta(\Delta n)(T)$ dependence for the annealed sample is presented. It is seen that the hysteretic shift between the heating and cooling curves of LB in the steep-variation region is equal to $\Delta T_{\mathrm{hys}} \approx 0.3$ K, while it was $\Delta T_{\mathrm{hys}} \approx 0.6$ K before annealing (figure 7, curves 2 and 3).

## 4. Discussion

Hence, our measurements with a high-accuracy experimental technique have allowed us to reveal a series of specific phenomena in the temperature dependence of the LB in LBO crystals, namely a staircase behaviour, an irreversibility during passing from heating to cooling runs and a memory effect. Although it seems very likely that all of the phenomena are well explained by the availability of the IC superstructure in LBO, a close examination of alternative (or additional) mechanisms is still needed. In this relation a pyroelectric effect mentioned in [10], [11] and [13] should be taken into account first of all, for it also can lead to staircase-like changes in the LB, when combined with the electrooptic effect. However the existence and abrupt changes of internal electric fields in the crystal are prevented at high temperatures by

the conductance (see [5, 14]). As a result, the scintillations due to the pyroelectroluminescence effect have only been observed at temperatures lower than 250 K [8]. According to [2], the pyroelectric coefficient of LBO decreases rapidly with increasing temperature and becomes small above room temperature. Another essential detail consists in the fact that the values of pyroelectric coefficient should differ considerably at room temperature and 480 K, although the character of the $\delta(\Delta n)(T)$ dependence remains the same throughout the temperature region under study. Finally, pyroelectricity in no case produces a memory-type behaviour. However the pyroelectric effect may indeed superimpose with the IC modulation at low temperatures. Perhaps just this factor leads to a strong dependence of properties of the LBO on thermal prehistory when the sample temperature is being cycled [9, 11].

In our opinion, the staircase-like behaviour in LBO can hardly be treated as the manifestation of a kind of Barkhausen pulses, despite the fact that Furusawa *et al* [14] suppose the existence of ferroelectricity and a paraelectric phase in this crystal. According to the careful analysis presented in subsection 2.3 and the numerical results of section 3, we may certainly conclude that the steplike temperature dependence of the LB is not a 'visual' behaviour imposed by the systematic error of data interpretation due to imperfections of our optical apparatus or the effects of optical activity, indicatrix rotation and linear dichroism in the LBO.

Among the other possible reasons, we mention again the effect of multiple internal reflections of light between the sample surfaces which can manifest itself in high-accuracy polarimetric experiments in a manner similar to that of figure 6 (see [27]). We have performed computer simulations for the temperature dependence of the LB, assuming that the 'true' retardation behaves linearly with temperature (the corresponding thermal coefficient $\mathrm{d}(\Delta n)/\mathrm{d}T \sim -1.6 \times 10^{-6}$ K, see section 3) and using formula (6$a$) and the value $\mathrm{d}\bar{n}/\mathrm{d}T \sim 5.8 \times 10^{-6}\ \mathrm{K}^{-1}$ taken from [13]. The measured optical retardation influenced by the multiple reflections does have the 'fine' structure similar to some extent to that of figure 6. However the amplitude of the corresponding 'plateaus' is notably less than in figure 6 (even without accounting for the factor $a < 1$), while the temperature period is more than four times larger. With the exact data [13] for $\mathrm{d}\bar{n}/\mathrm{d}T$, the temperature width of the plateaus in LB should increase with increasing temperature, again in disagreement with our experimental data.

Beside the above results, there are still more facts that also dispose us to exclude the multiple reflection effect as the reason for the staircase behaviour of the LB in LBO: (i) small inclinations of sample in the optical system did not affect notably the LB; (ii) our sample was relatively thick and ought to manifest small but inevitable scattering and absorption of light; (iii) it is our experience that the sample surfaces, though being of a high enough quality, did not answer the demands necessary for the efficient multiple reflections; (iv) variations in the character of the staircase-like behaviour in different temperature regions are difficult to explain with the hypothesis of multiple reflections and (v) the staircase behaviour is characteristic for the other physical parameters of LBO (refractive indices themselves, thermal expansion coefficients etc) which cannot be affected by the multiple reflection effect.

