

REFRACTOMETRY OF LiRbSO<sub>4</sub> CRYSTALS

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Making use of the Obreimov photographic method, the dependences of birefringence  $\Delta n_i$  of LiRbSO<sub>4</sub> crystals have been studied in wide spectral (250–800 nm) and temperature (100–600 K) ranges, as well as the influence of uniaxial mechanical stresses on them. The anomalies of  $\Delta n_i$  at successive phase transitions (PTs), namely, paraelectric – incommensurate – commensurate ferroelastic – ferroelectric – paraelectric phases, have been discovered. The values of  $\Delta n_i$  for LiRbSO<sub>4</sub> crystals are found to be rather sensitive to the uniaxial stress action. Displacements of PT points under the uniaxial stress action as well as both an extension and a narrowing of the temperature intervals of incommensurate and ferroelectric phases have been revealed.

## Introduction

Crystals of LiRbSO<sub>4</sub> possess a pseudo-hexagonal crystalline structure similar to that of NH<sub>4</sub>LiSO<sub>4</sub> crystals [1]. An unconventional sequence of PTs, namely, paraelectric phase I (*Pcmn*-symmetry,  $T_i = 477$  K) → incommensurate phase II ( $k_z = (2 - \delta)/5$ ,  $T_{c1} = 475$  K) → ferroelastic phase III (*P12<sub>1</sub>/c1*,  $T_3 = 458$  K) → ferroelectric phase IV (*P11n*,  $T_4 = 439$  K) → paraelectric phase V (*P112<sub>1</sub>/n*), was revealed in them [2–5].

In spite of a certain interest in PTs taking place in LiRbSO<sub>4</sub> crystals, their optical properties were not studied enough, with investigations of domain structure, using a polarizing microscope, and of Brillouin and Raman scattering spectra being known examples [6, 7]. The measurements of temperature variations of the birefringence with the help of a Berek compensator in a polarizing microscope and using white light allowed one to discover anomalies at the phase V – phase IV and phase IV – phase III transitions [8]. There are practically no data in the literature concerning the influence of uniaxial stresses on the optical indicatrix and the PT point parameters of those crystals. Although these stresses do not change, in general, the crystal symmetry, not affecting, therefore, quantities under investigation, they allow one to modify selectively certain bond groups and certain structural entities of the crystal, which results in facilitating the analysis of

the PT mechanisms. An influence of an electric field on dielectric properties of the crystal involved was studied earlier [4, 9]. Provided that an electric field is applied to a LiRbSO<sub>4</sub> crystal, a new ferroelectric phase was revealed in a narrow temperature interval near 473 K between the incommensurate phase II and phase III, where the satellite reflections are characterized by a wave vector  $k_z = \frac{3}{7}c^*$ . Moreover, a similar modulation with the same wave vector appears, under the action of an electric field, between phases III and IV.

The aim of this work is to study the birefringence  $\Delta n_i$  of LiRbSO<sub>4</sub> crystals in wide temperature (77–600 K) and spectral (300–750 nm) ranges, as well as an influence of uniaxial mechanical stresses on the birefringence properties and the shifts of PT points of the crystals concerned.

## 1. Method of Experiment

LiRbSO<sub>4</sub> crystals were grown by a slow evaporation of an aqueous stoichiometric solution of Li<sub>2</sub>SO<sub>4</sub> and Rb<sub>2</sub>SO<sub>4</sub> substances. The crystals grown were of a good optical quality and had a pseudo-hexagonal form. They comprised three well-defined blocks, the pseudo-orthorhombic axes *a* of which were oriented at 120° to one another.

To define the birefringence, a photographic recording of the interference pattern in the focal plane of a DFS-8 spectrograph was used, which ensured a spatial resolution of extrema of various orders, excluded “smeared” patterns, and allowed therefore their independent registrations. A transmittance of the polarizing system, composed of crossed polarizers, with a specimen being installed between them in a diagonal position and normally to the incident light beam, is determined according to the relation

$$I = I_0 \sin^2 \pi/\lambda(n_i - n_j)d, \quad (1)$$

where  $I_0$  and  $I$  are intensities of the incident and transmitted light beams, respectively,  $\lambda$  is a wavelength, and  $n_i - n_j$  is the birefringence. If a white light beam passes through such a system, then, due to the sinusoidal

