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Dilatometric and refractive parameters of rubidium sulfate crystals at low temperatures

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The temperature changes of the relative elongation $(\Delta l/l_0)_i$ and refractive indices $n_i(T)$ of rubidium sulfate crystals in the region of low temperatures are investigated in the work. The linear dimensions and volume of the crystal decrease with a decrease in temperature, and the parameters $(\Delta l/l_0)_i$ are anisotropic. The values of n_i increase with decreasing temperature for all crystal physical directions, and the intersection of the curves $n_z(T)$ and $n_x(T)$ at a temperature of $T = 85$ K occurs. This indicates the existence of an optical isotropic point in this crystal, which is confirmed by independent temperature measurements of the angle between the optical axes. It is shown that rubidium sulfate crystals are optically biaxial, with the angle between the optical axes equal $2V = 41.5°$ at room temperature. With decreasing temperature, it decreases almost linearly, so that at $T = 85$ K the crystal changes from optically biaxial to optically uniaxial ($2V = 0°$). The temperature changes of the values of electronic polarizability α_i were calculated. It was shown that α_i increases slightly as temperature decrease, so that in the region where the optical isotropic point exists, the values α_x and α_z are equal to each other.

Keywords: crystal, relative elongation, anisotropy, refractive index, optical isotropic point, angle between optical axes.

1. Introduction

Crystals of the $ABSO_4$ group (A, B = K, Li, Rb, NH_4) have an optical isotropic point (OIP), at which the symmetry of the optical indicatrix increases with changes in spectral range or temperature. The transition through OIP is accompanied by a change in the sign of birefringence of the crystal, that is, its inversion takes place. Therefore, the very phenomenon of the intersection of the dispersion curves of refractive indices is called the phenomenon of the birefringence sign inversion (BSI) [1–4]. OIP is a result of temperature-spectral deformations of optical indicatrices of crystals and consists in the fact that for each wavelength only at a certain temperature the phase transition of the crystal from uniaxial to isotropic or from biaxial to uniaxial state takes place. The presence and temperature dependence of an isotropic state of a crystal is associated with spectral and temperature changes in the refractive indices $n_i(\lambda, T)$ [5–8]. Therefore, independent studies of $n_i(\lambda, T)$ make it possible to detect and analyze the behavior of OIP in crystals.

Crystals with OIP are interesting due to the possibility of their use as crystal-optical sensors for measuring temperature and pressure, as well as acousto-optical modulators. They create better opportunities for temperature measurement in harsh conditions (high electric and magnetic fields, moving parts) and can provide sensitivity up to 10^{-3} K.

By measuring the temperature (77–1000 K) and spectral (300–700 nm) dependences of the refractive indices n_i and birefringence Δn_i, it was possible to detect OIP for a number of dielectric ferroic crystals of the $ABSO_4$ group ($LiKSO_4$, K_2SO_4, $RbNH_4SO_4$, $RbKSO_4$, $LiNH_4SO_4$, etc.) [9–11]. Despite the large number of crystals, the practical value of searching for new crystals with OIP is relevant, since many of the known ones reveal OIP in an inconvenient for practical use part of the spectrum, and almost all of them undergo phase transitions (PT) in a certain temperature range, which limits their technical characteristics.

Following this purpose, we have chosen one of the representatives of the $ABSO_4$ group, namely the crystal of rubidium sulfate (RS) Rb_2SO_4. Previously, it was found that the refractive indices n_z and n_y of this crystal are close in the visible part of the spectrum, so that at a wavelength of $\lambda = 495$ nm they intersect at room temperature ($n_z = n_y = 1.51705$), which indicates the existence of OIP along of the crystal physical direction x. The RS crystal is a typical representative of the $ABSO_4$ group, at a temperature of $T_c \sim 922$ K it undergoes PT from the pseudohexagonal paraelectric phase $P3m1$ to the orthorhombic ferroelastic phase (space group symmetry $D_{2h}^{16} - Pmcn$ [12–14].

