

# BARIC VARIATIONS OF THE OPTICAL PROPERTIES OF ROCHELLE SALT CRYSTALS

M.O. ROMANYUK, V.YO. STADNYK

UDC 535.323,535.53,537.226,548  
©2006

Ivan Franko Lviv National University  
(8, Kyrylo and Mefodii Str., Lviv 79005, Ukraine; e-mail: vasylstadnyk@ukr.net)

The influence of the uniaxial mechanical stress  $\sigma_m \leq 200$  bar on the spectral (300–800 nm) and temperature (77–320 K) dependences of the refractive indices  $n_i$  ( $i = x, y, z$ ) and the points of the birefringence sign inversion (BSI) of Rochelle salt (RS) crystals in the near infrared range has been studied. The parameters of the electron polarizabilities  $\alpha_i$  and refractions  $R_i$ , as well as the parameters  $\lambda_{0i}$  and  $B_{1i}$  of UV oscillators of mechanically clamped RS crystals, have been calculated. The temperature-spectral-baric diagram of the BSI points of RS crystals has been plotted. The anomalies of the birefringences  $\Delta n_i$  in the vicinity of 200 K and the differences between the dependences  $\Delta n_i(T)$  in nonpolar phases have been observed. These facts testify that the nonpolar phases are not identical, which is assumed to be caused by antipolarization. The baric changes of  $n_i(\sigma)$  have been demonstrated to be due to the variation of the oscillator concentration (by about 30%), the shift of the absorption band edge, the effective band maximum, and the oscillator strength (by about 70%).

## 1. Introduction

The influence of the pressure  $p$  upon the dielectric and optical properties of Rochelle salt  $\text{KNaCaH}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$  crystals has been studied in a number of works (see, e.g., works [1–4]), and the attention to such researches is renewed [5–8].

Under the action of hydrostatic pressure, the initial dielectric permittivity has been demonstrated to vary, the upper Curie point to be shifted by 0.0107 K/atm, and the lower one by 0.0038 K/atm, so that the interval where the polar phase exists becomes narrower. If a specimen is subjected to uni- or biaxial squeezing conjugated to its spontaneous deformation, the dielectric hysteresis loops become asymmetric and distorted. At high pressures, they degenerate into a straight line with a slope close to that of the saturation section of the hysteresis loop of a free specimen. By analyzing the baric dependence of the temperature, at which the domains disappear, the Curie temperature of the specimens with the faces at  $45^\circ$  to their axes has been found to increase, if those specimens are subjected to the uniaxial squeezing, and to decrease in the case of the biaxial squeezing. The numerical values that were

obtained for  $\partial T/\partial p$  substantially differ from the data deduced from dielectric measurements [1], but agree with the data of work [8].

A lot of attention has been paid recently to the theoretical study of how the pressure influences the dielectric properties of ferroics, including RS crystals [5–9]. It has been shown that, while considering the Mitsui model, the account of terms connected to the shear deformation  $\varepsilon_4$  improves the agreement between theoretical results and experimental data for spontaneous polarization and provides the correct temperature behavior of the relaxation times and the dynamic dielectric permittivity of RS in the vicinity of the phase transition (PT) point. The influence of various factors on the dielectric permittivity of RS crystals and the positions of their PT points have been studied in work [8].

In work [9], the influence of a uniaxial stress on the birefringence in RS crystals has been investigated, and the temperature and the spectral dependences of their absolute and combined piezooptic coefficients, as well as the BSI points, in the UV range of the spectrum have been found.

This work aims at studying the influence of uniaxial stresses on the spectral and temperature variations of the refractive indices of RS crystals and the shifts of their BSI points in the IR range of the spectrum.

