Temperature-and-Spectral Deformations of the Optical Indicatrix of Rubidium Sulphate Single Crystal

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The paper deals with newly investigated temperature-and-spectrum dependences of principal birefringences ($\Delta n_i(\lambda, T)$ — $i = X, Y, Z$; $\lambda = 250 \div 850$ nm; $T = 4.2\text{--}1100$ K), and temperature dependence of the optic-axial angle ($2V(T)$ — $T = 4.2\text{--}1100$ K) for two laser lines 632.8 nm and 441.1 nm of Rb_2SO_4 crystals. Based on the temperature dependence of the optic-axial angle, the second point of birefringence sign inversion has been found. Newly obtained is the temperature-and-spectrum diagram of the uniaxial state of the optical indicatrix at the "isotropic points" and in the hexagonal phase of Rb_2SO_4 . Based on the temperature behavior of the birefringence and optic-axial angle it was supposed that hexagonal-orthorhombic phase transition in rubidium sulfate can be a second-order phase transition. Found is the inversion of birefringence dispersion in the X and Y directions at 400 K and 620 K, respectively.

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1. Introduction

The A_2BX_4 -group crystals serve as model objects to investigate ferroelectric and ferroelastic phase transitions, as well as transitions between the commensurate and incommensurate phases. The prototype phase for this group of crystals is the high-temperature hexagonal phase with a symmetry space-group $P6_3/mmc$ ($\alpha\text{-K}_2\text{SO}_4$).

In Ref. [1], based on the discontinuous change in birefringence of K_2SeO_4 and Rb_2SeO_4 , it was supposed that the phase transition from the prototype phase $P6_3/mmc$ into the orthorhombic one must be a transition of the first order. In potassium sulfate, the change in symmetry $P6_3/mmc \rightarrow Pmcn$ takes place through an intermediate phase (853–860 K), and, based on the thermal studies [2], it was supposed that the phase transition (PT) in K_2SO_4 is the transition of the first order, while the polarization studies by means of a microscope [3], the changes in the indices of refraction [4] and birefringence [5] showed that the hexagonal-orthorhombic transition in K_2SO_4 is very close to the PT of the second order, because of the change $n_i(T)$ and $\Delta n_i(T)$ during PT which takes place very quickly but continuously.

Additionally, in K_2SO_4 , the points of birefringence sign inversion ("isotropic points") have been found at $T' = 617$ K ($\Delta n_y = 0$), and $T'' = 700$ K ($\Delta n_x = 0$) [5, 6]. Similar points of birefringence sign inversion also exist in K_2SeO_4 ($\Delta n_x = 0$ at $T \approx 680$ K, and $\Delta n_y = 0$ at $T \approx 740$ K) [1]. In Ref. [5] it was shown that "isotropic points" in potassium sulfate are "isospectral", i.e. $\Delta n_i = 0$ ($i = 1, 2$) simultaneously for the entire spectral range.

Given the above, it should be interesting to investigate the temperature-and-spectrum dependence of the

birefringence and optic-axial angle in the isomorphous crystal of rubidium sulfate (RS) — Rb_2SO_4 in order to determine how the total isomorphous replacement of the K^+ ion by the R^+ ion influences the character of "isotropic points" and the nature of the high-temperature hexagonal-orthorhombic phase transition.

Crystals of rubidium sulfate are poorly studied. It is known that at near-room temperatures a crystal has an "isotropic point" featuring the temperature-and-spectrum dependence of birefringence sign inversion [7]. The results of structural studies allowed one to determine that the hexagonal-orthorhombic PT in Rb_2SO_4 takes place at $T_c = 930$ K [8].

2. Experimental

The Rb_2SO_4 crystals have been grown in a water solution by the temperature-decreasing method. For measurement purposes, samples of regular shape, monodomain, without internal strains and stresses have been taken, this being checked by means of a polarizing microscope. The crystal axes have been designated using a hexagonal setup, as it was for potassium sulfate [4].