The crystal structure of RS was studied, and it was found that the obtained crystals belong to the *Pnma* spatial symmetry group having the following refined lattice parameters: $a = 7.82079(10)$ Å, $b = 5.97778(7)$ Å, and $c = 10.44040(13)$ Å. The band-energy structure of the crystal is characterized by the band gap of the direct type ($E_g = 4.89$ eV) and a weak dispersion of energy levels. It was found that for the Rb_2SO_4 crystal, as for many other crystals of the A_2BX_4 group, the top of the valence band is formed by the $2p$ states of oxygen atoms, and the bottom of the conduction band is formed by the $4s$ electrons of rubidium [15].

However, there is no information in the literature on the optical-spectral parameters of the Rb_2SO_4 crystal in the region of low temperatures. Therefore, the purpose of this work is to establish the possibility of the existence of an isotropic state in the RS crystal in the region of low temperatures, as well as to clarify the effect of the cationic substitution $Rb^+ \rightarrow (NH_4)^+ \rightarrow Na^+ \rightarrow K^+$ on the optical and electronic parameters of crystals of the $ABSO_4$ group in order to influence and regulate the spectral and temperature ranges of OIP existence.

2. Methodology of the experiment

The studied crystals were obtained by the method of slow evaporation of repeatedly recrystallized aqueous solution of salts of pure rubidium sulfate Rb_2SO_4 at room temperature. The temperature of the solution was 310 K, which was controlled by a thermostat with an accuracy of 0.5 K. The growth was carried out from spontaneously formed seeds with pseudo-hexagonal morphology for 20 days. The obtained crystals were of good optical quality and had the shape of elongated prisms, the size of which was approximately 6 × 8 × 8 mm.

The thermal expansion of Rb_2SO_4 crystals was studied using a quartz dilatometer [16–21]. This device allows measuring the thermal expansion of samples with dimensions within a few centimeters, and the relative changes in sample sizes were determined with an accuracy of 0.001 mm. The studied sample was placed in a nitrogen cryostat, the temperature was lowered by liquid nitrogen vapors blowing, and measured with a copper-constantan thermocouple. The duration of stabilization for each temperature point was several minutes.

The temperature-spectral dependences of the refractive indices of the studied crystals were carried out by the well-known photographic Obreimov method [6, 22], which is based on the fact that during the passage of a parallel light beam along the boundary of a plane-parallel crystal plate and the external environment with a refractive index n_{en}, a path difference occurs:

$$\Delta = d\left(n_{\text{cr}} - n_{\text{en}}\right). \tag{1}$$

Light beams that have passed through the sample and the medium partially overlap and will interfere, and the refractive index of the crystal under study can be written as

$$n_{\text{cr}}(\lambda) = 1 + k\lambda / d. \tag{2}$$

Here, n_{cr} and d are the refractive index and the thickness of the sample, respectively; λ is the wavelength, k is the order of the interference extremum.

3. Results and discussion

3.1. Dilatometric properties

Figure 1(a) shows the temperature dependence of the relative linear elongation of the RS crystal for three crystal-physical directions in the region of low temperatures. One can see that as the temperature decreases, the linear dimensions decrease. For the x and y directions, these changes are not significant and are practically the same $\alpha_{x,y} = \frac{1}{l_0}\left(\frac{\Delta l}{\Delta T}\right) \sim 1.8 \cdot 10^{-7}\ \text{K}^{-1}$ and $2.2 \cdot 10^{-7}\ \text{K}^{-1}$, respectively. In the z direction of occurrence of ferroelastic deformation, these changes are somewhat larger $\alpha_z \sim 3.6 \cdot 10^{-7}\ \text{K}^{-1}$.