## 2. Experimental technique

The baric variations of the refractive indices  $n_i(\lambda, T)$  ( $i = x, y, z$ ) were calculated, making use of the known temperature and spectral dependences of the absolute piezooptic coefficients  $\pi_{im}$  [9] and the refractive indices  $n_{io}$  of a mechanically free crystal [10], by the relationship

$$n_i(\lambda, T) = n_{io}(\lambda, T) - 1/2\pi_{im}(\lambda, T)\sigma_m n_{io}^3(\lambda, T). \quad (1)$$

The birefringences  $\Delta n_i$  were calculated by analyzing the interference pattern created by polarized rays, the extrema  $k$  of which were determined by the difference

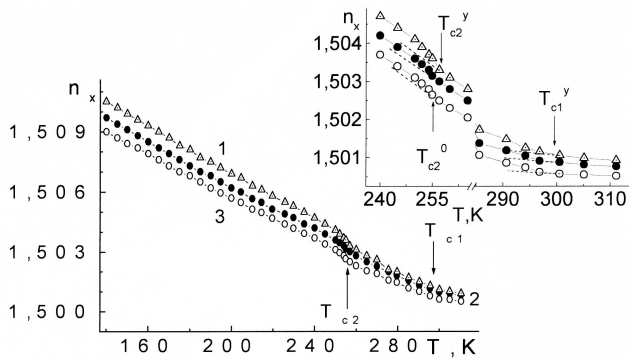


Fig. 1. Temperature dependences of the refractive index  $n_x$  of an RS crystal at  $\lambda = 500$  nm:  $\sigma_y = 200$  bar (1),  $\sigma_z = 200$  bar (2), and  $\sigma_i = 0$  (3). The temperature variations of  $n_x$  in the vicinity of the PT point are shown in the inset

between the optical paths

$$\Delta n_i = d(n_j - n_m) = k\lambda, \quad (2)$$

with the temperature dependence of the crystal thickness  $d$  in the translucence direction being taken into account [11]. The positions of the PT points were found by considering the anomalies observed in the  $\Delta n_i(T)$  dependences, and the BSI points by the conditions  $\Delta n_i = 0$ .

### 3. Results and Their Discussion

#### 3.1. Influence of Uniaxial Stresses on the Refractive Indices of RS Crystals

The uniaxial mechanical stresses along various crystallophysical axes were found to be responsible for the changes of the refractive indices  $\delta n_i$  different by amplitude and sign; in particular, we determined that  $\delta n_z(\sigma_y = 200 \text{ bar}) = 4.1 \times 10^{-5}$ ,  $\delta n_z(\sigma_x = 200 \text{ bar}) = -3.9 \times 10^{-5}$ ,  $\delta n_y(\sigma_z = 200 \text{ bar}) = 3.7 \times 10^{-5}$ , and  $\delta n_y(\sigma_x = 200 \text{ bar}) = -3.1 \times 10^{-5}$ .

In Fig. 1, the temperature dependences of the parameter  $n_x$ , which were obtained provided that the RS crystal was subjected to the action of the  $\sigma_z$  or the

**Table 1.** Spontaneous increments of the refractive indices  $\delta n_i$  of RS crystals in the vicinity of their PT point at  $\lambda = 500$  nm and for various directions of the stress application ( $\sigma_m = 200$  bar)

$T, \text{K}$	$\sigma_x$		$\sigma_y$		$\sigma_z$	
	250	290	250	290	250	290
$\delta n_x$			2.6	2.7	3.7	3.1
$\delta n_y$	3.4	3.1			4.2	4.0
$\delta n_z$	2.7	2.2	1.7	1.1		

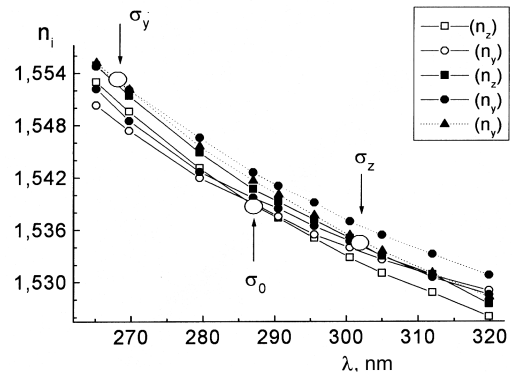


Fig. 2. Dispersion curves of the refractive indices of an RS crystal in the vicinity of the BSI point for various applied stresses:  $\sigma_z$  (solid) and  $\sigma_y$  (dotted curves). The measurements were done at room temperature. Hollow points correspond to the mechanically free crystal, and solid points to the mechanically clamped one

$\sigma_y$  stress of 200 bar, are shown. The temperature variations of  $n_i$  are nonlinear, with  $dn_i/dT < 0$  and  $|dn_y/dT| < |dn_x/dT| \approx |dn_z/dT|$  within the whole investigated spectral and temperature ranges. At the PT points, there are certain anomalies in the dependence  $n_i(T)$ , which are connected with the spontaneous electrooptical effect (EOE).

