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PACS 78.20. Fm; 78.20.hb; 61.50.Ks

BIREFRINGENCE PROPERTIES OF UNIAXIALLY COMPRESSED K_2SO_4 CRYSTALS

The influence of the uniaxial mechanical pressure $\sigma_m \leq 200$ bar on the temperature dependence of the birefringence Δn_i in K_2SO_4 crystals in an interval of 300–1000 K has been studied. The uniaxial pressure was found to affect only the magnitude but not the behavior of $d\Delta n_i/dT$. A significant baric shift of the ferroelastic phase transition point toward higher (for σ_x) and lower (for σ_y and σ_z pressures) temperatures was observed, as well as a baric shift of the temperature interval, where the intermediate phase exists, near the phase transition point.

K e y w o r d s: birefringence, uniaxial press, phase transition.

1. Introduction

Crystals of potassium sulfate, K_2SO_4 (PS), are typical ferroelastics, with a phase transition (PT) at the temperature $T = 860$ K from the high-temperature paraelectric phase into a low-temperature orthorhombic ferroelastic one with the spatial symmetry group $D_{2h}^{16} - Pmcn$ ($c_0 = 7.48$ Å, $b_0 = 10.07$ Å, $a_0 = 5.76$ Å, and $Z = 4$ [1]). An X-ray diffraction study [2] showed that the structure of the paraelectric phase of PS crystals is characterized by the central symmetry with the spatial group $D_{6h}^{6} - P6_3/mmc$ ($c_1 = 7.90$ Å, $b_1 = 10.12$ Å, $a_1 = 5.84$Å, and $Z = 2$, with $a_0 || c_1$ [3]). The ferroelastic PT in PS crystals occurs through an intermediate phase (853–860 K), being a phase transition of the first kind with some features of a second-kind phase transition and being associated with the softening of acoustic vibrations [4]. The authors of the cited work revealed a longitudinal acoustic mode that arises at the ferroelastic PT and is connected with the ordering of SO_4^{2-} groups.

Earlier measurements of the dispersion dependence for the refractive, $n_i(\lambda)$, and birefringence, $\Delta n_i(\lambda)$, indices at room temperature showed that the dispersion of all $n_i(\lambda)$ is normal in the spectral interval from 250 to 800 nm, it drastically grows when approaching the absorption edge, and it can be well described by the two-term Sellmeier formula [5]. At room temperature, the PS crystal is optically biaxial, positive, with a sharp bisectrix directed along the axis Z; the angle between the optical axes amounts to $2V = 60°$ ($\lambda = 632.8$ nm) and $58°$ ($\lambda = 441.1$ nm). As the temperature grows, the dispersion of $2V$ decreases, whereas the angle increases, passes through a value of 90° at a temperature of 540 K, and then decreases. The crystal itself changes the optical sign from positive to negative at that [6].

Despite the fact that the PS crystals attract a considerable interest, there is practically no information in the literature concerning the influence of the uniaxial pressure on the temperature-induced changes in the parameters of their optical indicatrix. Researches on the influence of mechanical stresses on the spectral dependences of the refractive and birefringence indices in PS crystals at room temperature [7, 8] proved their baric sensitivity. In general, such stresses change a crystal symmetry and, hence, can affect the studied parameters. In addition, they make it possible to selectively affect the corresponding groups of bonds and the corresponding structural units, by facilitating the analysis of phase transition mechanisms.

This work aimed at studying the influence of the uniaxial pressure on temperature-induced variations in the birefringence Δn_i of PS crystals in the range of their phase transition. The researches were carried out with the use of a conventional technique [7, 9].

2. Results and Their Discussion

In Fig. 1, the temperature dependences of the PS crystal birefringence at $\lambda = 500$ nm are shown for various directions of the uniaxial compression. In the ferroelastic phase, the dependences $\Delta n_i(T)$ are nonlinear for all physical directions in the crystal. The most

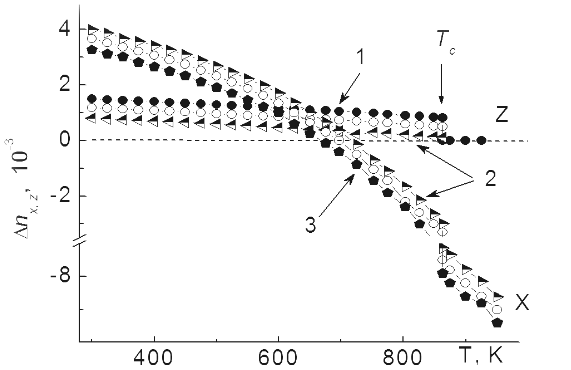


Fig. 1. Temperature dependences of the birefringence coefficients $\Delta n_{x,z}$ in K_2SO_4 crystals for various directions of the uniaxial compression: $\sigma_x = 200$ bar (*1*), $\sigma_y = 200$ bar (*2*), and $\sigma_z = 200$ bar (*3*)