Figure 1(b) also shows the relative changes in the volume of the sample, calculated on the basis of the data and according to the obvious formula:

$$\Delta V / V_0 \sim \left(\Delta l / l_0\right)_x + \left(\Delta l / l_0\right)_y + \left(\Delta l / l_0\right)_z. \tag{3}$$

One can see that as the temperature decreases, the volume of the crystal decreases almost linearly so the coefficient of temperature change of the volume $\beta = \frac{1}{V_0}\left(\frac{\Delta V}{\Delta T}\right) \sim$ $\sim 7.2 \cdot 10^{-7}\ \text{K}^{-1}$. As can be evidenced from Fig. 1(a), the parameters $(\Delta l / l_0)_i$ are strongly anisotropic. It is known that the following relations are used to estimate the quantitative parameters A describing the anisotropy of a certain physical characteristic f (in our case the relative linear thermal expansion) [23, 24]:

$$A = \sum_{i \neq j}^{n} \frac{\left|f_i - f_j\right|}{\left|f_i\right| + \left|f_j\right|} = \frac{\left|f_x - f_y\right| + \left|f_x - f_z\right| + \left|f_y - f_z\right|}{\left|f_x + f_y + f_z\right|}. \tag{4}$$

It was found that the anisotropy coefficient for RS at room temperature is $A = 0.053$, and it changes slightly with temperature: the decrease in temperature is accompanied by a decrease in A, which is due to the approaching of the crystal to the isotropic state. At a temperature of $T = 85$ K,

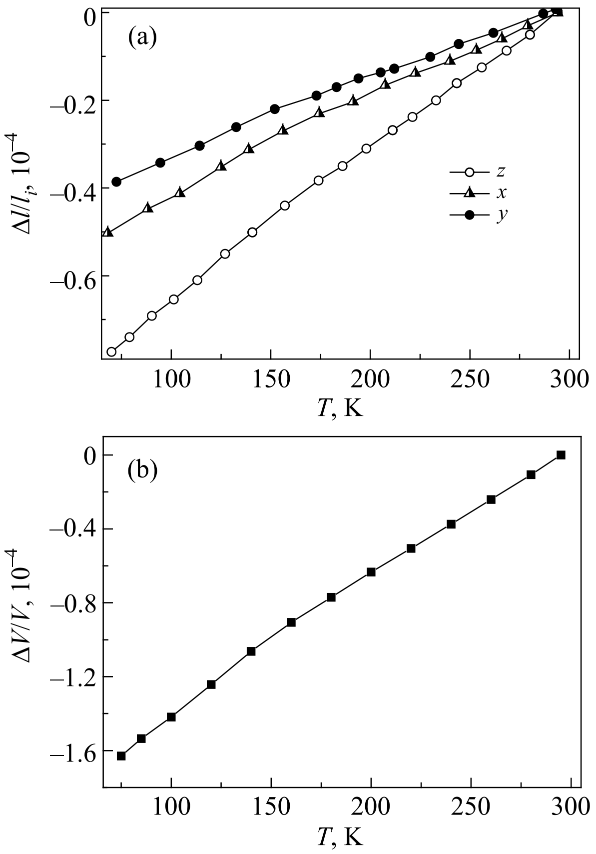

Fig. 1. Temperature dependence of relative elongation (a) and volume (b) of Rb_2SO_4 crystals in the region of low temperatures.

the value of $A = 0.037$. The dependences $A(T)$ make it possible to analyze the main regularities of the temperature behavior of dilation anisotropy in crystals.

3.2. Refractive parameters

Figure 2 shows the temperature dependence of the refractive indices n_i of Rb_2SO_4 crystals in the region of low temperatures. One can see that the n_i values increase with decreasing temperature: $dn_x/dT = 3.95 \cdot 10^{-5}$ K^{-1}, $dn_y/dT = 4.085 \cdot 10^{-5}$ K^{-1}, and $dn_z/dT = 4.85 \cdot 10^{-5}$ K^{-1}. Since $dn_z/dT > dn_x/dT$, this leads to the intersection of the curves $n_z(T)$ and $n_x(T)$, so that at a temperature of $T = 85$ K we can observe the equality $n_z = n_x = 1.51936$. This fact confirms the existence of OIP, which was previously discovered using temperature measurements of birefringence $\Delta n_y(T)$, and a value of $\Delta n_y = 0$ was observed [25].