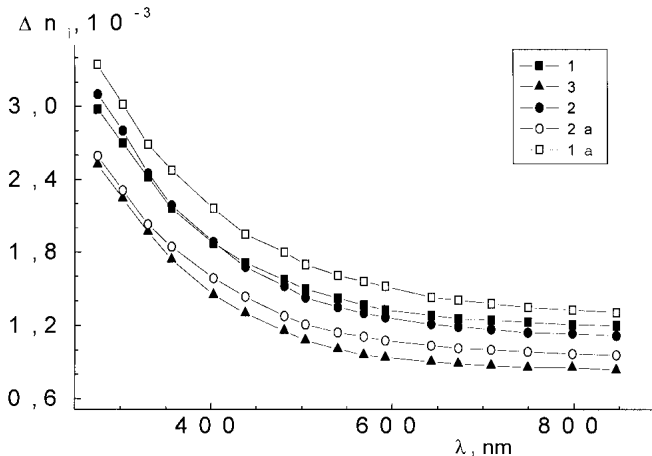


Fig. 1. Birefringence dispersion of LiRbSO<sub>4</sub> crystals at ambient temperature for various stress directions. Hollow symbols correspond to an unstressed crystal: Δ*n<sub>x</sub>* (1*a*) and Δ*n<sub>y</sub>* (2*a*). Solid symbols correspond to a mechanically stressed crystal: Δ*n<sub>x</sub>* at σ<sub>z</sub> = 200 bar (1), Δ*n<sub>y</sub>* at σ<sub>z</sub> = 200 bar (2), and Δ*n<sub>y</sub>* at σ<sub>x</sub> = 200 bar (3)

dependence *I*(λ), the spectrum in the focal plane of the spectrograph will consist of a number of alternating bright and dark stripes. The extremum positions satisfy the relation

$$d(n_i - n_j) = k\lambda, \tag{2}$$

where *k* is an interference order.

Under the variation of the temperature and due to the *d*(*T*)- and *n<sub>i</sub>*(*T*)-dependences, the positions of interference extrema will shift, and the birefringence will be determined by the expression

$$\Delta n_i(\lambda, T) = k\lambda/d_i(T). \tag{3}$$

An uniaxial mechanical stress was developed making use of a special attachment to a nitrogen cryostat and an electric furnace, which allowed us to obtain a stress of about 200 kg/cm<sup>2</sup>. Provided the mechanical stress, the birefringence is determined by the expression

$$\Delta n(T, \sigma, \lambda) = \frac{k(T, \sigma)\lambda}{d(T)}, \tag{4}$$

where *d* is a crystal thickness in the direction of the incident light beam. The temperature variations of Δ*n* and *d* were investigated independently for unstressed and stressed specimens. By varying either of the parameters (*T* or σ), with another one being fixed, one can unambiguously determine the temperature or baric dependence of Δ*n* from the displacements of the interference pattern extrema.

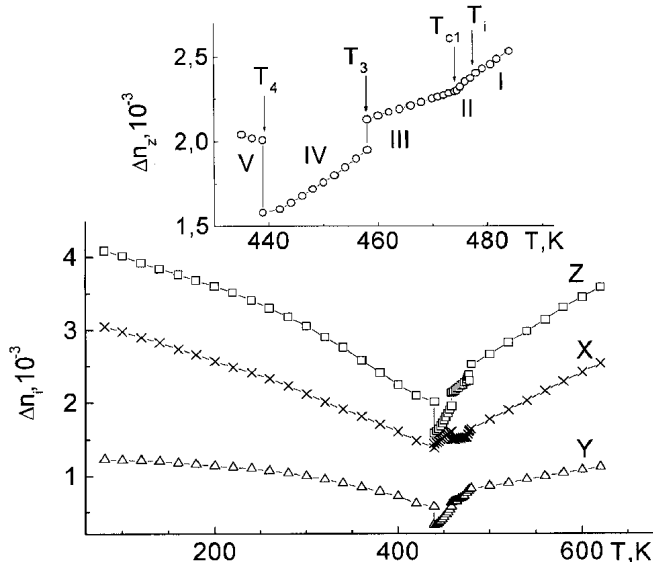


Fig. 2. Temperature dependences of the birefringence Δ*n<sub>i</sub>* of LiRbSO<sub>4</sub> crystals at λ = 500 nm for the principal crystallophysical directions. The same dependence but for the *c*-direction and in the interval of PTs is shown in the inset

