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The baric changes of the refractive properties of K_2SO_4 crystals

V.Yo.Stadnyk, M.O.Romanyuk, O.Z.Chyzh, V.F.Vachulovych

Franko Lviv National University, Kyrylo and Mefodij, 8 Str., Lviv, 79005 Ukraine

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The dependencies of the birefringence Δn_i of K_2SO_4 crystals in wide spectral (250–800 nm) ranges, as well as the effect of uniaxial mechanical stress on them have been studied. The values of n_i for K_2SO_4 are found to be rather sensitive to the uniaxial stress. The spectral characteristics of the refractive indices n_i of free and mechanically clamped K_2SO_4 crystals have been studied. The refractive indices turned out to increase under the effect of uniaxial stress. The variations in the refraction, electron polarizability and the position of the center of the effective ultraviolet absorption band have been calculated. It is shown that the positions of the isotropic points in these crystals can be controlled by thermal and spectral methods.

Key words: *bireringence, refractive indices, uniaxial pressure, phase transition, isotropic state, structure, energy band*

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1. Introduction

Crystals K_2SO_4 (PS) – are classic ferroelastics. The phase transition (PT) at 860 K from paraelastic to ferroelastic phase of space group symmetry D_{2h}^{16} (c_0 = 7.48 Å, b_0 = 10.07 Å, a_0 = 5.76 Å, Z = 4) was revealed [1–4]. In spite of a certain interest in PTs taking place in K_2SO_4 crystals [5,6], their optical properties have not been studied well enough. There are practically no data in the literature concerning the effect of uniaxial stress on the optical indicatrix of these crystals. Although this stress does not generally change the crystal symmetry without affecting the quantities under investigation, they make it possible to selectively modify certain bond groups and certain structural entities of the crystal.

The study of the temperature and spectral characteristics of the refractive indices n_i of the A_2BX_4 [K_2SO_4, Rb_2SO_4, $LiKSO_4$, and $(NH_4)_2BeF_4$] crystals made it possible to establish the isotropic points, i.e. the intersection of the dispersion curves of the refractive indices n_i at certain temperatures and wavelengths. The Rb_2SO_4 crystals have three isotropic points. In the short wavelength range of the spectrum, the isotropic points slightly depend on temperature with $|\frac{\partial\lambda_0 y}{T}| < |\frac{\partial\lambda_0 x}{T}|$, where, like in the long wavelength range, the shifts of the isotropic points are quite pronounced, especially along the Y – direction [7]. The $(NH_4)_2BeF_4$ crystals also have two isotropic points [8]. In the $LiKSO_4$ crystals, a decrease of the temperature causes the shift of the point of the intersection of the n_x and n_z curves toward the long wavelength range of the spectrum [4]. The K_2SO_4 crystals have two isotropic points in the spectral range 250–850 nm as well as demonstrate the property of *isospectrality* [8].

The aim of this work is to study the birefringence Δn_i and the principal refractive indices n_i of K_2SO_4 crystals in a wide spectral (300–800 nm) range, as well as the effect of uniaxial mechanical stress applied along the main crystallophysical directions and the bisectors of the angles formed by these directions on the birefringence properties and on the behavior of the isotropic points.

2. Experiments

K_2SO_4 crystals were grown by a slow evaporation of an aqueous solution. The grown crystals were of good optical quality and were of an orthrombic shape. The spectral dependencies of the Δn_i were measured using the interference technique.

To define the birefringence, a photographic recording of the interference pattern in the focal plane of a DFS-8 spectograph was used, which ensured a spatial resolution of extrema of various orders, excluded "smeared" patterns, and therefore allowed for their independent registration. 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

$$I = I_0 \sin^2 \left(\frac{\pi(n_i - n_j)d}{\lambda} \right), \tag{1}$$

where I_0 and I are intensities of the incident and transmitted light beams, respectively, λ is a wavelength, and $n_i - n_j$ is the birefringence and d is a crystal thinkness in the direction of the incident light beam. 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_i(T)-dependencies, the positions of interference extrema will shift, and the birefringence will be determined by the expression

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

An uniaxial 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 bar. Assuming the mechanical stress, the birefringence is determined through the expression

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

The temperature variations of Δn 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 Δn .

The principal refractive indices were determined using the immersion Obreimov method at room temperature.