At this point, the deformation of the optical indicatrix occurs. At temperatures $T > 85$ K, the relation between the refractive indices $n_x > n_z > n_y$ in the vicinity of the OIP is valid for the RS crystal: $n_x = n_z > n_y$, while at temperatures $T < 85$ K we have the following relation $n_z > n_x > n_y$.

In order to additionally verify the existence of OIP, a study of the angle between the optical axes of the crystal was conducted. To do this, the sample was pre-oriented using a polarizing microscope so that in the field of view there is a section perpendicular to the bisector of the acute angle between the optical axes. The crystal was placed in a cryostat between the crossed polarizer and the analyzer. The polarizer ensures a constant ratio of the amplitudes of the two waves in the crystal. The crystal itself, which is placed in a diagonal position (the crystal physical axes, in our case, x and z, are located at the angle of 45° to the polarizer and the analyzer), creates a constant difference in path $\Delta = l(n_x - n_z)$. The analyzer reduces the oscillations that occur in the crystal to one plane, which is a necessary condition for interference.

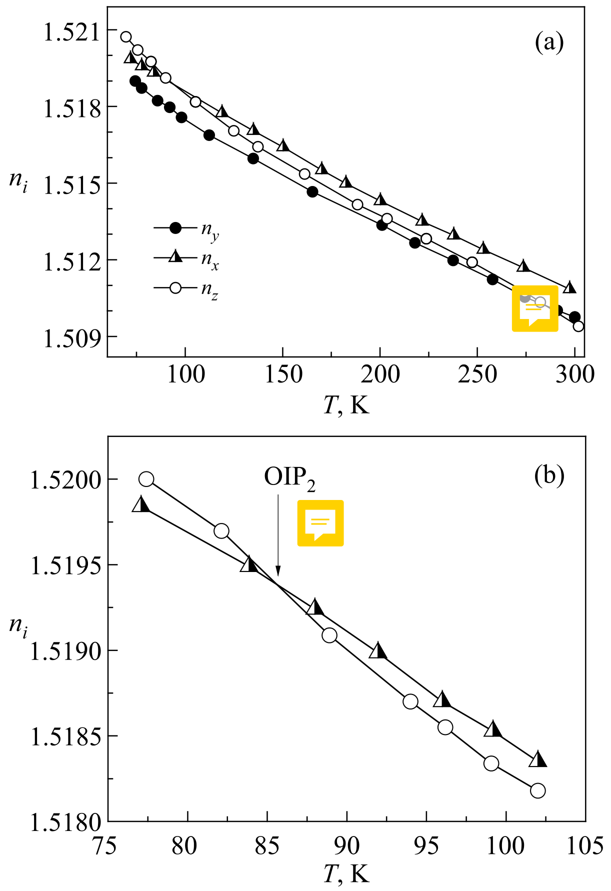

Fig. 2. Temperature dependence of the refractive indices of Rb_2SO_4 crystals in the region of low.

The provided schema ensures obtaining the interference (conoscopic) pattern on the screen. In the temperature range $T > 85$ K, the crystal is optically biaxial, and its conoscopic figure is a set of isochromes (corresponding to interference bands of the same order) and two hyperbolas — isogyres (corresponding to the output of the optical axes). As the temperature decreases, the isogyres approach each other and at the temperature of the existence of the isotropic point ($T = 85$ K) they transform, so that the conoscopic figure is a combination of a dark cross (Maltese cross) and concentric isochrome rings (Fig. 3). The position of the beams of the central cross indicates the oscillations of the electric vector in the polarizer and the analyzer.

To determine the angle between the optical axes, we measured the linear distance between the optical axes $2l$ on

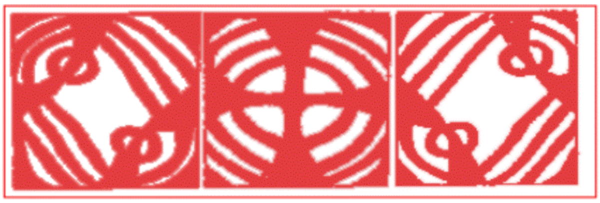

Fig. 3. View of the conoscopic figures of the Rb_2SO_4 crystal: (a) for the case $T > 85$ K (approaching OIP); (b) near OIP($T = 85$ K); (c) for the case $T < 85$ K (distance from OIP).