It also looks tempting to assume that the non-monotonic temperature dependence of the LB in LBO originates from non-trivial light interference effects at a periodic incommensurate superstructure. However the attempt almost surely fails. First, the calculations for the multi-soliton (domain-like) and sinusoidal modulated structures [28–30] performed with Jones calculus have shown a weak influence of the modulation on the propagation constants, which are related mainly to the LB, with lack of such the impressive effects as the existence of forbidden gaps etc, characteristic for the other periodic systems (see [31]). The reason lies in very small incommensurate order parameter value and, therefore, very small refractive index perturbations.

Secondly, Stasyuk *et al* [32] (see also [33]) have calculated, with the $4\times4$ matrix technique [34, 35], the multiple reflection interference of light at the domain-wall-like phase solitons in incommensurate crystals. Although spatial regions with different phase of the modulation indeed possess slightly different refractive indices and may, in principle, cause the multiple reflections, the latter turn out to be too small to be detected experimentally. Working in the 'long-wavelength approximation' ($\Lambda/\lambda \ll 1$, with $\Lambda$ being the spatial period of the modulation) justified in both sinusoidal and multi-soliton regions (see, e.g., [28] and [30]), the authors of [32] have demonstrated that the optical parameters are corrected due to the light interference effects by the factor $1 + (\Delta n/\bar{n})^2$ which may be disregarded in any practical situation.

Thus we assume the peculiarities observed in the LBO crystals to be a result of the IC modulation and the coupling between the ideal modulated structure and defects. According to the considerations of Mogeon *et al* [25], a crossover to quasi-discontinuous temperature variations of LB may be caused by attaining a regime of 'viscous' interaction of mobile defects with the phase solitons. The attempt at such an interpretation implies realization of a few important features occurring in LBO. First, we were unable to detect the upper threshold for $\mathrm{d}T/\mathrm{d}t$ at which the crossover takes place. Maybe it is located in the region of high $\mathrm{d}T/\mathrm{d}t$ where the sample temperature would not be kept homogeneous†. Second, in accordance with the theoretical conclusions [24] but unlike the corresponding experimental results, our plateau width $\Delta T$ does not depend on $\mathrm{d}T/\mathrm{d}t$, at least in the investigated $\mathrm{d}T/\mathrm{d}t$ range. Within the model [24], observation of the viscous interaction between the IC structure and defects at relatively high $\mathrm{d}T/\mathrm{d}t$ should mean a high mobility of defects in LBO. To our knowledge, these defects may be $Li^+$ ions and the corresponding vacancies which diffuse fairly easy through the lattice (see e.g. [5]). On the other hand, a staircase character of the LB may be not related to the temperature change rate. Then it is better understood as a result of strongly pronounced lock-ins of the modulation wave vector $\boldsymbol{q}$ at relatively low-index commensurate values. The effect is accompanied by relatively large $q(T)$ and $\delta(\Delta n)$ jumps, similarly to the case of BCCD [18].

In the spirit of the treatment adopted in the present work, a non-monotonic temperature behaviour can be expected for the other optical properties of LBO (e.g., indicatrix rotation, optical activity, linear dichroism etc), the more so because those properties are often characteristic for incommensurate materials, in spite of the requirements of the macroscopic symmetry (see [28–30]). In this respect we should note that the latter effects are studied in much less detail than the LB, due to their weakness and the corresponding experimental difficulties. Probably this is the reason why, to our knowledge, no steplike or other non-smooth temperature dependences for these parameters have been reported up to now for incommensurate phases. Even relatively strong effects of the global thermal hysteresis and the optical memory have been mainly studied on the LB.