## 2. Experimental Results and Their Discussion

### 2.1. Unstressed LiRbSO<sub>4</sub> Crystals

As is seen from Fig. 1, the dispersion of the birefringence Δ*n<sub>i</sub>* is normal in the whole spectral interval under investigation, with  $d\Delta n_z/d\lambda = -2.51 \times 10^{-6} \text{ nm}^{-1}$ ,  $d\Delta n_x/d\lambda = -1.58 \times 10^{-6} \text{ nm}^{-1}$ , and  $d\Delta n_y/d\lambda = -1.56 \times 10^{-6} \text{ nm}^{-1}$ , so that  $|d\Delta n_z/d\lambda| > |d\Delta n_x/d\lambda| \geq |d\Delta n_y/d\lambda|$ . It is of interest that the values of |Δ*n<sub>x</sub>*| and |Δ*n<sub>y</sub>*| are very close to each other. The temperature dependences of Δ*n<sub>i</sub>* for LiRbSO<sub>4</sub> crystals at λ = 500 nm are depicted in Fig. 2. It has been established that the dependences Δ*n<sub>i</sub>*(*T*) are almost linear for phase I with  $d\Delta n_y/dT = 2.3 \times 10^{-6} \text{ K}^{-1}$ ,  $d\Delta n_x/dT = 6.4 \times 10^{-6} \text{ K}^{-1}$ , and  $d\Delta n_z/dT = 7.6 \times 10^{-6} \text{ K}^{-1}$ . The further temperature decrease results in step-like changes of Δ*n<sub>i</sub>* at *T* = 458 K, namely, δΔ*n<sub>x</sub>* = 1.1 × 10<sup>-4</sup>, δΔ*n<sub>y</sub>* = 0.7 × 10<sup>-4</sup>, and δΔ*n<sub>z</sub>* = 1.6 × 10<sup>-4</sup>, which evidences for the availability of the PT of the first kind. Additionally, a slight temperature hysteresis of about 1.5 K was revealed. The following changes, δΔ*n<sub>x</sub>* = 0.6 × 10<sup>-4</sup>, δΔ*n<sub>y</sub>* = 2.7 × 10<sup>-4</sup>, and δΔ*n<sub>z</sub>* = 4.4 × 10<sup>-4</sup>, were detected at the IV–V PT point, which takes place at *T* = 439 K.

The largest changes of Δ*n<sub>i</sub>* were measured in the *c*-direction of the incommensurate modulation. In paraphase V, Δ*n<sub>i</sub>*'s increase nonlinearly with the

temperature decreasing:  $d\Delta n_x/dT = 4.4 \times 10^{-6} \text{ K}^{-1}$ ,  $d\Delta n_y/dT = 2.2 \times 10^{-6} \text{ K}^{-1}$ , and  $d\Delta n_z/dT = 6.5 \times 10^{-6} \text{ K}^{-1}$ .

Our results agree well with the temperature dependences of  $\Delta n_z$  and  $\Delta n_x$  obtained in [8]. A small discrepancy in absolute values of  $\Delta n_x$  and  $\Delta n_y$  is probably due to the fact that the measurements in [8] were carried out by the Senarmon method in white light, i.e. the dispersion of  $\Delta n_i$ , which is rather significant for the crystal concerned, was neglected. In contrast to isomorphous crystals of LiKSO<sub>4</sub> [10], LiRbSO<sub>4</sub> crystals did not manifest essential dependences of the PT features and positions on the annealing time. For the as-prepared specimens, only an insignificant increase of PT hystereses was observed, namely, about 1.7 K for the phase II — phase III transition, about 2.6 K for the phase III — phase IV transition, and about 2.1 K for the phase IV — phase V one.

The minimal time of annealing, after which a complete reproducibility of experimental results for LiRbSO<sub>4</sub> crystals is observed, amounts to 6–8 hrs. An as-grown crystal involves a significant number of defects of the “crystallization water” type, the existence of which leads to the PT smearing and displacement. The largest hysteresis takes place at the incommensurate—commensurate PT, which is probably due to an additional fixation of phase solitons at those defects. Crystal annealing stabilizes the defects. The time needed for a total reproducibility of PT temperatures can be considered as a minimal one required to stabilize completely those defects.

The temperature and spectral dependences of the birefringence are in a good agreement with relevant dependences for the refractive indices  $n_i$  of the crystals concerned [11]. A comparison of  $\Delta n_i$  with corresponding values for K<sub>2</sub>SO<sub>4</sub> and LiKSO<sub>4</sub> isomorphous crystals showed [12,13] that the cation substitution  $\text{Rb}^+ \rightarrow \text{K}^+$  in the sublattice results in a birefringence growth by 0.008–0.010 on the average, while the  $\text{Li}^+ \rightarrow \text{K}^+$  and  $\text{Li}^+ \rightarrow \text{Rb}^+$  substitutions result in an average decrease of  $\Delta n_i$  by 0.02 and 0.03, respectively. The results are primarily due to the variations of the refractive indices, to the shifts of UV and IR absorption bands, and to the changes of relevant additive refractions and electron polarizability [14].