The temperature-and-spectrum dependence of the principal birefringences ($\Delta n_i(\lambda, T)$ — $i = X, Y, Z$; $\lambda = 250 \div 850$ nm; $T = 4.2\text{--}1100$ K) has been measured by the interference method [9], and the temperature dependence of optic-axial angle ($2V(T)$ — $T = 4.2\text{--}1100$ K) has been measured by the conoscopic method for two laser lines 632.8 nm and 441.1 nm. In calculating $\Delta n_i(T)$ account has been taken of a thermal dilatation independently measured by means of a quartz dilatometer. Low-temperature investigations have been carried out respec-

tively in a helium and nitrogen cryostat using the temperature control system "Utrex", and the high-temperatures ones have been carried out in an electrically heated oven using BPT-2.

It was determined that at room temperature the crystal of rubidium sulfate is optically positive with acute bisectrix directed along the X -axis: at the wavelength $\lambda_0 = 490$ nm the birefringence sign inversion occurs, for 632.8 nm — $2V = 25^\circ$ (plane of optic axes XOZ), and for 441.1 nm — $2V = 15^\circ$ (plane of optic axes XOY). Our results somewhat disagree with those in [7], however there are other values of $2V$ at room temperature which are known in literature. Based on the temperature dependence of the optic-axial angle (Fig. 1), it was determined that the Rb_2SO_4 crystal has another "isotropic point" in the Y direction at near nitrogen temperatures.

3. Results and discussion

Let us consider in more detail the behavior of the optic-axial angle of rubidium sulfate. As seen in Fig. 1, at near $4.2 \div 40$ K, the dependence of $2V(T)$ features saturation, at $T = 73$ K — $2V = 0$ for 632.8 nm, and at $T = 79$ K — $2V = 0$ for 441.1 nm. At temperature ≈ 200 K the optic-axial angle transits 90° , and the optical sign of the crystal changes from negative into positive. Further temperature increase results in decrease the optic-axial angle down to zero at 284 K and 299 K for 632.8 nm and 441.1 nm, respectively. At temperatures near 400 K the optical-axis angle again transits 90° , and the optical sign changes from (+) into (−). After this, the $2V(T)$ reaches saturation at near 550–800 K, in which case the spectral dependence of $2V$ almost disappears, starting from 500 K. In the hexagonal phase the crystal becomes optically uniaxial, and remains negative. As seen in Fig. 1, no step changes in $2V$ during the hexagonal-orthorhombic phase transition take place, and, starting from 800 K, the optic-axial angle slowly decreases down to zero at T_c .

Figure 2 shows the temperature-and-spectrum diagrams of the uniaxial state of the optical indicatrix of rubidium sulfate, which have been measured by the interference method, using DFS-8 and KSVU-23 spectrographs. The insets show the orientations of the optical indicatrices of Rb_2SO_4 on the 632.8 nm laser line at various temperatures. In the short-wave region of the spectrum the "isotropic points" feature a weak temperature dependence of the uniaxial state, with $|d\lambda_{0y}/dT| < |d\lambda_{0x}/dT|$, and in the long-wave spectral region the movement velocity of the "isotropic point" is significant, especially in the Y direction, but in this case with $|d\lambda_{0y}/dT| > |d\lambda_{0x}/dT|$. For example, in the Y direction, $d\lambda_{0y}/dT = -2$ nm K^{-1} at $T = 100 \div 150$ K for $330 \text{ nm} \geq \lambda \geq 250$ nm, and at near 73 K for $\lambda \geq 500$ nm, $d\lambda_{0y}/dT = -80$ nm K^{-1} ; in the X direction — $d\lambda_{0x}/dT = -3.5$ nm K^{-1} at $T = 320 \div 350$ K for $350 \text{ nm} \geq \lambda \geq 300$ nm, and at $T = 276 \div 286$ K for $800 \text{ nm} \geq \lambda \geq 600$ nm, $d\lambda_{0x}/dT = -20$ nm K^{-1} .

The spectrum-and-temperature dependence $\lambda_{0x}(T)$ of rubidium sulfate is well described by the function

Fig. 1. Temperature dependences of the optic-axial angle ($2V(T)$) for 441.1 nm (1) and 632.8 nm (2); temperature changes of birefringences ($\Delta n_i(T)$, $i = X, Y, Z$) for 300 nm (1) and 700 nm (2).