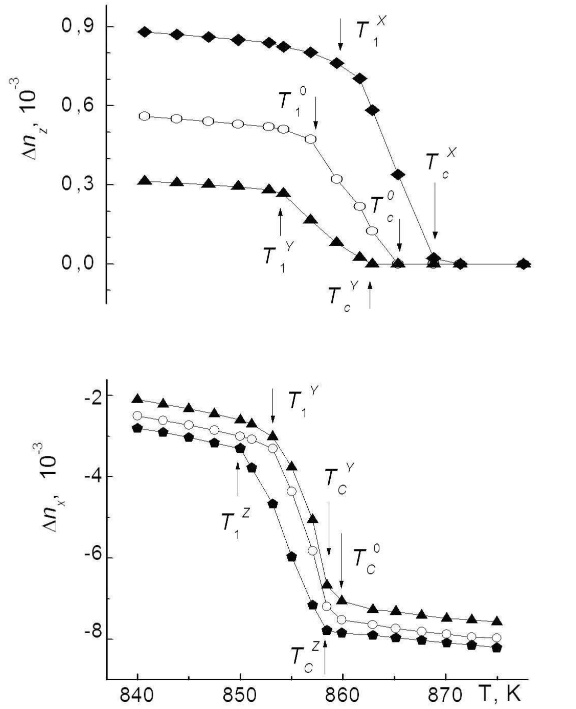


Fig. 2. Temperature dependences of the birefringence in K_2SO_4 crystals in a vicinity of the ferroelastic phase transition for $\lambda = = 500$ nm and various uniaxial stresses: $\sigma_x = 200$ bar (*1*), $\sigma_y = 200$ bar (*2*), and $\sigma_z = 200$ bar (*3*)

substantial variations of Δn_i are observed for the directions X and Y ($\partial \Delta n_{x,y}/\partial T \sim -2.5 \times 10^{-5}$ K^{-1}), whereas they are insignificant in the direction Z ($\partial \Delta n_{x,y}/\partial T \sim -0.1 \times 10^{-5}$ K^{-1}).

Near the ferroelastic PT, all Δn_i drastically decrease ($\delta \Delta n_x = 4.8 \times 10^{-3}$, $\delta \Delta n_y = 4.1 \times 10^{-3}$, $\delta \Delta n_z = 0.7 \times 10^{-3}$), but no well-pronounced jump is observed. Such a behavior is associated with the fact that the phase transition in the PS crystal is of the first kind, but with some features of the PT of the second kind. The interval of drastic Δn_i changes equals 7 K and corresponds to an intermediate phase, in which $\partial \Delta n_i/\partial T \sim -50 \times 10^{-5}$ K^{-1}. In the paraelectric phase, $\Delta n_i(T)$ changes linearly with $\partial n_{x,y}/\partial T \sim -1 \times 10^{-5}$ K^{-1}, whereas $\Delta n_z = = 0$ because the crystal becomes optically uniaxial, $\Delta n_z = n_x = n_y$.

The uniaxial stresses $\sigma_m (m = X, Y, Z)$ were found to result in Δn_i variations different by magnitude. For instance, at room temperature and the light wavelength $\lambda = 500$ nm, $\delta n_z = 1.12 \times 10^{-4}$ for $\sigma_x = 100$ bar and -1.80×10^{-4} for $\sigma_y = 100$ bar; $\delta n_x = 1.56 \times 10^{-4}$ for $\sigma_y = 100$ bar and 1.89×10^{-4} for $\sigma_z = 100$ bar. In general, the uniaxial stresses along mutually perpendicular directions always result in birefringence changes that are different by magnitude and sign. The curves $\Delta n_i(T)$, similarly to $\Delta n_i(\lambda)$, do not change qualitatively under the action of uniaxial stresses. Only an insignificant variation of the dispersion $\partial n_i/\partial \lambda$ takes place.