3. Results and discussion

3.1. Effect of the uniaxial stress on the birefringence

The dispersion of the Δn is normal in the whole spectral interval of investigation. A comparison of Δn with the corresponding values for Rb_2SO_4 and $LiKSO_4$ isomorphous crystals showed that the cation substitution $Li^+ \to K^+$ in the sublattice causes a birefringence growth by 0.008-0.010 on the average, while the $Li^+ \to K^+$ and $Rb^+ \to Li^+$ substitutions cause an average decrease of Δn_i by 0.02 and 0.03, respectively. The results are primarily due to the variations of the n_i, to the shifts of UV and IR absorption bands, as well as due to the changes of relevant additive refractions and electron polarizability.

The values of Δn_i for this crystal are sensitive to the uniaxial stress and change almost linearly with the stress as follows: Δn_z: $\delta(\Delta n_z) = +0.15 \cdot 10^{-4}$ and $-1.80 \cdot 10^{-4}$ (for σ_x and $\sigma_y = 100$ bar, respectively). In general, although σ_m stress affects the Δn_i values, it does not substantially change their dispersion.

The analogous dependencies were observed for value Δn_x at pressures σ_y and σ_z: $\delta(\Delta n_x) = 1.58 \cdot 10^{-4}$ and $-1.92 \cdot 10^{-4}$(for σ_y and $\sigma_z = 100$ bar, respectively).

It was found that if the uniaxial stress is X-directed, then Δn_z increases and Δn_y decreases, for Y- directed, then Δn_x increases and Δn_z decreases (figure 1). Since the relations $n_x > n_z > n_y$ and $\Delta n_x = n_z - n_y$, $\Delta n_y = n_x - n_z$ and $\Delta n_z = n_x - n_y$ of K_2SO_4 crystals were established, the increase of the anisotropy of optical indicatrix under σ_m uniaxial stress action was observed.

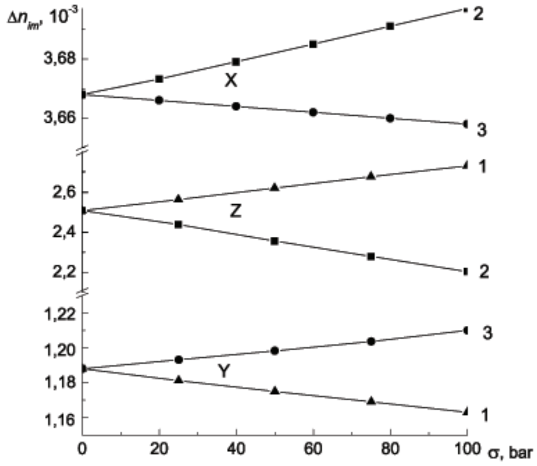

Figure 1. The stress dependencies of birefringence of K_2SO_4 crystal at room temperature for $\lambda = 500$ nm: $1 - \sigma_x, 2 - \sigma_y, 3 - \sigma_z$.

By extrapolation of lines $\Delta n_i = f(\sigma_m)$ and by solving the solution $\Delta n_{z(\sigma=0)} + b_1\sigma_x = \Delta n_{x(\sigma=0)} - b_2\sigma_z$ it was determined that $\Delta n_z \sim \Delta n_x \sim 3.49 \cdot 10^{-3}$ at $\sigma_z \sim \sigma_x \sim 1.66$ kbar. It means that the application of the uniaxial stress leads to the appearance of the pseudo-isotropic point of K_2SO_4 crystal.

3.2. Refractive indices

The variations in the refractive indices of the K_2SO_4 crystals were studied through analyzing the effect of uniaxial σ_m on Δn_i.

It has been established that the dispersion of the n_i has no anomalies and is well described by the single-oscillator Sellmeier formula

$$n_i^2(\lambda, T) = 1 + \frac{B_i(T)\lambda_{0i}^2(T)\lambda^2}{\lambda^2 - \lambda_{0i}^2(T)}\,, \tag{5}$$

where B_i is the parameter related to the strength, effective mass, and charge of UV-oscillators and λ_{0i} is the position of the effective center of the UV absorption band. Using the experimental dependencies $n_i(\lambda)$ and the well-known Lorenz-Lorentz formula,

$$\frac{(n_i^2 - 1)}{(n_i^2 + 2)} = \frac{4}{3}\pi N_0 \alpha_i = (\rho/\mu) R_i \tag{6}$$

we calculated the effective parameters of the Sellmeier formula, electron polarizability α_i, and specific refractivity R_i of the crystals (table 1) (ρ and μ are the density and the molar mass of the crystal and N_0 is the Avogadro number). The comparison with the analogous characteristics of the isomorphic Rb_2SO_4 crystal showed that the cation substitution $K^+ \to Rb^+$ causes an increase of the n_i by 0.004–0.007, the α_i by $(2-4) \cdot 10^{-25}$ cm^3, and R_i by 0.8–1.0 cm^3.