The spontaneous increments  $\delta n_x$  of the refractive index  $n_x$  for a mechanically free RS crystal are somewhat smaller than those for a clamped one:  $\delta n_x = 3.1 \times 10^{-4}$ ,  $2.7 \times 10^{-4}$ , and  $2.4 \times 10^{-4}$  at  $T = 290$  K, and  $\delta n_x = 3.7 \times 10^{-4}$ ,  $2.6 \times 10^{-4}$ , and  $1.8 \times 10^{-4}$  at  $T = 250$  K for the stresses  $\sigma_z = 200$  bar,  $\sigma_y = 200$  bar and  $\sigma_i = 0$ , respectively.

The slopes of the linear sections of the curves  $n_i(T)$  for the high- and low-temperature phases do not coincide. In particular, at  $T < T_{c1}$ ,  $dn_x/dT = 0.77 \times 10^{-5}$  for  $\sigma_i = 0$  and  $1.61 \times 10^{-5}$  for  $\sigma_y = 200$  bar, whereas, at  $T < T_{c2}$ , this quantity amounts to  $6.25 \times 10^{-5}$  for  $\sigma_i = 0$  and  $6.68 \times 10^{-5}$  for  $\sigma_y = 200$  bar; i.e. the slopes are steeper in the low-temperature phase, which can be explained by the spontaneous antipolarization and its baric dependence and testifies that those phases are not identical. The baric dependence of the spontaneous antipolarization can be calculated, making use of the knowing piezooptic coefficients and the measured values for  $\Delta n_i$  or  $n_i$ . The BSI point is the third characteristic temperature of RS crystals.

In Fig. 2, the fragments of the spectral dependences of  $n_i$  of an RS crystal in the vicinity of its BSI point ( $\lambda_0 \approx 287$  nm) are depicted. The figure demonstrates that, as the specimen is subjected to the  $\sigma_y$  or  $\sigma_z$  stress,

the curves  $n_i(\lambda)$  elevate, and the BSI point moves along the spectrum: at  $\sigma_z = 200$  bar,  $n_z = n_y = 1.53465$  and  $\lambda_0 \approx 302$  nm; whereas at  $\sigma_y = 200$  bar,  $n_z = n_y = 1.55342$  and  $\lambda_0 \approx 268$  nm. Below the BSI point, the dispersion of the dependence  $n_i(\lambda)$  is smaller than that above  $\lambda_0$ . For clamped specimens, this difference becomes more pronounced.

Consider the correlation between the  $n_i(\lambda, \sigma)$  dependences and other characteristics of the crystal, which follow from the Selmeier dispersion formula and the Lorenz-Lorentz formula, the latter describing the refraction  $R$  and the electron polarizability  $\alpha$ :

$$n_i^2 = 1 + \frac{B_{1i}\lambda^2\lambda_{01}^2}{\lambda^2 - \lambda_{01}^2} + \frac{B_{2i}\lambda^2\lambda_{02}^2}{\lambda_{02}^2 - \lambda^2}, \quad (3)$$

$$\alpha = \frac{3}{4\pi N} \frac{n^2 - 1}{n^2 + 2}, \quad (4)$$

$$R = 4\pi/3N_A\alpha = \frac{\mu}{\rho} \frac{n^2 - 1}{n^2 + 2}. \quad (5)$$

Here,  $N$  is the number of particles per unit volume;  $N_A$  the Avogadro constant;  $\mu$  the molar mass;  $\rho$  the density of the crystal;  $\lambda_{01}$  and  $\lambda_{02}$  are the wavelengths at the maxima of the absorption bands of UV and IR oscillators, respectively;  $B_1 = \frac{e^2 f}{\pi m c_0^2}$  is the effective strength of an UV oscillator;  $e$  and  $m$  are the electron charge and mass, respectively;  $c_0$  is the speed of light in vacuum; and  $f$  the oscillator strength.