## 2.2. Influence of the Uniaxial Stress on the Birefringence Properties of the Crystals

The baric dependences of  $\Delta n_i$  at  $\lambda = 500 \text{ nm}$  for a LiRbSO<sub>4</sub> crystal at ambient temperature are shown in

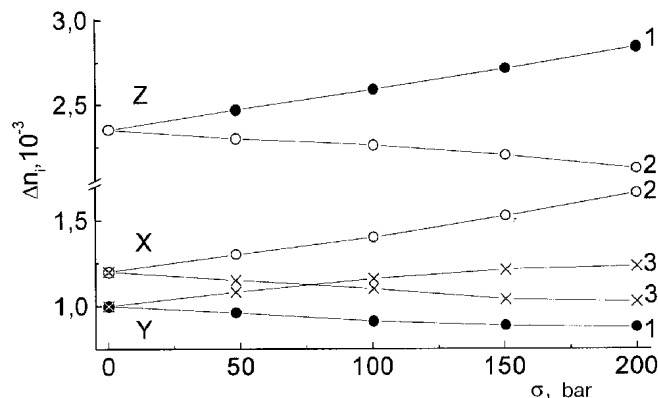


Fig. 3. Baric dependences of the LiRbSO<sub>4</sub> crystal birefringence at  $\lambda = 500 \text{ nm}$  and ambient temperature for various stress directions:  $\sigma_x$  (1),  $\sigma_y$  (2), and  $\sigma_z$  (3)

Fig. 3. The values of  $\Delta n_i$  for this crystal are seen to be rather sensitive to the uniaxial stress action and change almost linearly with the stress as follows:  $\delta(\Delta n_x) = +4.2 \times 10^{-4}$  and  $-2.6 \times 10^{-4}$  (for  $\sigma_y$  and  $\sigma_z = 200 \text{ bar}$ , respectively),  $\delta(\Delta n_y) = +2.3 \times 10^{-4}$  and  $-1.4 \times 10^{-4}$  ( $\sigma_z$  and  $\sigma_x = 200 \text{ bar}$ ), and  $\delta(\Delta n_z) = +4.9 \times 10^{-4}$  and  $-2.7 \times 10^{-4}$  ( $\sigma_x$  and  $\sigma_y = 200 \text{ bar}$ ).

It was found that if the uniaxial stress is  $z$ -directed, then  $\Delta n_x$  decreases and  $\Delta n_y$  increases, and at  $\sigma_z = 77 \text{ bar}$  they become equal,  $\Delta n_x = \Delta n_y = 1.11 \times 10^{-3}$ . Since a relation  $n_y \geq n_z \geq n_x$  between the refractive indices of LiRbSO<sub>4</sub> crystals was established, the equality  $\Delta n_x(\sigma_z) = \Delta n_y(\sigma_z)$  will be valid for the following relation between  $n_i$  of the deformed LiRbSO<sub>4</sub> crystal:  $n_y - n_z = n_z - n_x$  or  $n_x + n_y = 2n_z$ . It means that the application of the uniaxial stress  $\sigma_z$  results in an averaging of one of the refractive indices.

According to Fig. 1, curves 1 and 2, which correspond to the variations of  $\Delta n_x$  and  $\Delta n_y$ , respectively, if the stress  $\sigma_z = 200 \text{ bar}$  is applied, intersect at  $\lambda \approx 423 \text{ nm}$ , i.e. if the stress increases, the “pseudo-isotropic” state point shifts towards shorter wavelengths at a rate  $d\lambda_0/d\sigma = 0.51 \text{ nm/bar}$ , which corresponds to a baric modification of the isotropic state of the isomorphous LiRbSO<sub>4</sub> crystal under the  $\sigma_z$ -stress influence [15]. For the same crystal, the stress  $\sigma_y$  shifts the isotropic point towards the long-wave region at a rate  $d\lambda_0/d\sigma = 4.8 \times 10^{-2} \text{ nm/bar}$ , and the stress  $\sigma_z$  towards the short-wave one at a rate  $d\lambda_0/d\sigma = -3.4 \times 10^{-2} \text{ nm/bar}$ .

In general, although mechanical stresses affect the  $\Delta n_i$ -values, they do not change substantially their dispersion. For example,  $d\Delta n_a/d\lambda = 1.56 \times 10^{-6}$  and

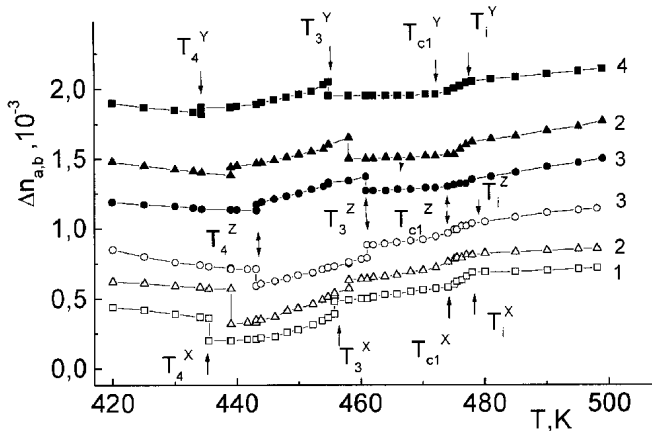


Fig. 4. Temperature variations of the birefringences  $\Delta n_x$  (hollow symbols) and  $\Delta n_y$  (solid symbols) of LiRbSO<sub>4</sub> crystals at  $\lambda = 500$  nm and for various stress directions:  $\sigma_x = 200$  bar (1), unstressed specimens ( $\sigma_i = 0$ , curve 2),  $\sigma_z = 200$  bar (3), and  $\sigma_y = 200$  bar (4)

$1.54 \times 10^{-6} \text{ nm}^{-1}$  ( $\sigma_z$  and  $\sigma_y = 200$  bar), and  $d\Delta n_b/d\lambda = 1.59 \times 10^{-6}$  and  $1.62 \times 10^{-6} \text{ nm}^{-1}$  ( $\sigma_z$  and  $\sigma_x = 200$  bar).