Using the data on the spectral variations of Δn_i under the pressure σ_m, we calculated the spectral dependencies of the piezooptical constants of the K_2SO_4 crystals in the spectral ranges of 300–700 nm, respectively, by the formula

$$\pi_{im}^0 = 2\delta\Delta n_i/\sigma_m + 2\Delta n_i s_{im}\,, \tag{7}$$

where δn_i is the induced change in birefringence for the light propagating along the i-axis, s_{im} are the coefficients of elastic compliance. The second term in formula (7) describing the variations in the geometric dimensions of the crystal under pressure was ignored, because its contribution to the change of π_{im} did not exceed 2–5%, i.e., it was comparable with the experimental accuracy. Using the well-known expressions for piezobirefringence of orthorhombic crystals (the traditional Pockels method [9]) we calculated the spectral characteristics of the absolute piezooptical constants of the K_2SO_4 crystals by solving the systems of equations with nine unknowns π_{im}

$$\delta\Delta n_i^m = \frac{1}{2}\left(n_m^3\pi_{mm} - n_k^3\pi_{km}\right), \qquad (i,k,m = 1,2,3), \tag{8}$$

where $\delta\Delta n_i^m$ is the change in birefringence along the i-direction under uniaxial stress applied along the m-axis, and n_k and n_m are the absolute values of the refractive indices of a free K_2SO_4 crystal.

The analysis of the variations of the principal n_i of K_2SO_4 crystals was performed using the piezooptic constants and the formula

$$n_i(\lambda,\sigma) = n_{i0}(\lambda) - \frac{1}{2}\pi_{im}(\lambda)\sigma_m n_{i0}^3(\lambda), \tag{9}$$

where $n_{oi}(\lambda)$ are the spectral dependencies of the refractive indices for a mechanically free crystal.

Figure 2 shows the stress dependence of the principal n_i for $\lambda = 500$ nm and various directions of the applied mechanical stresses at room temperature. The n_i increase with stresses application. In the UV spectrum range, the n_i are very sensitive to pressures, which is explained by a considerable dispersion of the absolute piezooptic constants.

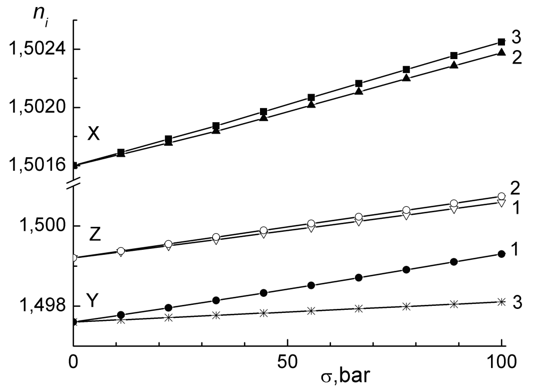

Figure 2. The stress dependencies of the refractive indices of K_2SO_4 crystal at T_{room} and $\lambda = 500$ nm: $1-\sigma_x, 2-\sigma_y, 3-\sigma_z$.

For the light propagating along the X-, Y-, and Z-axes, the dependencies $n_i(\lambda,\sigma)$ and formula (6) provide the calculation of the changes in α_i and R_i of the crystal (table 1).

It is established that the pressures up to $\sigma_m \sim 200$ bar raise the R_i (on the average by $\sim 1E2\cdot10^{-25}$ cm^3) as well as the α_i of the K_2SO_4 crystal.

Probably, uniaxial pressures change the degree of ordering of the crystal and lead to a slight deformation and rotation of the framework formed by SO_4^{2-}-tetrahedra and to displacements of K^+ ions, which can be seen from the changes in α_i and R_i. Using the dependencies $n_i(\lambda,\sigma)$ and formula (5), we also calculated the baric dependencies of the parameters of ultraviolet (λ_{0i}, B_i) oscillators (table 1).