Making use of the obtained dependences  $n_i(\lambda, \sigma)$  and the formulas displayed above, we calculated the values of the parameters which are quoted in Table 2. One can see from the table that, at stresses of about 200 bar, the parameters  $\alpha_i$  increase by about of  $2 \times 10^{-26}$  cm<sup>3</sup> on the average, which coincides, by the order of magnitude, with baric variations of the specimen's volume and its linear dimensions along the squeezing direction calculated on the basis of the Hooke law

$$(\Delta l/l_0)_i = s_{im}\sigma_m, \quad (6)$$

where  $(\Delta l/l_0)_i$  are the relative stretchings, and  $s_{im}$  the components of the elastic compliance tensor. Provided that  $\sigma_m \approx 200$  bar and  $s_{im} \approx 10^{-11}$  m<sup>2</sup>/N [12], we obtain that  $(\Delta l/l_0)_i \approx 10^4$ .

From Eq. (5), we obtain the relationship

$$\frac{dR}{d\sigma} = - \left( \frac{\mu}{\rho^2} \frac{n^2 - 1}{n^2 + 2} \frac{d\rho}{d\sigma} \right)_n + \left( \frac{\mu}{\rho} \frac{6n}{(n^2 + 2)^2} \frac{dn}{d\sigma} \right)_N \quad (7)$$

which allows the contributions of the components, which include the derivatives  $\partial\rho/\partial\sigma$  and  $\partial n/\partial\sigma$ , to the baric variations of  $R_i$  to be evaluated. Using the numerical data  $\mu = 282$  g/mol,  $\rho \approx 1.56$  g/cm<sup>3</sup>,  $\partial\rho/\partial\sigma \approx s_{im} = 0.4 \times 10^{-10}$  bar<sup>-1</sup>,  $n_i = 1.5$ , and  $\partial n/\partial\sigma \approx 5 \times 10^{-6}$  bar<sup>-1</sup>, we obtain  $2 \times 10^{-4}$  bar<sup>-1</sup> for the first term in Eq. (7) and  $4.8 \times 10^{-4}$  bar<sup>-1</sup> for the second, i.e. the contribution of the geometrical factor is about 30% of the total baric increment of  $R$ .

On the basis of the Selmeier formula for a single oscillator, we obtain

$$\frac{\partial n}{\partial \sigma} \approx \frac{1}{2n} \frac{e^2}{\pi m c_0^2} \left\{ \frac{\lambda^2 \lambda_0^2}{\lambda^2 - \lambda_0^2} \left[ f \frac{\partial N}{\partial \sigma} + N \frac{\partial f}{\partial \sigma} \right] + \frac{2Nf\lambda_0\lambda^4}{(\lambda^2 - \lambda_0^2)^2} \frac{\partial \lambda_0}{\partial \sigma} \right\} = 0,03 \frac{\partial f}{\partial \sigma} + 10^{-7} f + 3 \cdot 10^{-6} f \frac{\partial \lambda_0}{\partial \sigma}, \quad (8)$$

whence it follows that the dominating contributions to the baric variations of the refractive indices are given by the components that include the derivatives  $\partial\rho/\partial\sigma$  and  $\partial n/\partial\sigma$ .

Knowing the baric variations of the refractive indices  $n_i$  enables the corresponding alterations of the energy gap width  $E_g$  to be estimated by Moss's relationship [13]

$$n^4 E_g = \text{const}, \quad (9)$$

whence it follows that

$$\frac{\partial E_g}{\partial \sigma} = - \frac{4}{n} E_g \frac{\partial n}{\partial \sigma}. \quad (10)$$

**Table 2.** Baric dependences of the electron polarizability  $\alpha_i$ , the specific refraction  $R_i$  at  $\lambda = 500$  nm, and the parameters of effective oscillators in the Selmeier single-oscillator formula for an RS crystal at  $T = 294$  K

