A NEW LiNH$_4$SO$_4$ CRYSTAL WITH AN ISOTROPIC POINT

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LiNH$_4$SO$_4$ crystals of α-modification were grown up, and the spectral dependences of their refractive indices and birefringence are studied. The intersection of $n_i(\lambda)$ curves is found, which testifies to the inversion of birefringence sign ($\Delta n_y = 0$) at the light wavelength $\lambda_0 \approx 683$ nm at room temperature. For higher temperatures, this point shifts toward the short-wave spectral range. The temperature dependence of the angle between the optical axes is examined, and the change of the optic axial plane at the transition into the isotropic state is demonstrated.

1. Introduction

The isotropic point phenomenon or the inversion of birefringence sign is a result of temperature-spectral distortions of the optical indicatrix in crystals. It consists in that, for every wavelength, a crystal can transform from the optically uniaxial state into the isotropic one or from the optically biaxial state into the uniaxial one only at a certain temperature.

A number of crystals belonging to the A$_2$BX$_4$ group are known, which demonstrate the isotropic point in a wide temperature and spectral ranges; these are K$_2$SO$_4$, RbKSO$_4$, Rb$_2$SO$_4$, LiKSO$_4$, RbNH$_4$SO$_4$, and (NH$_4$)$_2$BeF$_4$ [1, 2]. However, in some of them, this point is located in the spectral interval, which is inconvenient for practice. Searching for new crystals of this group, which would possess the isotropic point, is an interesting task, which aims at expanding the scope of materials that are practically important for thermometry. Another task consists in finding how the substitution of structural elements affects the temperature and spectral intervals, which are already known for the given crystal and in which birefringence changes its sign.

With this end in view, we selected lithium ammonium sulfate (LiNH$_4$SO$_4$, LAS) crystals to study. LAS crystals have phase transitions at temperatures of 459 and 285 K. At temperatures above 459 K, the LAS crystal have the structure $G_0 = Pmcn$, $Z = 4$. The phase transition at the temperature $T = 459$ K is of the first kind and with the polarization jump $\Delta P_c \approx 2 \times 10^3$ μC/cm^2. The structure of phase $G_1 = P2_1cn$, $Z = 4$ of LAS crys-

tals represents one of the possible versions for the ordering of tetrahedral (T)-groups with respect to rotations about the pseudo-hexagonal axis c. This phase is ferroelectric. At a temperature of 285 K, the phase transition $G_1 \rightarrow G_2$ into the ferroelastic phase (the phase symmetry is $G_2 = P2_1/c11$) takes place [3–5]. The indicated sequence of phase transitions exists in the β-modifications of LAS crystals. Typical of them is a pseudo-hexagonal tridymite-like structure, which consists of SO$_4$ and LiO$_4$ tetrahedra connected by their vertices and forming six-link rings oriented perpendicular to the Z-axis. Half of the tetrahedra are oriented vertex down, the other half vertex up, where they are connected with the next layer of tetrahedra. The emerged voids are filled with the ammonium groups. The α-modification of LAS crystals is also known. It differs from the β-modification in that SO$_4$ and LiO$_4$ tetrahedra can have not only common vertices in the Z-direction, but also common edges. Neighbor layers interact with nitrogen atoms in the ammonium groups by means of hydrogen bonds and form a layered structure. Therefore, crystals of the α-modification are grown at room or lower temperature, whereas those of β-modification at temperatures higher than 30 °C [4–6]. In this work, LAS crystals of the α-modification (α-LAS) were fabricated, and their indices of refraction and birefringence were studied. The crystals were grown using the evaporation method at temperatures of about 20 °C. They looked like elongated hexagons. The refraction properties of α-LAS crystals were analyzed within standard methods [1, 2].

2. Research Results and Their Discussion

The dispersion of the refractive index $n_1(\lambda)$ of LAS crystal at room temperature was found to be normal, i.e. $\partial n/\partial \lambda < 0$ (see Fig. 1 and Table), and described well by the two-oscillator Sellmeier formula,

$$n_i^2 = 1 + \frac{B_1 \lambda_{01}^2 \lambda^2}{\lambda^2 - \lambda_{01}^2} - \frac{B_2 \lambda_{02}^2 \lambda^2}{\lambda^2 - \lambda_{02}^2}, \quad (1)$$

where λ_{01} and λ_{02} are the positions of the effective centers of ultra-violet and infra-red, respectively, absorption
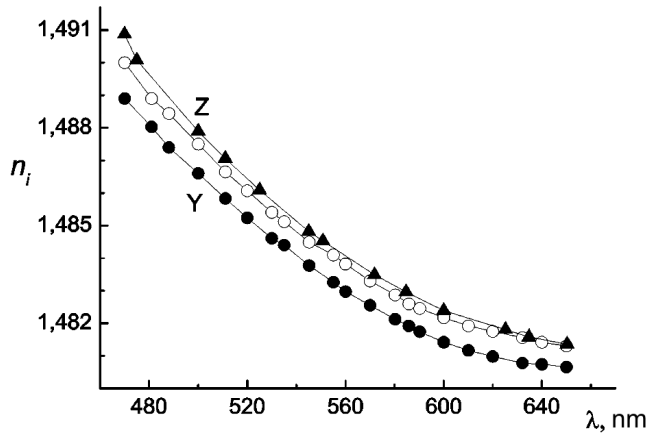
Fig. 1. Dispersion of the refractive indices in LiNH$_4$SO$_4$ crystals of the α-modification at room temperature