Fig. 2. Temperature-and-spectrum diagram of the uniaxial state of the optical indicatrix of rubidium sulfate at the "isotropic points" and in the hexagonal phase; λ_0 — a wavelength at which the birefringence sign inversion takes place. The insets show the characteristic conoscopic figures corresponding to the state of the optical indicatrix at 632.8 nm laser wavelength (2); 1 — 441.1 nm laser wavelength.

$$\lambda_{0x}(T) = A_{\text{exp}}(b - aT) + B, \quad (1)$$

where $A = 1$ nm, $b = 21.42$, $a = 0.0551 \text{ K}^{-1}$, $B = 300$ nm.

The temperature dependence of the uniaxial state of the optical indicatrix of rubidium sulfate in the Y direction is described by a complex function

$$\lambda_{0x}(T) = A(T_0 - T)_{\text{exp}}\{[a(T_0 - T)]^\alpha\} + B \quad (2)$$

with coefficients $A = 1.388 \text{ nm K}^{-1}$, $a = 0.0147 \text{ K}^{-1}$, $T_0 = 146 \text{ K}$, $\alpha = 5.5$, $B = 250$ nm.

Table summarized the parameters of the optical indicatrices of rubidium sulfate for 500 nm at various temperatures. As seen in these figures and table, the change in the characteristics of the optical indicatrix of rubidium sulfate has a tendency similar to that in K_2SO_4 [5], however the Rb_2SO_4 "isotropic points" are shifted into the region of more lower temperatures, and feature the

temperature-and-spectrum dependence of the birefringence sign inversion. This is also confirmed by the

temperature-and-spectrum dependences of birefringence that we have first measured.

TABLE
Change in the parameters of the optical indicatrix of Rb_2SO_4 .

Temperature [K]	Optical axis plane	Acute bisectrix	Optical sign	Axiality	Refractive indices
4.2–75	ZOY	Y	–	biaxial	$N_z > N_x > N_y$
75	OO $\parallel$ Y	–	–	uniaxial	$N_z > N_x > N_y$
75–193	YOX	Y	–	biaxial	$N_x > N_z > N_y$
193–293	YOX	X	+	biaxial	$N_x > N_z > N_y$
293	OO $\parallel$ X	–	+	uniaxial	$N_x > N_z > N_y$
293–430	XOZ	X	+	biaxial	$N_x > N_y > N_z$
430–930	XOZ	Z	–	biaxial	$N_x > N_y > N_z$
930–1100	OO $\parallel$ Z	–	–	uniaxial	$N_x > N_y > N_z$

Figure 1 shows the dependences $\Delta n_i(T)$ for 300 nm and 700 nm. The birefringence dispersion $d\Delta n/d\lambda$ at low temperatures in all crystallographic directions is normal with a clearly marked anisotropy: $d\Delta n_x/d\lambda = -1 \times 10^{-6} \text{ nm}^{-1}$, $d\Delta n_y/d\lambda = -0.25 \times 10^{-6} \text{ nm}^{-1}$, $d\Delta n_z/d\lambda = -0.5 \times 10^{-6} \text{ nm}^{-1}$ for 500 nm at 70 K. In the direction of the polar Z-axis, when being heated, the birefringence dispersion tends to decrease. Thus, at 800 K, $d\Delta n_z/d\lambda = -0.3 \times 10^{-6} \text{ nm}^{-1}$ for 500 nm, and during PT $\Delta n_z \rightarrow 0$ and $d\Delta n_z/d\lambda \rightarrow 0$. The normal dispersion of birefringence at low temperatures in the X and Y directions results in a situation where a temperature increase causes a change in the birefringence sign, firstly for 700 nm, then for 300 nm. This is also well seen in the temperature-and-spectrum diagram of the uniaxial state of the optical indicatrix of rubidium sulfate (Fig. 2). However, as seen in Fig. 1, at 400 K (T'') in the Y direction, and at 620 K (T'') in the X direction, the curves Δn for 300 nm and 700 nm merge with one another ($\Delta n(300 \text{ nm}) = \Delta n(700 \text{ nm})$), i.e. the birefringence dispersion practically disappears. Temperature changes in the dispersion Δn_x are detailed in Fig. 3. As seen in this figure, with the temperature being increased, the birefringence dispersion decreases, and at 620 K the $d\Delta n_x/d\lambda$ becomes equal to zero, further temperature rise results in an increase in the dispersion reversed in sign: $d\Delta n_x/d\lambda = -0.25 \times 10^{-6} \text{ nm}^{-1}$ at 493 K and $d\Delta n_x/d\lambda = +0.25 \times 10^{-6} \text{ nm}^{-1}$ at 703 K. It can be said that at 620 K for the X direction, the inversion of the birefringence dispersion sign of rubidium sulfate takes place. A similar inversion of the dispersion takes place in the Y direction at 400 K, and this is not given here. In the isomorphous K_2SO_4 there is a similar change in the dispersion [5] at 617 K and 700 K, but in this case the birefringence sign inversion and the dispersion inversion