the screen, changed the temperature of the sample and recorded the change in the position of the outputs of the optical axes. Then the temperature dependence of the angle between the optical axes can be determined by the following ratio:

$$2V(T) = 2\arcsin\frac{\sin E}{n_m(T)} = 2\arcsin\left(\frac{l/L}{n_m(T)\sqrt{1+(l/L)^2}}\right), \quad (5)$$

where $n(T)$ is the index of refraction for a beam propagating along the optical axis, L is the distance between the crystal and the screen on which the conoscopic figure is observed.

It has been confirmed that RS crystals are optically biaxial crystals, in which the angle between the optical axes at room temperature is $2V = 41.5°$. As the temperature decreases, the angle between the optical axes decreases almost linearly, so that at $T = 85$ K the crystal changes from optically biaxial to optically uniaxial (the optical indicatrix transforms from an ellipsoid of the general type into an ellipsoid of rotation) and at the same time $2V = 0^{\circ}$ (Fig. 4).

Additionally, the angle between the optical axes can be estimated from the experimental values of the refractive index using the relation [6]:

$$\mathrm{tg}V = \sqrt{\frac{N_p^{-2}-N_m^{-2}}{N_m^{-2}-N_g^{-2}}} \quad \text{or} \quad \sin V = \frac{N_g}{N_m}\sqrt{\frac{N_m^2-N_p^2}{N_g^3-N_m^2}}, \quad (6)$$

where N_g, N_m, and N_p are the largest, middle, and smallest refractive indices of the crystal, respectively. In our case, $N_g \equiv n_x$, $N_m \equiv n_z$, and $N_p \equiv n_y$. The calculated value of the angle between the optical axes is equal to $2V = 41.8°$. Therefore, the results of the calculation using formula (6) agree well with direct measurements of the angle between the optical axes. Using the experimentally obtained results on $n_i(T)$, the temperature dependence of the angle between the optical axes was estimated according to formula (6). The theoretically obtained dependence $2V(T)$ fully reproduces the given experimental dependence.

Based on known ratios

$$\frac{n^2-1}{n^2+2} = \frac{4}{3}\pi N\alpha \quad \text{and} \quad R = 4\pi/3N_A\alpha = \frac{\mu}{\rho}\frac{n^2-1}{n^2+2} \quad (7)$$

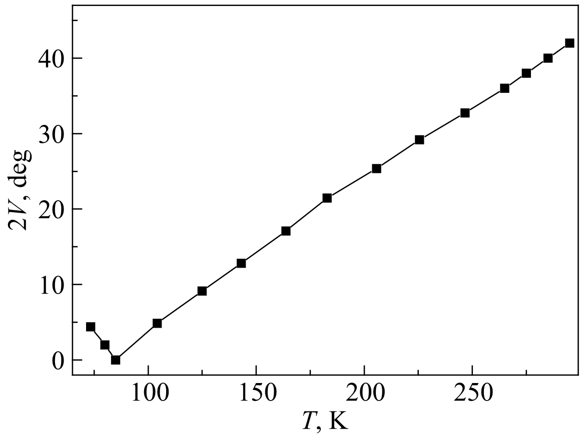

Fig. 4. Temperature angle between the optical axes of Rb_2SO_4 crystals for the light wavelength $\lambda = 633$ nm.

(where N is the number of particles per unit volume; N_A is Avogadro's number; μ is the molar mass; ρ is the crystal density, respectively) the changes in electronic polarizability α in the region of low temperatures are estimated. Electronic polarizability characterizes the degree of polarization (displacement of structural elements from the equilibrium positions) of a dielectric crystal under the action of an external electric field (in our case, the field of an incident light wave).