The temperature dependences of  $\Delta n_x$  and  $\Delta n_y$  for various directions of uniaxial mechanical stresses are shown in Fig. 4. It has been found that uniaxial stresses do not change the temperature behavior of  $\Delta n_i$  in essence, i.e. the profiles of the curves  $\Delta n_i(T)$  and the PT patterns are practically reproducible in every phase. But the values of  $\Delta n_i$ , the positions of PT points, and the values of the jumps  $\delta\Delta n_i$  were revealed to be affected substantially. For example, at  $T = T_4$ ,  $\delta\Delta n_b = 1.5 \times 10^{-4}$  for  $\sigma_x = 200$  bar and  $0.7 \times 10^{-4}$  for  $\sigma_z = 200$  bar, while at  $T = T_3$  the corresponding values are  $1.25 \times 10^{-4}$  and  $0.6 \times 10^{-4}$ . The temperature-induced differences of the dependences  $\Delta n_i(\sigma)$  for unstressed and gripped specimens are notable only for the incommensurate phase:  $d\Delta n_x/dT = 7.5 \times 10^{-5} \text{ K}^{-1}$  for an unstressed specimen,  $3.9 \times 10^{-5} \text{ K}^{-1}$  for  $\sigma_y = 200$  bar, and  $2.8 \times 10^{-5} \text{ K}^{-1}$  for  $\sigma_z = 200$  bar, while for  $d\Delta n_y/dT$ , the corresponding values are  $14.8 \times 10^{-5}$ ,  $9.8 \times 10^{-5}$ , and  $22.8 \times 10^{-5} \text{ K}^{-1}$ . Therefore, uniaxial stresses suppress, as a rule, the temperature sensitivity of the birefringence in the incommensurate phase.

It is known that uniaxial stresses lead to displacements of PT points [16, 17]. For LiRbSO<sub>4</sub> crystals, the PT points were found to shift at  $\sigma_x = 200$  bar towards lower temperatures, namely, the IV–V PT point by 3.1 K ( $T_4^x = 435.9$  K), the IV–III PT point by 2.1 K ( $T_3^x = 455.9$  K), the III–II PT point by 1.3 K ( $T_{c1}^x = 473.7$  K), and the II–I PT point by 0.8 K ( $T_i^x = 476.2$  K). The stress  $\sigma_y = 200$  bar also shifts the

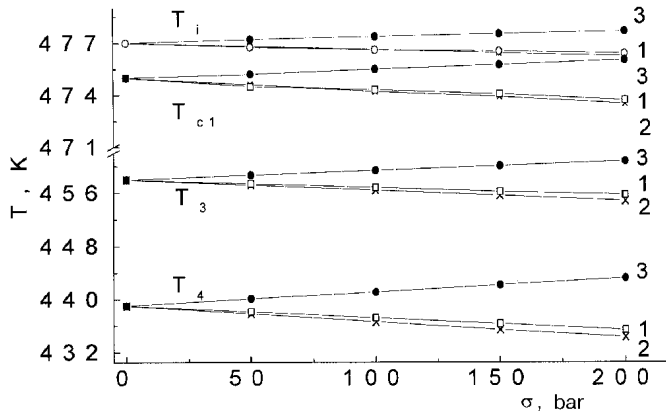


Fig. 5. Baric displacements of the paraelectric–incommensurate ( $T_i$ ), incommensurate–commensurate ( $T_{c1}$ ), commensurate–ferroelectric ( $T_3$ ), and ferroelectric–paraelectric ( $T_4$ ) phase transition points of LiRbSO<sub>4</sub> crystals for various stress directions:  $\sigma_x$  (1),  $\sigma_y$  (2), and  $\sigma_z$  (3)

PT points towards lower temperatures:  $T_4^y = 435.0$  K (the variation is 4.0 K),  $T_3^y = 455.0$  K (the variation is 3.0 K),  $T_{c1}^y = 473.7$  K (the variation is 1.3 K), and  $T_i^y = 476.2$  K (the variation is 0.8 K). Contrary to  $\sigma_x$  and  $\sigma_y$ , the stress  $\sigma_z = 200$  bar shifts the PT points towards higher temperatures:  $T_4^z = 443.2$  K (the variation is 4.2 K),  $T_3^z = 460.8$  K (the variation is 2.8 K),  $T_{c1}^z = 476.0$  K (the variation is 1.0 K), and  $T_i^z = 477.4$  K (the variation is 1.4 K).