are superimposed, and we have an “isospectral isotropic point”. In Ref. [10], anomalies of the electrical conductivity near 673 K have been found. This effect is due to the beginning of the thermoreactive rotational motion of the SO_4^{2-} group. Maybe, the observed changes of the birefringence dispersion sign in potassium and rubidium sulfates are also due to this effect, however, to fully answer this question, it is necessary to measure the optical properties of these crystals in a wider spectral range.

Fig. 3. Spectrum dependences $\Delta n_x(\lambda)$ for a series of temperatures: 1 — 77 K, 2 — 294 K, 3 — 493 K, 4 — 620 K, 5 — 703 K, 6 — 837 K, 7 — 997 K.

The temperature changes in the birefringence ($d\Delta n_i/dT$) of rubidium sulfate for all crystallographic directions are nonlinear, with temperature increase all $d\Delta n_i/dT$ increase smoothly: thus, at a room temperature $d\Delta n_i/dT$ is equal to $6.8 \times 10^{-6} \text{ K}^{-1}$, $6.4 \times 10^{-6} \text{ K}^{-1}$, $0.2 \times 10^{-6} \text{ K}^{-1}$, and at 850 K — $29.0 \times 10^{-6} \text{ K}^{-1}$, $26.1 \times 10^{-6} \text{ K}^{-1}$, $3.0 \times 10^{-6} \text{ K}^{-1}$ for the X , Y , Z directions, respectively. In the paraelectric phase $\Delta n_z = 0$, and $\Delta n_x = \Delta n_z$ and the temperature changes of the birefringence take place linearly, with a temperature coefficient equal to $15 \times 10^{-6} \text{ K}^{-1}$. The temperature course of spontaneous increments in birefringence ($\delta\Delta n_i(T)$) in the ferroelastic phase has a tendency of a phase transition of the second kind, this being confirmed by the absence of step changes in $\Delta n_i(T)$ and $2V(T)$ during phase transition.

Thus, based on the temperature dependence of the optic-axial angle in rubidium sulfate, the second point of birefringence sign inversion has been found. The temperature-and-spectrum diagram has been first obtained for the uniaxial state of the optical indicatrix at the “isotropic points” and in the hexagonal phase of Rb_2SO_4 . Based on the temperature behavior of the birefringence and optic-axial angle, it was supposed that the hexagonal-orthorhombic transition in rubidium sulfate can be a phase transition of the second kind. Found is the birefringence dispersion inversion in the X and Y directions at 400 K and 620 K, respectively. Comparison of the characteristics of the optical indicatrices of rubidium and potassium sulfates shows that the “isotropic points”

of Rb_2SO_4 are shifted into a lower temperature range and feature the temperature-and-spectrum dependence of the birefringence sign inversion. In both crystals, the birefringence dispersion inversion takes place in the X and Y directions, however in K_2SO_4 the birefringence sign inversion and the dispersion inversion are superimposed, which allows us to have an “isospectral isotropic point”.

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