In Fig. 2, the temperature dependences of the birefringence in PS crystals near the PT point are shown. One can see that the uniaxial stresses do not change the $\Delta n_i(T)$ dependence, but substantially shift the point of the paraelectric–ferroelastic PT. In particular, the pressure $\sigma_x = 200$ bar shifts the PT toward higher temperatures ($T_c^X = 863.1$ K), whereas the pressures along the Y and Z axes do it toward lower temperatures ($T_c^Y = 858.1$ K and $T_c^Z = 858.2$ K). The total coefficient of baric shift of the ferroelastic PT point (an analog of the hydrostatic one) amounts to

$$\frac{\partial T_c}{\partial \sigma_m} = \frac{\partial T_c}{\partial \sigma_X} + \frac{\partial T_c}{\partial \sigma_Y} + \frac{\partial T_c}{\partial \sigma_Z} =$$
$$= +0.0155 - 0.009 - 0.0095 = -0.003 \text{ K/bar}.$$

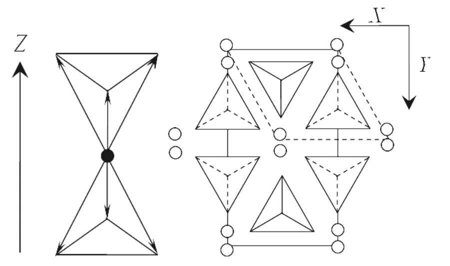
Similar baric shifts of PT points were revealed earlier for a number of crystals isomorphic to K_2SO_4, such as $LiKSO_4$, $LiRbSO_4$, and $(NH_4)_2SO_4$ [9–11]. They were explained by the influence of uniaxial stresses on the crystal structure and the mechanism of phase transition. It was found that, depending on the uniaxial compression direction, the PT points of those crystals can shift into different temperature regions. Let us consider a PS crystal from this viewpoint.

It is known that if the temperature decreases, and the orientational mobility of tetrahedral groups (SO_4^{2-} or T-group) diminishes, then the hexagonal phase becomes unstable and transforms into another structural type. The symmetry of a new phase is determined by the position and the relative orientation of SO_4^{2-} tetrahedra in the crystal lattice. In Fig. 3, the structure of a PS crystal in the initial phase is shown schematically. The position of every tetrahedron is given by an arrow that corresponds to a vector S-O which is the nearest to the axis Z. In the paraphase, the tetrahedron can have two possible orientations (up/down), which can deviate from the axis Z at a certain angle in the symmetry planes m [13, 14].

The phase transition from the initial high-temperature phase into the low-temperature ferroelastic one is classed to the "order–disorder" type. Tetrahedral groups SO_4 are an ordering factor of the structure. Tetrahedra mainly rotate around the axis Z in the plane XY. The shifts of the PT point in different directions on the temperature scale under the action of uniaxial pressures along three crystallographic directions, which were revealed by us, may probably be explained as either a "deceleration" or an "acceleration" of tetrahedra rotation around the axis Z by uniaxial pressures (Fig. 3, *b*).

The shift of the PT point under the action of uniaxial pressures is also associated with the influence of the latter on twins that arise when the crystal passes into the ferroelastic state. It was shown earlier [15, 16] that the PS crystal trillings can shift under the action of a mechanical loading and, when the stresses achieve a certain magnitude depending on the temperature, the domains of different orientations may arise in the volume of one of the components. The magnitudes of threshold mechanical pressures decrease, as the temperature grows. The analysis of the influence of mechanical stresses on the domain structure allowed us to compare the interaction energies of a trilling with external stresses and to show that it is the squeezing stress along the axis Z in the plane of the initial phase of a domain that gives rise to the growth to this domain at the expense of the others. Repeating this procedure every 60°, it is possible to create a single-domain ferroelastic crystal, allowing one (any) of the trilling components to survive in the specimen.

Abnormal variations of $\Delta n_i(T)$ in the PS crystal in the transition region are not typical of PTs of the first kind (the jump Δn_i), but are as a result of the combination of PTs of the first and second kinds. From Fig. 2, one can see that the considerable variations of $\Delta n_i(T)$ take place in the intermediate phase ($853 \div 860$ K, $\Delta T_{\rm im} = 7$ K). The existence of such a phase follows from the fact that, in a vicinity of the PT, there may locally arise and disappear the regions with a structure that is "wrong" with respect to the given domain in the ferroelastic phase, as well as the fact that the process of orientation ordering often runs in several stages, as the temperature falls down. This can reveals itself as a sequence of partially or completely ordered phases, which are either related or not to one another by the symmetry relations "group–subgroup."



a *b*

Fig. 3. Structure of K_2SO_4 crystal (*a*) in the initial paraphase (small arrows indicate possible orientations of SO_4^{2-} groups) and (*b*) in the ferroelastic phase (light circles stand for potassium). Large arrows indicate the directions the crystal axes and, accordingly, the direction of the uniaxial pressure application

We have established that the uniaxial stresses affect the temperature interval, where the mentioned intermediate phase exists. In particular, at the pressure $\sigma_x = 200$ bar, this phase was observed in the interval $856 \div 863.1$ K ($\Delta T_{\rm im} = 7.1$ K) and, at $\sigma_y = \sigma_z = 200$ bar, in the intervals $850.7 \div 858$ K ($T_{\rm im} = 7.3$ K) and $850 \div 858.2$ K ($T_{\rm im} = 8.2$ K), respectively.