The baric dependences of the PT points of LiRbSO<sub>4</sub> crystals are exhibited in Fig. 5. The figure testifies to that the most sensitive to stresses is the ferroelectric–paraelectric PT. The paraelectric–incommensurate–commensurate PTs turned out to be less sensitive to uniaxial stress actions: the stresses  $\sigma_x$  and  $\sigma_y$  led to almost identical shifts of those PT points.

The coefficients of the baric shifts of the PT points under the action of the uniaxial stresses along the principal crystallophysical directions of LiRbSO<sub>4</sub> crystals are quoted in Table, as well as the summary

**Coefficients of the baric shifts of the phase transition points of LiRbSO<sub>4</sub> crystals ( $dT_i/d\sigma_m$ , K/bar)**

Phase transition temperature	$T_4$	$T_3$	$T_{c1}$	$T_i$
Stress $\sigma_m$ direction				
$x$	-0.0155	-0.0105	-0.0065	-0.004
$y$	-0.02	-0.015	-0.006	-0.005
$z$	+0.021	+0.0014	+0.005	+0.008
$\Sigma$	-0.0145	-0.0115	-0.0075	-0.001

coefficients, calculated as

$$\sum_{im}^3 \frac{dT_i}{d\sigma_m} = \frac{dT_i}{d\sigma_x} + \frac{dT_i}{d\sigma_y} + \frac{dT_i}{d\sigma_z}. \quad (5)$$

If the summary coefficients of the shifts of the PT points under the influence of the uniaxial stresses along the principal crystallophysical directions are considered as analogues of the hydrostatic pressure  $p$ , then we are brought to a conclusion that the PT points shift in the general case towards lower temperatures.

Since the coefficients of the baric displacements of the PT points are different, e.g.,  $dT_{c1}/d\sigma_z > dT_i/d\sigma_z$ , one may expect that the temperature interval of the incommensurate phase existence in LiRbSO<sub>4</sub> crystals will narrow under the influence of the stress  $\sigma_z$ . At  $\sigma_z \approx 1$  kbar and  $T \approx 481$  K, the incommensurate phase disappears and there will be a paraelectric—ferroelastic PT bypassing the incommensurate phase and thus resulting in a “triple point”. Similar phenomena were revealed in LiKSO<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>BeF<sub>4</sub> crystals [18, 19]. The “triple point” in the isomorphous LiKSO<sub>4</sub> crystal exists at  $\sigma_z \approx 1.4$  kbar and  $T = 353$  K. The uniaxial stresses  $\sigma_x$  and  $\sigma_y$ , in their turn, stimulate an extension of the temperature interval of the incommensurate phase towards lower temperatures. Moreover, since  $dT_4/d\sigma_z > dT_3/d\sigma_z > dT_{c1}/d\sigma_z$ , the stress  $\sigma_z$  will also narrow the temperature intervals of the ferroelectric and commensurate phases. An extrapolation of the  $T(\sigma_z)$ -lines allowed us to find out that at  $\sigma_z \approx 2.71$  kbar and  $T \approx 496$  K, the ferroelectric phase would disappear and a commensurate ferroelastic—paraelectric PT would take place, while at  $\sigma_z \approx 2.13$  kbar and  $T \approx 488$  K, the commensurate ferroelastic phase would disappear and an incommensurate—ferroelectric PT would occur.

The quoted results coincide in part with those of [20], where a thermal expansion of LiRbSO<sub>4</sub> crystals was studied. On the basis of the Clausius—Clapeyron relation and using experimental data on  $\Delta l/l_i$ , it was evaluated that  $dT_4/dp = -0.38$  K/kbar, whereas  $dT_3/dp = +2.48$  K/kbar and  $dT_2/dp = +0.21$  K/kbar.

Let us analyze those values making allowance for the structure of the crystal concerned. The structure of phase I is disordered [3, 21] with respect to the orientation of tetrahedral (T) groups which librate with large amplitudes around the pseudo-hexagonal axis  $c$  and axis  $b$ . The unit cell of the LiRbSO<sub>4</sub> crystal includes two pseudo-hexagonal frames with tetrahedra SO<sub>4</sub> and LiO<sub>4</sub>. Rb atoms occupy the positions of vacant lattice sites between two frames. Each SO<sub>4</sub>- and LiO<sub>4</sub>-tetrahedrons are rotated in the frame around