Fig. 2. Dispersion of a birefringence in LiNH$_4$SO$_4$ crystals of the α-modification at room temperature

bands; and B_1 and B_2 are some quantities connected with the effective forces of ultra-violet and infra-red oscillators.

The refractive indices and their dispersion satisfy the inequalities $|\partial n_{x,z}/\partial\lambda| > |\partial n_y/\partial\lambda|$ and $n_z \geq n_x > n_y$. The refractive indices in the X- and Z-directions are very close to each other and tend to converge in the near infra-red spectral range. Such a behavior allowed us to suppose that there is an isotropic point in the crystal concerned. We used experimental values for the refractive indices and the Lorentz–Lorenz relation,

$$\frac{n_i^2 - 1}{n_i^2 + 2} = \frac{4}{3}\pi N_0\alpha_i = \frac{\rho}{\mu}R_i, \qquad (2)$$

to calculate the electron polarizabilities α_i and the total refraction coefficients R_i of the crystals under investigation (see Table). The obtained values agree well with the sum of refraction coefficients for each elements of the structure [9],

$$R_{\text{LiNH}_4\text{SO}_4} + R_{\text{Li}^+} + R_{\text{NH}_4^+} + R_{\text{SO}_4^{2-}} =$$

$$= 0.2 + 11.96 + 14.5 = 26.66 \ \ \text{cm}^3. \qquad (3)$$

This fact testifies that NH_4^+ cations give a considerable contribution of about 45% to the total refraction in examined crystals.

A comparison of optical indicatrix parameters for LiNH$_4$SO$_4$ crystals with those for isomorphic K$_2$SO$_4$, Rb$_2$SO$_4$, (NH$_4$)$_2$SO$_4$, and RbNH$_4$SO$_4$ crystals revealed the following modifications as a result of the cation substitution. The substitution Li$^+$ $\rightarrow$ Rb$^+$ leads to increases of refraction indices on the average by $(3 \div 5) \times$
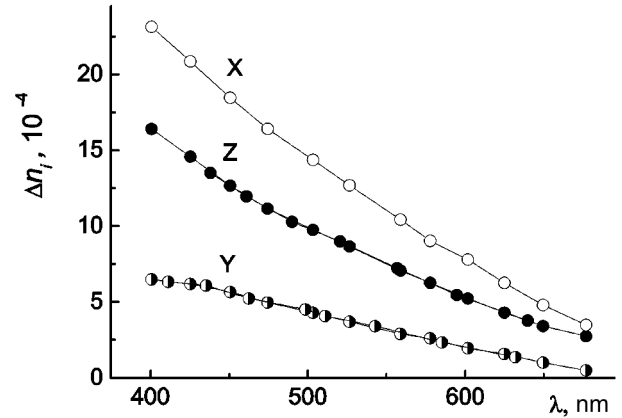
10^{-3}, a displacement of λ_{0x} by approximately 7 nm toward the short-wave spectral section, and a displacement of λ_{0y} by 3 nm toward long-wave one.

In general, we found that the substitutions Li$^+$ $\rightarrow$ K$^+$ $\rightarrow$ NH$_4^+$ $\rightarrow$ Rb$^+$ induced reductions of n_i on the average by 0.02–0.03, whereas the corresponding changes to λ_{01}, λ_{02}, B_1, and B_2 were minor.

The measurements of birefringence Δn_i for all crystalline directions showed that the dispersion of Δn_i is normal in the X- and Z-directions ($\partial\Delta n_x/\partial\lambda = -4.78 \times 10^{-6}$ nm^{-1} and $\partial\Delta n_z/\partial\lambda = -7.12 \times 10^{-6}$ nm^{-1}) and abnormal in the Y-one, which testify to the existence of inversion point for the birefringence sign in this direction (Fig. 2). Really, the temperature researches of $\Delta n_y(\lambda, T)$ showed that Δn_y decreases with the temperature growth so that the point $\Delta n_y = 0$ shifts toward the short-wave spectral range.