We also studied the temperature dependences of the combined piezooptic constants π^0_{im} of K_2SO_4 crystals, with the use of the well-known relation

$$\pi^0_{im} = \frac{2\delta\Delta n_i}{\sigma_m} + 2s_{im}\Delta n_i,$$

where δn_i are the birefringence increments experimentally obtained as a difference between the birefringence indices in mechanically loaded and free crystals, σ_m is the magnitude of mechanical pressure ap-

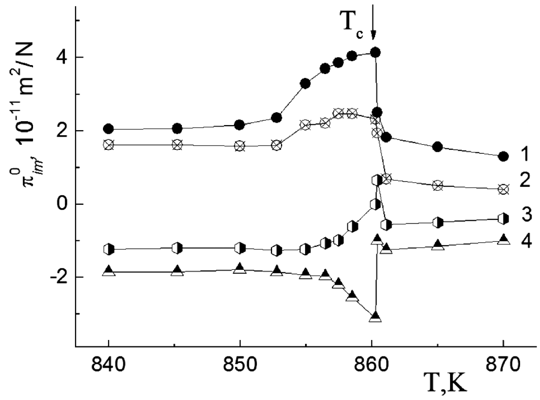


Fig. 4. Temperature dependences of the combined piezo-optic constants of K_2SO_4 crystals in a vicinity of the phase transition: (*1*) π^0_{12}, (*2*) π^0_{31}, (*3*) π^0_{32}, and (*4*) π^0_{13}

plied to the crystal in the direction perpendicular to the direction of light propagation, and s_{im} are the elastic ductilities of the crystal. One can see (Fig. 4) that the piezoconstants π^0_{12} and π^0_{13}, as well as π^0_{31} and π^0_{32}, have different signs, which testifies that the uniaxial stresses along mutually perpendicular physical directions in the crystal bring about variations in the birefringence that are different by sign.

We also found that the piezoconstants π^0_{im} change by $(1.4 \div 2.3) \times 10^{-11}$ m^2/N in a jump-like manner in the course of PT. The intermediate phase also reveals abnormal variations of π^0_{im}, which consist in a considerable growth of $d\pi^0_{im}/dT$.

To summarize, we have studied the influence of uniaxial stresses along the main physical directions in the crystal on the temperature dependences of the birefringence in PS crystals. It is found that the uniaxial stresses give rise to changes in the birefringence that are different by their magnitude and sign. However, the qualitative character of the curves $\Delta n_i(T)$ did not change. We detected a substantial baric shift of the ferroelastic PT point toward either higher (σ_x) or lower (σ_y and σ_z) temperatures. The total coefficient (an analog of hydrostatic pressure) for the baric shift of the PT point amounts to -0.003 K/bar. We also revealed the baric shift of the temperature interval of the existence of an intermediate phase near the PT point. Such a behavior stems from the influence of uniaxial stresses on the crystal structure, namely, on the rotation and the ordering of SO_4^{2-} tetrahedra, which are the dominating mechanism of the phase transition in this crystal. The behavior of combined piezo-optic constants in a vicinity of both the intermediate phase and the phase transition point was also analyzed.

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Received 29.10.12.
Translated from Ukrainian by O.I. Voitenko

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ДВОПРОМЕНЕЗАЛОМЛЮЮЧІ ВЛАСТИВОСТІ ОДНОВІСНО СТИСНУТИХ КРИСТАЛІВ K_2SO_4

Р е з ю м е

Досліджено вплив одновісного механічного навантаження $\sigma_m \leq 200$ бар на температурну (300–1000 K) залежність двопроменезаломлення Δn_i кристалів K_2SO_4. Установлено, що одновісне навантаження не змінює характеру, а лише величину $d\Delta n_i/dT$. Виявлено суттєве баричне зміщення точки сегнетоеластичного ФП як в бік вищих (σ_x), так і нижчих (σ_y, σ_z) температур. Виявлено також баричне зміщення температурного інтервалу проміжної фази поблизу ФП.