It has been established that an increase of the n_i $(\partial n/\partial\sigma \cong 5\cdot10^{-6}\ \mathrm{bar}^{-1})$ under pressure is caused by a decrease of the strength of the effective UV oscillator and by the displacement of the center of the effective UV absorption band to the long wavelength range $(\partial\lambda_0/\partial\sigma \approx 0.5E2\cdot10^{-2}$Å/bar $\approx 15\cdot10^{-5}$ eV/bar).

Indeed, upon differentiation of (5), we arrive at

$$\frac{\mathrm{d}n}{\mathrm{d}\sigma_m} \approx \frac{1}{2n}\frac{\lambda^2\lambda_{0i}^2}{\lambda^2-\lambda_{0i}^2}\left(\frac{\mathrm{d}B_i}{\mathrm{d}\sigma_m} + \frac{B_i}{\lambda_{0i}}\frac{\mathrm{d}\lambda_{0i}}{\mathrm{d}\sigma_m}\right). \tag{10}$$

Table 1. The stress dependencies of the electron polarizability i, specific refractivity R_i ($\lambda =$ 500 nm) and effective parameters of Sellmeier formula for K_2SO_4 crystals at $T = 294$ K.

Parameters	$\sigma_i = 0$ bar	$\sigma_x = 200$ bar	$\sigma_y = 200$ bar	$\sigma_z = 200$ bar
$\alpha_x \times 10^{24}$, nm^3	7.642	7.662	7.682	7.683
$\alpha_y \times 10^{24}$, nm^3	7.588	7.620	7.592	7.612
$\alpha_z \times 10^{24}$, nm^3	7.608	7.612	7.632	7.611
R_x, nm^3	19.402	19.421	19.423	19.451
R_y, nm^3	19.275	19.298	19.279	19.289
R_z, nm^3	19.302	19.321	19.339	19.330
λ_{0x}, nm	91.130	91.185	91.235	91.256
λ_{0y}, nm	90.329	91.392	90.521	91.026
λ_{0z}, nm	90.332	90.832	91.523	91.421
$B_x \times 10^6$, nm^{-2}	146.175	146.021	146.002	145.992
$B_y \times 10^6$, nm^{-2}	147.527	147.532	147.529	148.023
$B_z \times 10^6$, nm^{-2}	148.033	149.001	148.563	148.365

The baric displacement of the effective UV oscillator is very large. It showed that UV oscillator is situated in a high energy spectrum region.

Thus, studying the spectral dependencies of the refractive indices of free K_2SO_4 crystals mechanically clamped by the stresses along the main crystallophysical directions, we established that the refractive indices n_i increase because the applied pressure effects the electronic subsystem of the crystal.

We also calculated the variations in the electron polarizability, refraction and the parameters of the UV oscillators of free and mechanically clamped K_2SO_4 crystals. It is seen that uniaxial pressures shift the center of the effective absorption band to the visible range of the spectrum, which seems to be associated with a decrease of the band gap.

It has been found that the birefringence is rather sensitive to the uniaxial stresses applied along the principal crystallophysical axes. Those stresses, applied along mutually perpendicular crystallophysical axes, $\sigma_{i,m}$, result in the changes Δn_j different in signs and values ($i, j, m = 1, 2, 3$).

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Баричні зміни рефрактивних параметрів кристалів K_2SO_4

В.Й.Стадник, М.О.Романюк, О.З.Чиж, В.Ф.Вахулович

Львівський національний університет ім. І.Франка, Львів 79005, вул. Кирила і Мефодія 8, Україна

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Досліджено залежності двопроменезаломлення Δn_i кристалів K_2SO_4 в широкому спектральному (250–800 нм) діапазоні під впливом одновісних тисків. Виявлено, що величини ni кристалів K_2SO_4 є досить чутливими до впливу одновісних тисків. Досліджено спектральні залежності показників заломлення n_i вільних та механічно затиснутих кристалів K_2SO_4. Встановлено, що показники заломлення зростають під дією одновісних тисків. Розраховано зміни рефракцій, електронної поляризовності та положень центрів ефективних ультрафіолетових смуг поглинання. Показано, що положення ізотропних точок в цих кристалах можна змінювати температурним та спектральним методами.

Ключові слова: *двопроменезаломлення, показник заломлення, фазовий перехід, ізотропний стан, енергетична смуга*

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