The polarizability values at room temperature are $\alpha_x = 8.85 \cdot 10^{-24}$ cm^3, $\alpha_y = 8.85 \cdot 10^{-24}$ cm^3, and $\alpha_z = 8.85 \cdot 10^{-24}$ cm^3, and as the temperature decreases, the value of α_i increases slightly with the coefficient $d\alpha/dT \sim 4 \cdot 10^{-28}$ cm^3/K. In the region of OIP_2, the values of α_x and α_z are equal to each other, which is due to the equality of the corresponding refractive indices. The behavior of $\alpha(T)$ of the RS crystal is similar to the behavior of electronic polarizabilities of isomorphic crystals of the $ABSO_4$ group [26–30].

Using relation (4), the value of the anisotropy coefficient was also determined based on measurements of temperature changes of refractive indices. The value f in this case corresponds to the refractive index. It was established that at room temperature the value of anisotropy is $A = 0.048$, and its temperature changes fully reproduce the changes in A calculated from the changes of $(\Delta l/l_0)_i$: the anisotropy decreases with temperature decreasing.

4. Conclusions

The work examines temperature changes in relative elongation and refractive indices of Rb_2SO_4 crystal in the region of low temperatures. It was found that as the temperature decreases, the linear dimensions and volume of the crystal decrease: $\frac{1}{l_0}\left(\frac{\Delta l}{\Delta T}\right) \sim 1.8 \cdot 10^{-7} \ldots 3.6 \cdot 10^{-7}$ K^{-1}, $\frac{1}{V_0}\left(\frac{\Delta V}{\Delta T}\right) \sim 7.2 \cdot 10^{-7}$ K^{-1}. It is shown that the parameters

$(\Delta l / l_0)_i$ are strongly anisotropic, the anisotropy value decreases as the temperature decreases.

It was established that with a decrease in temperature, the refractive indices n_i for all crystal physical directions increase at different rates ($dn_z/dT > dn_x/dT$), which leads to the intersection of the curves $n_z(T)$ and $n_x(T)$, so that at a temperature of $T = 85$ K the equality $n_z = n_x = 1.51936$ is observed. This indicates the existence of an optical isotropic point in this crystal, which is confirmed by independent temperature measurements of the angle between the optical axes. It is shown that rubidium sulfate crystals are optically biaxial; at room temperature the angle between the optical axes is $2V = 41.5°$, and with decreasing temperature it decreases almost linearly, so that at $T = 85$ K the crystal changes from optically biaxial to optically uniaxial ($2V = 0$).

The temperature changes of the values of electronic polarizability α_i were calculated, and it was shown that they slightly increase as the temperature decrease, so that in the region where the optical isotropic point exists, the values α_x and α_z are equal to each other. This behavior of $\alpha(T)$ of the rubidium sulfate crystal is similar to the behavior of electronic polarizabilities of isomorphic crystals of the ABSO$_4$ group.

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Дилатометричні та рефракційні параметри кристалів сульфату рубідію за умов низьких температур

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Досліджено температурні зміни відносного подовження $(\Delta l/l_0)_i$ та показників заломлення $n_i(T)$ кристалів сульфату рубідію в області низьких температур. Зі зниженням температури лінійні розміри та об’єм кристала зменшуються, а параметри $(\Delta l/l_0)_i$ є анізотропними. Значення n_i зростають зі зниженням температури для всіх фізичних напрямів кристала, і відбувається перетин кривих $n_z(T)$ та $n_x(T)$ при температурі $T = 85$ К. Це вказує на існування оптичної ізотропної точки в цьому кристалі, що підтверджується незалежними вимірюваннями температури кута між оптичними осями. Показано, що кристали сульфату рубідію оптично двовісні з кутом між оптичними осями $2V = 41{,}5°$ при кімнатній температурі. Зі зниженням температури вона зменшується майже лінійно, так що при $T = 85$ К кристал переходить від оптично двовісного до оптично одновісного ($2V = 0°$). Розраховано температурні зміни значень електронної поляризовності α_i. Показано, що зі зниженням температури α_i дещо зростає, тому в області наявності оптичної ізотропної точки значення α_x та α_z рівні між собою.

Ключові слова: кристал, лінійне розширення, анізотропія, показник заломлення, оптична ізотропна точка, кут між оптичними осями.