Parameters	$\sigma_i=0$	$\sigma_x=200$ bar	$\sigma_y=200$ bar	$\sigma_z=200$ bar
$\alpha_x \times 10^{24}$ , cm <sup>3</sup>	18.370	18.395	18.396	18.394
$\alpha_y \times 10^{24}$ , cm <sup>3</sup>	18.260	18.305	18.312	18.291
$\alpha_z \times 10^{24}$ , cm <sup>3</sup>	18.190	18.407	18.412	18.394
$R_x$ , cm <sup>3</sup>	46.351	46.370	46.369	46.368
$R_y$ , cm <sup>3</sup>	46.081	46.113	46.097	46.092
$R_z$ , cm <sup>3</sup>	45.896	46.001	45.912	45.994
$\lambda_{0x}$ , nm	109.67	109.38	108.95	109.92
$\lambda_{0y}$ , nm	105.60	106.31	106.10	106.24
$\lambda_{0z}$ , nm	108.99	108.28	109.89	108.56
$B_x \times 10^6$ , nm <sup>-2</sup>	100.1	100.5	101.2	100.0
$B_y \times 10^6$ , nm <sup>-2</sup>	108.8	107.8	110.1	111.1
$B_z \times 10^6$ , nm <sup>-2</sup>	102.6	104.2	101.9	103.1

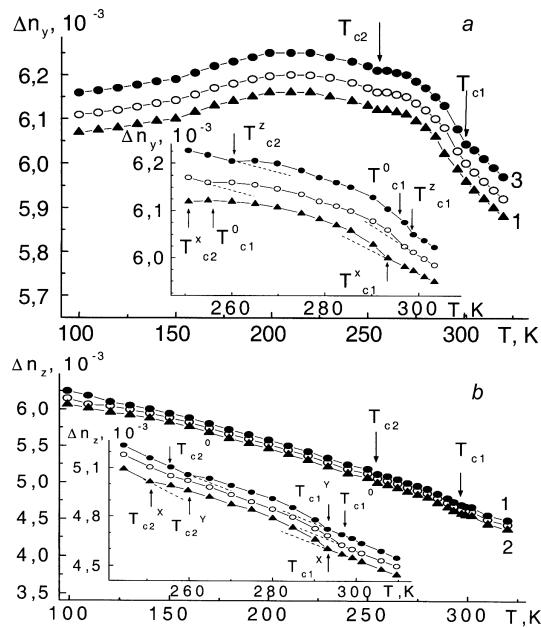


Fig. 3. Temperature variations of the birefringences  $\Delta n_y$  (a) and  $\Delta n_z$  (b) of the RS crystals at  $\lambda = 500$  nm for various directions of a 200-bar stress:  $\sigma_x$  (1),  $\sigma_y$  (2), and  $\sigma_z$  (3). Hollow points correspond to the mechanically free specimen, and solid points to the mechanically clamped one. The variations  $\Delta n_y$  and  $\Delta n_z$  in the vicinity of the PT points  $T_{c1}$  and  $T_{c2}$  are shown in the insets

Taking the known values  $\partial n/\partial \sigma \approx \times 10^{-6} \text{ bar}^{-1}$ ,  $n_i \approx 1.5$ , and  $E_g \approx 5.1 \text{ eV}$  into account, we find  $\partial E_g/\partial \sigma \approx 2 \times 10^{-5} \text{ eV/bar}$ , which agrees with the results of the direct studies of the baric shift of the fundamental absorption edge of an RS crystal.

In order to determine the baric shift of the fundamental absorption edge of RS, we repeated the routine of measuring the absorption in the range of phonon manifestations [14], using the clamped specimens, and revealed the following. For a free RS crystal,  $E_{gx} = 5.125 \text{ eV}$ ,  $E_{gy} = 5.152 \text{ eV}$ , and  $E_{gz} = 5.162 \text{ eV}$ . At the same time, the energy gap width  $E_{gx}$  amounts to 5.121 eV if  $\sigma_z = 200$  bar and to 5.119 eV if  $\sigma_y = 200$  bar, i.e.  $\partial E_g/\partial \sigma_z = 2 \times 10^{-5} \text{ eV/bar}$  and  $\partial E_g/\partial \sigma_y = 3 \times 10^{-5} \text{ eV/bar}$ .