the  $c$ -axis counterclockwise or clockwise, respectively. Such a frame for the LiRbSO<sub>4</sub> crystal is dubbed as positive. Then, phase I is characterized as disordered, i.e. there are rotations “+” and “-” in each layer. When approaching  $T_i = 477$  K from above, well-pronounced peaks of diffuse X-ray scattering were observed. Their arrangement and forms evidenced for the availability of correlations in the T-group orientations along the pseudo-hexagonal axis. A conclusion was made that the modulation in phase II is due, most probably, to the rotations of T-groups, or a static distribution of dimensions of microdomains with various rotation angles in neighbor layers may take place. The phase transition into phase III is accompanied by a partial ordering of the structure in such a manner that a following tetrahedron sequence occurs: “+ + - -”. It is clear that the uniaxial stresses, applied along the  $a$ - and  $b$ -axes, will impede the rotations of T-groups around the  $c$ -axis, because those stresses will grip the unit cell. Then the condition of thermodynamic phase equilibrium at the PT will be valid at lower temperatures and, correspondingly, the temperatures of the paraelectric— incommensurate and incommensurate—commensurate PTs will shift towards lower values under the action of the stresses  $\sigma_x$  and  $\sigma_y$ . The displacements of PT points towards higher temperatures under the  $\sigma_z$ -stress action are evidently due the fact that this stress favors the tetrahedron group ordering, the latter occurring mainly in the  $ab$ -plane for the mentioned PTs. The phase III – phase IV transition is accompanied by either “+ + - + - - + - -” or “- - + - - + + - + +” ordering of the T-groups. Provided those sequences of T-group orientations, Rb atoms have small displacements along the  $a$ -axis. A trigonal antiprism is made up of the oxygen atoms O<sub>2</sub>, O<sub>3</sub>, and O<sub>4</sub> of the adjacent T-groups in the case of the “+ -” rotation sequence around a Rb atom, and a trigonal prism in the case of the “+ +” or “- -” sequence. The phase V structure is a deformed phase I structure with the same number of formula entities in a unit cell. All T-groups are also rotated around the  $c$ -axis but with opposite signs. The baric coefficients of the point shifts for the III—IV and IV—V PTs are somewhat larger than their counterparts for the I—II PT. It is stipulated by the fact that the stresses  $\sigma_x$  and  $\sigma_y$  impede not only the rotations of the T-groups around the  $c$ -axis but also their ordering in the  $ac$ -plane, although the character of their behavior does not change. As is seen from the Table, the summary coefficients of the baric displacements of the PT points are negative. It means that if the uniaxial stresses act simultaneously in all three crystallophysical directions, the processes

of “impeding” the T-group rotations and their ordering will be dominant, i.e. the PT points shift towards lower temperatures.

The baric displacement values of the PT points of LiRbSO<sub>4</sub> crystals correlate to some extent with the results of studies concerning the substitution of Rb atoms for Cs ones in solid solutions LiRbSO<sub>4</sub>–CsRbSO<sub>4</sub> [22], where the increase of the Cs concentration was found to shift the PT points and to result in a disappearance of some phases. In particular, phases II and IV are already absent from the Cs<sub>0.25</sub>Rb<sub>0.75</sub>LiSO<sub>4</sub> compound, and the phase I – phase III transition occurs at  $T = 255$  K. One may assume that the substitution of Rb for Cs in LiRbSO<sub>4</sub> crystals is adequate to an application of mechanical stresses. The results correlate also qualitatively with those of the investigation of the concentration phase diagrams of Cs<sub>x</sub>Rb<sub>1-x</sub>LiSO<sub>4</sub> and (NH<sub>4</sub>)<sub>x</sub>Rb<sub>1-x</sub>LiSO<sub>4</sub> systems in the range of small concentrations  $x < 0.09$  [23]. It was found that if the Cs concentration in the Cs<sub>x</sub>Rb<sub>1-x</sub>LiSO<sub>4</sub> compound increases, the temperature intervals of phases II and IV narrow and the PT temperatures decrease, so that both phases disappear at  $x \approx 0.06$ .

## Conclusions

Thus, the temperature and spectral dependences of the birefringence in LiRbSO<sub>4</sub> crystals have been studied.

It has been found that the birefringence is rather sensitive to the uniaxial mechanical stresses applied along the principal crystallophysical axes. Those stresses, applied along mutually perpendicular crystallophysical axes,  $\sigma_{i,m}$ , result in the changes  $\Delta n_j$  different in signs and values ( $i, j, m = 1, 2, 3$ ). A “pseudo-isotropic” state has been discovered, for which  $\Delta n_x = \Delta n_y$  and whose PT point, if the mechanical stress grows, shifts towards shorter wavelengths.

An application of uniaxial mechanical stresses along the principal crystallophysical axes was found to result in the PT point displacements towards both lower and higher temperatures. Those baric displacements are due to an influence of the uniaxial stresses on the crystal structure, and their determination allows one to connect the temperature variations of the birefringence at the PT with baric lattice deformations. In general cases, the stress  $\sigma_z$  enhances the rotation of SO<sub>4</sub><sup>2-</sup> tetrahedra and, in so doing, shifts the PT point towards higher temperatures, while the  $\sigma_x$  and  $\sigma_y$  ones impede the rotation of tetrahedra and shift the points of thermodynamic phase equilibrium towards lower temperatures. A “triple point” has been discovered

as well as the points of disappearance of the ferroelectric and commensurate phases in LiRbSO<sub>4</sub> crystals.