On the other hand, it should be very natural that the indicatrix rotation and optical activity also reveal a pronounced behaviour associated with temperature features of the modulation phase and the coupled structural defects. Unfortunately, theoretical models describing the behaviour of, e.g., optical activity in ideal or defect-influenced incommensurate phases are still absent. It is understood that these phenomena are determined by the optical susceptibility components different from those related to the LB, so that they can exhibit another temperature behaviour (for example, oscillations but not steps). Experimental verification of those arguments is now in progress, although the effects seem to be out of the capability of the experimenter in the case of LBO.

† Note that the staircase-like $\delta(\Delta n)(T)$ dependences in the IC phase of $(N(CH_3)_4)_2FeCl_4$ crystals [19] are observed starting at $\mathrm{d}T/\mathrm{d}t \approx 0.5\,\mathrm{K\,h^{-1}}$, the rate that exceeds notably the mean threshold reported for quartz ($\mathrm{d}T/\mathrm{d}t = 5\times10^{-3}$–$0.25\,\mathrm{K\,h^{-1}}$ [24]).

In the following discussion of optical properties of LBO we have to consider more closely the results [14] on the second harmonic intensity $I_{2\omega}$. It is well-known that in the non-depleted input approximation

$$I_{2\omega} \propto I_{\omega}^2 \frac{\chi_{NL}^2 d^2}{n^{2\omega}(n^{\omega})^2} \left[\frac{\sin(\Delta K d/2)}{\Delta K d/2}\right]^2 \tag{10}$$

where $I_{\omega}$ is the input fundamental intensity, $\chi_{NL}$ the nonlinear susceptibility coefficient, $n^{\omega}$ and $n^{2\omega}$ the refractive indices at fundamental and second harmonic frequencies, respectively, and $\Delta K$ the phase mismatch, $\Delta K = (2\pi/\lambda)(n^{2\omega} - n^{\omega})$. It is seen from (10) that the temperature dependence $I_{2\omega}(T)$ is influenced by the changes in the factor $\Delta K(T)d/2$ but not only the $\chi_{NL}(T)$ dependence as assumed in fact by Furusawa *et al* [14]. Using the data [11], we conclude that the thermal expansion effect in $I_{2\omega}(T)$ is negligible, in compliance with the estimations made in [14]. At the same time, accounting for the data $n_e^{2\omega}(T)$ [13] arrives at the conclusion that the global decrease in $I_{2\omega}(T)$ starting from room temperature up to 800 K can mainly be attributed to the last term in formula (10) (the variation of $\Delta K(T)d/2$ is approximately equal to 2.1). That is why the hypotheses of nonpolar phase and spontaneous polarization in LBO [14] are not necessary for the explanation of temperature behaviour $I_{2\omega}(T)$ on the whole. However, the attempt to justify local temperature oscillations of the second harmonic intensity in a similar manner faces difficulties, because both the $d(T)$ and $n_e(T)$ dependences are monotonic and the same is believed of $\chi_{NL}(T)$. Perhaps the only reasonable idea is a quasi-phase matching which is possible if a periodic superstructure is available in LBO. Then the nonlinear effect can be considerably enhanced, provided that the following condition is fulfilled:

$$\Delta \boldsymbol{K} = l\boldsymbol{q} \tag{11}$$

where $\boldsymbol{q}$ means here the wave vector that describes a spatial periodicity and $l$ is a not too large integer. Temperature variations would violate the equality (11), giving rise to oscillations in the second harmonic intensity. With the coherence length value characteristic for the nonlinear wave interaction of the *eee*-type observed in [14] ($d_c = 20$ $\mu$m) and the IC modulation parameter $\delta = 0.35$ [9] (the corresponding wavelength $\Lambda \approx 3 \times 10^{-2}$ $\mu$m), we conclude that the condition $\Lambda = l d_c$, equivalent to (11), can in no case be answered. In other words, the IC modulation does not explain the $I_{2\omega}(T)$ oscillations in LBO (see also [36]), the more so because formula (11) needs, in the case of collinear nonlinear interaction, a periodicity along the principal axis $x$, unlike the results reported in [9].