The baric shift of the effective UV oscillator –  $\partial \lambda_0/\partial \sigma \approx (2 \div 4) \times 10^{-2} \text{ \AA/bar} \approx 25 \times 10^{-5} \text{ eV/bar}$  – turned out larger, which may be connected with its “location” in a higher-energy interval of the spectrum as compared to that of a real one (at about 7 eV). Therefore, its displacement has to be formally larger in order to achieve the agreement with experiment.

### 3.2. Influence of uniaxial stresses on the birefringences in and the BSI points of the RS crystals

In Fig. 3, the temperature variations of the birefringences  $\Delta n_y$  and  $\Delta n_z$  of RS crystals are plotted. As is seen from the figure, the variation  $\Delta n_y$  is characterized by a complicated behavior: as the temperature decreases, the dependence  $\Delta n_y(T)$  grows, reaches the maximum at  $T \approx 200$  K, and starts to fall down. In the case of the  $\Delta n_z(T)$  dependences, such features are less pronounced. The temperature, at which the change of the sign of the temperature factor of birefringence  $d\Delta n_y/dT$  ( $d\Delta n_y/dT \approx -5.35 \times 10^{-7} \text{ K}^{-1}$  at  $T > 200$  K and  $+8.85 \times 10^{-7} \text{ K}^{-1}$  at  $T < 200$  K) is observed, coincides with the temperature of abnormal variations of other parameters of the crystal [15–17], which evidences for the existence of the third critical temperature in RS crystals.

Some insignificant anomalies in  $\Delta n_y$  and  $\Delta n_z$  are also observed in the vicinity of the PT points, being more manifested at the lower-temperature PT. The slopes of the linear sections of the high-temperature ( $d\Delta n_y/dT = -0.416 \times 10^{-6} \text{ K}^{-1}$  and  $d\Delta n_z/dT = -9.13 \times 10^{-6} \text{ K}^{-1}$ ) and low-temperature ( $d\Delta n_y/dT = -7.71 \times 10^{-6} \text{ K}^{-1}$  and  $d\Delta n_z/dT = -0.301 \times 10^{-6} \text{ K}^{-1}$ ) paraphases are different, which may testify that those phases are not identical.

In their turn, the anomalies in the temperature behavior of the quantities  $\Delta n_y$  and  $\Delta n_z$  evidence for a certain “non-homogeneity” of the low-temperature RS phase.

The uniaxial stresses do not affect the dependences  $\Delta n_i$  qualitatively: the curves  $\Delta n_y(T)$  become either elevated ( $\sigma_z \neq 0$ ) or lowered ( $\sigma_x \neq 0$ ); similarly, the curves  $\Delta n_z(T)$  become shifted towards either greater ( $\sigma_x \neq 0$ ) or smaller ( $\sigma_y \neq 0$ ) birefringence values. The slopes of the curves for the high-temperature paraphase also vary:  $d\Delta n_y/dT = -4.28 \times 10^{-7}$  and  $-4.02 \times 10^{-7} \text{ K}^{-1}$  for the stresses  $\sigma_z$  and  $\sigma_x$ , respectively; and  $d\Delta n_z/dT = -9.25 \times 10^{-7}$  and  $-9.01 \times 10^{-7} \text{ K}^{-1}$  for the stresses  $\sigma_y$  and  $\sigma_x$ , respectively.

The uniaxial stresses displace the PT points considerably. In particular, the point  $T_{c1}$ , under the influence of the 200-bar stress  $\sigma_x$  or  $\sigma_z$ , becomes shifted towards a lower ( $T_{c1} = 295.1 \text{ K}$ ) or a higher ( $T_{c1} = 299.3 \text{ K}$ ) temperature, respectively. In this case, the corresponding baric coefficients of the PT point displacement amount to  $\partial T_{c1}/\partial \sigma_x \approx -0.012 \text{ K/bar}$  and  $\partial T_{c1}/\partial \sigma_z \approx +0.098 \text{ K/bar}$ .