1. *Aleksandrov K.S., Beznosikov B.V.* Structural Phase Transitions in Crystals (the Potassium Sulfate Family). — Novosibirsk: Nauka, 1993 (in Russian).
2. *Steurer W., Wittmann H., Jagodzinski H.* // Acta Crystallogr. B. — 1986. — **42**. — P.11–16.
3. *Kunishige A., Mashiyama H.* // J. Phys. Soc. Jpn. — 1987. — **56**, N 9. — P.3189–3195.
4. *Mashiyama H., Unruh H.-G.* // Ibid. — 1985. — **54**, N2. — P.822–828.
5. *Hasebe K., Asari T.* // Phys. Rev. B. — 1990. — **41**, N10. — P.6794–6800.
6. *Kurishima T., Izumi T., Sawada S.* // J. Phys. Soc. Jpn. — 1987. — **56**, N2. — P.554–559.
7. *Ganot F., Farhi R., Moch P.* // Ferroelectrics. — 1988. — **80**. — P.173–178.
8. *Ganot F., Farhi R., Dugautier C., Moch P.* // Phys. Rev. B. — 1989. — **40**, N1. — P.273–284.
9. *Shiroishi Y., Sawada S.* // J. Phys. Soc. Jpn. — 1979. — **48**, N1. — P.148–153.
10. *Romanyuk N.A., Gaba V.M., Stadnyk V.I.* // Kristallogr. — 1992. — **37**, N4. — P.1039–1040.
11. *Stadnyk V.I., Romanyuk N.A., Vakhulovych V.F.* // Opt. Spekt. — 1993. — **75**, N4. — P.800–804.
12. *Romanyuk N.A., Gaba V.M., Ursul Z.M., Stadnyk V.I.* // Ibid. — 1987. — **62**, N1. — P.94–100.
13. *Zheludev I.S., Gaba V.M., Romanyuk N.A., Ursul Z.M.* // Izv. AN SSSR, Ser. Fiz. — 1986. — **7**, N2. — P.386–390.
14. *Batsanov S.S.* Structural Refractometry. — Moscow: Vysshaya Shkola, 1976 (in Russian).
15. *Romanyuk M.O., Stadnyk V.Y., Brezvin R.S.* // Ukr. Fiz. Zh. — 1995. — **40**, N10. — P.1068–1070.
16. *Vysochanskii Yu.M., Slivka V.Yu.* Ferroelectrics of the Sn<sub>2</sub>P<sub>2</sub>S<sub>6</sub> Family. Properties in the Vicinity of the Lifshits Point. — Lviv: 1994 (in Russian).
17. *Vlokh O.G., Kityk A.A.* Crystalline Insulators with an Incommensurately Modulated Structure. — Lviv: 2002 (in Ukrainian).
18. *Romanjuk M.O., Stadnyk V.Y.* // Ferroelectrics. — 1997. — **192**, N1–4. — P.235–241.
19. *Romanjuk M.O., Stadnyk V.Yo.* // Cond. Matter Phys. — 1999. — **2**, N4(20). — P.711–720.
20. *Dohata H., Kawada S.* // J. Phys. Soc. Jpn. — 1988. — **57**, N12. — P.4284–4287.
21. *Pietraszko A.* // Acta Crystallogr. A. — 1981. — **37**, Suppl. C. — P.109.
22. *Hasebe K., Asahi T.* // Ferroelectrics. — 1989. — **96**. — P.63–66.
23. *Kawamura K., Kuramashi A., Nakamura H.* // Ibid. — 1990. — **105**. — P.279–284.

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РЕФРАКТОМЕТРІЯ КРИСТАЛІВ LiRbSO<sub>4</sub>*В.Й. Стадник, М.О. Романюк, Л.Т. Карплюк*

## Резюме

Фотографічним методом Обреїмова для кристалів LiRbSO<sub>4</sub> досліджено температурні і спектральні залежності двопронезаломлення  $\Delta n_i$  в широкому спектральному (250–800 нм) і

температурному (100–600 К) діапазонах, а також вплив на них одновісних механічних тисків. Виявлено аномалії  $\Delta n_i$  при фазових переходах (ФП): параелектрична—несумірна—сумірна сегнетоеластична—сегнетоелектрична—параелектрична фази. Встановлено, що величина  $\Delta n_i$  кристалів LiRbSO<sub>4</sub> досить чутлива до дії одновісних тисків. Виявлено зміщення точок ФП, а також розширення чи звуження температурної області несумірної і сегнетоелектричної фаз під впливом одновісних тисків.