In order to additionally verify the existence of the isotropic state in the LAS crystals, we carried out an independent research of the temperature dependence of the angle $2V$ between the optical axes. The crystal was preliminarily oriented with the help of a polarization microscope so that the microscopic field should include

T a b l e. **Optical indicatrix parameters for LiNH$_4$SO$_4$ crystals at room temperature**

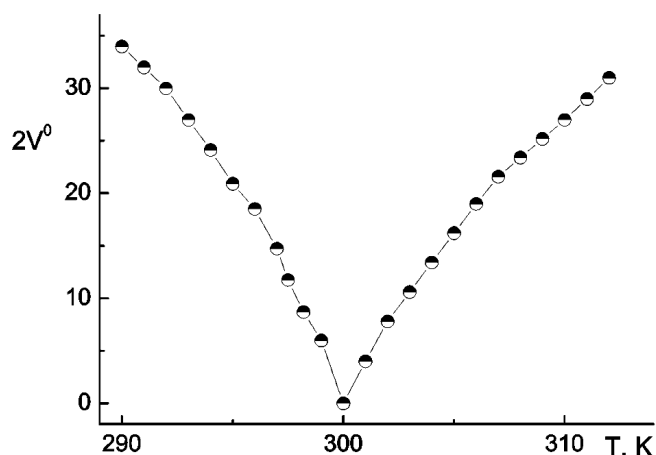| $\partial n_i/\partial\lambda$, 10^{-5} nm^{-1}					
$\lambda = 500$ nm		X	Y		Z
		-5.2	-4.6		-5.4
axis	λ_{01}, nm	λ_{02}, nm	B_i, 10^{-6} nm	B_i', 10^{-9} nm^{-2}	α_i, 10^{-24} cm^3	α_i, cm^3
X	105.4	1020.21	104.1	1.46	8.41	26.12
Y	108.7	8413.9	97.5	3.56	8.52	26.23
Z	109.3	3636.57	96.7	2.41	8.48	26.14

Fig. 3. Temperature dependence of the angle between the optical axes in a LAS crystal for $\lambda = 633$ nm

the cut oriented perpendicularly to the bisectrix of the acute angle between the optical axes (in our case, it was the Y-cut). The crystal was mounted between crossed polarizers in the diagonal position, which provided the maximum enlightenment of the microscopic field. It was found that, at room temperature, $T = 293$ K, the angle $2V = 26°$ for $\lambda = 633$ nm. As the temperature grew, the angle concerned decreased and achieved the value $2V = 0°$ at a temperature of 300 K, which confirmed the existence of isotropic point in this crystal. If the temperature continued to grow, the optical axes changed from the plane XOZ into the plane XOY, and the crystal became optically biaxial again.

Within the experimental accuracy, no temperature hysteresis was observed for a variation of the angle $2V$ between the optical axes.

A comparison of the optical indicatrix parameters among isomorphic crystals belonging to group A_2BX_4 can serve for the substantiation of criteria for the search for crystals with an isotropic point, if one takes into consideration that K_2SO_4, $RbKSO_4$, Rb_2SO_4, $LiKSO_4$, $RbNH_4SO_4$, and $(NH_4)_2BeF_4$ crystals demonstrate it in wide temperature and spectral ranges. Since the cation substitution leads to minor changes in the optical indicatrix parameters, one may expect that it will result in a variation of the spectral or temperature range, in which the isotropic state exists, depending on the ratios between mixed substances.

To summarize, in this work, $LiNH_4SO_4$ crystals of the α-modification were fabricated, and the spectral dependences of their refractive indices and birefringence were studied in the room temperature interval. The intersection of curves $n_x(\lambda)$ and $n_z(\lambda)$ was found, which testifies to the presence of isotropic point ($\Delta n_y = 0$) in those crystals, which is located at the wavelength $\lambda_0 \approx 683$ nm at room temperature. The temperature measurements of the angle between the optical axes evidence a change of the optic axial planes at the transition through the isotropic state. The results obtained enable us to propose $LiNH_4SO_4$ as a new crystal with the isotropic point that is located in the accessible spectral region at room temperatures.

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ПРО НОВИЙ КРИСТАЛ LiNH$_4$SO$_4$ З ІЗОТРОПНОЮ ТОЧКОЮ

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Р е з ю м е

Вирощено кристали LiNH$_4$SO$_4$ α-модифікації та досліджено їх спектральні залежності показників заломлення і двопроменезаломлення. Виявлено перетин кривих $n_i(\lambda)$, що свідчить про наявність за кімнатної температури інверсії знака двопроменезаломлення ($\Delta n_y = 0$), яка знаходиться на довжині світлової хвилі $\lambda_0 \approx 683$ нм. У випадку підвищення температури ця точка зміщується в короткохвильову ділянку спектра. Досліджено температурну залежність кута між оптичними осями, показано зміну площини оптичних осей під час переходу в ізотропний стан.