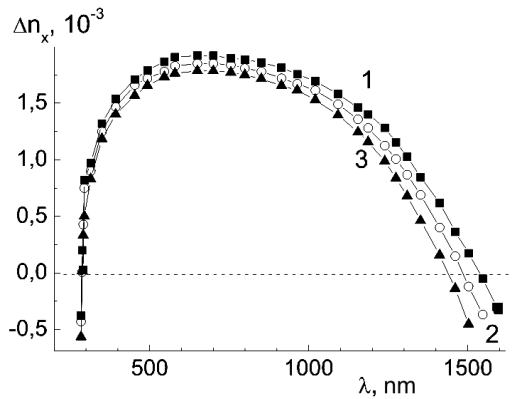


Fig. 4. Dispersion curves for the birefringence  $\Delta n_x$  of an RS crystal at room temperature for various directions of the uniaxial stress  $\sigma_m = 150$  bar:  $\sigma_z$  (1),  $\sigma = 0$  (2), and  $\sigma_y$  (3)

The BSI of RS crystals reveals itself along the  $X$  axis. In accordance to that, the spectral dependences of  $\Delta n_x$  in RS crystals subjected to the uniaxial  $\sigma_y$  or  $\sigma_z$  stress at room temperature are depicted in Fig. 4. The figure shows that, as the light wavelength grows, the amplitude of  $\Delta n_x$  increases drastically; at  $\lambda \approx 500$  nm, the dispersion  $d\Delta n_x/d\lambda$  decreases substantially; and, within the range  $\lambda \approx 610 \div 690$  nm,  $\Delta n_x$  remains almost constant ( $d\Delta n_x/d\lambda \approx 0$ ).

The further increase of the wavelength results in reducing  $\Delta n_x$  and growing its dispersion ( $d\Delta n_x/d\lambda = 1.23 \times 10^{-6} \text{ nm}^{-1}$ ). The extrapolation of the curve obtained until it intersects the straight line  $\Delta n_x = 0$  enabled us to determine the position of the second BSI point, namely,  $\lambda_{02} \approx 1490$  nm at room temperature.

Since the stresses along  $Z$  and  $Y$  axes bring about the variations  $\Delta n_x$ , which are different by sign and amplitude, the spectral position of the BSI points is also changed. In Fig. 5, the baric displacements of the BSI points in the near UV [17] and IR ranges are shown. The figure demonstrates that the uniaxial stress  $\sigma_y$  shifts the UV BSI point towards the long-wave range at a rate  $d\lambda_0/d\sigma_y = 0.0725 \text{ nm/bar}$ , and the IR BSI point towards short waves ( $d\lambda_0/d\sigma_y = -0.095 \text{ nm/bar}$ ).

Extrapolating the obtained dependences  $\lambda_0 = f(\sigma_m)$  or solving the equation

$$\lambda_{01} + (d\lambda_{01}/d\sigma)\sigma_y = \lambda_{02} + (d\lambda_{02}/d\sigma)\sigma_y, \quad (11)$$

provided that  $d\lambda_{0i}/d\sigma$  are constant, one can establish that, if the stress  $\sigma_y \approx 7.2$  kbar is applied, these BSI points “merge” together at  $\lambda_{02} \approx 810$  nm. A similar situation occurs in  $(\text{NH}_4)_2\text{BeF}_4$  crystals, but it is realized there through varying the temperature of the specimen [18].

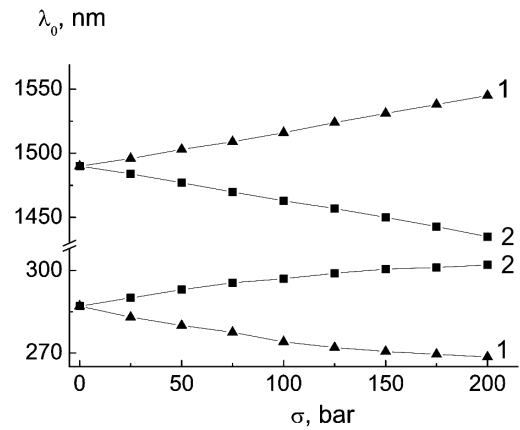


Fig. 5. Baric displacements of the BSI points of an RS crystal at  $T = 294$  K:  $\sigma_z$  (1) and  $\sigma_y$  (2)

The uniaxial stress  $\sigma_z$  moves, on the contrary, the BSI points apart: the first point makes its way towards the UV-range at a rate  $d\lambda_{01}/d\sigma = -0.094 \text{ nm/bar}$ , and the second towards the IR-range at a rate  $d\lambda_{02}/d\sigma = 0.185 \text{ nm/bar}$ .