Hence, some long-wavelength periodicity ($\Lambda \sim 10$ $\mu$m) should be available in LBO. Since the relative changes in $I_{2\omega}$ due to the oscillations do not exceed 50%, the periodicity might be not so regular but represent rather some tendency for arranging partly structural elements or (extrinsic or intrinsic) defects. In principle, such phenomena are specific for the compounds possessing the so-called quasi-one-dimensional ionic conductance, e.g. $KTiOPO_4$ and $\alpha$-$LiIO_3$ [37]. In this case the space charge distribution is known to acquire a quasi-periodic component in the plane normal to the maximum conductivity direction. In $KTiOPO_4$ crystals that component even causes diffraction of light whenever a dc voltage is applied along the mentioned direction [37]. It is worth noting that, at temperatures higher than room temperature, LBO indeed exhibits a strong ionic ($Li^+$) conductance anisotropy, and its conductivity along the $z$ axis is five orders of magnitude larger than that in perpendicular directions [5]. Therefore it is very likely that the second harmonic yield in LBO oscillates with temperature for the reason that a weak, temperature-dependent effect of quasi-phase-matching occurs owing to a specific charge carrier distribution. Of course, the origin of a periodic field potential that forces the space charges to arrange preferably at the given period remains unclear as yet, similarly to the case of $KTiOPO_4$.

In relation to this problem, we have tried, with no success, to observe light diffraction under the circumstances described in [37]. One of the possible reasons is a small value of electrooptic coefficients ([3], cf also the nonlinear coefficients [14]) which determine the efficiency of light diffraction by a phase-type grating. Finally, one cannot exclude that the ill defined periodicity in LBO originates from the process of crystal growth and is, therefore, rather sample dependent. By the way, this periodicity is also able to impose the diffraction of light transmitted through the crystal [38].

## 5. Concluding remarks

In this paper combined polarimetric studies of the dielectric LBO crystals have been performed using both the universal null-polarimeter of the HAUP type and the common Senarmont technique. The region above the room temperature is concentrated on, which is rather difficult to deal with if the dielectric properties or pyroelectricity are under test. The results obtained for the optical indicatrix rotation and the optical activity show the absence (at least, extreme smallness) of those effects, in good agreement with simple symmetry considerations. The LB is further investigated in detail with the aid of the experimental method whose sensitivity and accuracy are higher when compared with the methods employed in [11] and [13]. We have observed in LBO a series of specific effects, namely a staircase-like temperature variation of LB, irreversibility of the latter manifesting itself in a temperature hysteresis and an optical memory effect.

A careful analysis proves that the above phenomena are not imposed by the instrumental systematic errors of our optical apparatus and thus can be regarded as being firmly established. It is demonstrated that the most reasonable interpretation of the observed effects involves the assumption that the LBO crystals possess an incommensurately modulated superstructure, although the latter still remains a matter of controversy. Our results indicate that the IC phase stretches over a wide temperature range, the normal-to-IC phase transition point being at least higher than 480 K. The properties of this phase differ in many details from those studied in the other IC systems such as BCCD, quartz and the $A_2BX_4$ family crystals. In this relation, less known $\alpha$-$ZnP_2$ crystals [39] seem to be worth mentioning. They belong to the tetragonal symmetry group and manifest the IC phase of which the temperature limits are not found yet. $\alpha$-$ZnP_2$ exhibits an incomplete devil's staircase behaviour which can be observed in the temperature dependences of different physical properties. We suppose that LBO represents another similar, to some extent, example of such IC crystals. In order to elucidate the subject more, further experiments on LBO are necessary, in particular detailed structural studies.

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