The temperature variation also stimulates the shift of the BSI points. Therefore, we may draw a conclusion that the IR BSI point should shift towards the long-wave range of the spectrum if the temperature would rise, and towards the visible spectral range otherwise. The evaluation of the temperature-induced displacements of the BSI points of the RS crystal showed that, provided  $T \approx 332$  K, they should coincide at  $\lambda_0 \approx 737$  nm, and, in such a case, a “double” BSI point would emerge, as it does in FBA crystals [18]. However, RS crystals do not withstand the heating above 340 K and the uniaxial stresses of about 8 kbar; therefore, one may only talk about a hypothetical “double BSI point” in the RS crystal.

The corresponding temperature-spectral diagram for the UV BSI point of RS crystals is already known [17]. The temperature-induced displacement for the IR BSI point can be determined on the basis of the known temperature dependences of  $\Delta n_x$ . Taking advantage of the obtained baric dependences of the spectral position of the IR BSI point and the known diagram for the UV BSI one, we have plotted the temperature-spectral-baric diagram of the isotropic state of the RS crystal in the wide temperature (77–300 K), spectral (240–2300 nm), and baric (0–200 bar) ranges (see Fig. 6), which may be of use while applying this crystal as a crystalloptical sensor of temperature and pressure.

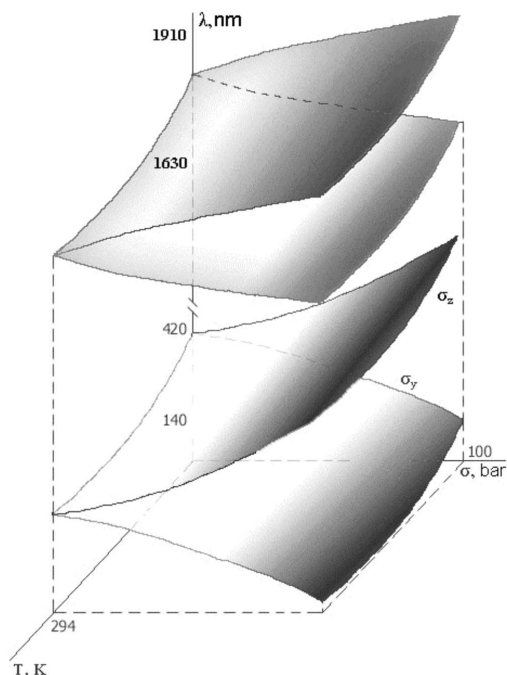


Fig. 6. Temperature-spectral-baric diagram of the isotropic state of the RS crystal

#### 4. Conclusions

In this work, the baric variations of the refractive indices have been studied, the BSI point in the near IR-range has been investigated, and the electron polarizabilities  $\alpha_i$  and refractions  $R_i$ , as well as the parameters  $\lambda_{0i}$  and  $B_{1i}$  of UV oscillators, of mechanically deformed RS crystals have been calculated. On the basis of the results obtained, it has been found that the uniaxial stresses increase the refractions  $R_i$  and the polarizabilities  $\alpha_i$  and modify the parameters of effective oscillators.

It has been shown that the growth of the refractive index under the action of a uniaxial stress is mainly caused by the growth of the refractions (about 70% of the total effect), which takes place owing to the change of the energy gap width  $E_g$  ( $dn/d\sigma \approx 10^{-6} \text{ bar}^{-1}$  and  $dE_g/d\sigma \approx 2 \times 10^{-5} \text{ eV/bar}$ ) and the long-wave shift of the UV absorption band maximum, and the concentration of effective oscillators (about 30% of the total effect) in the RS crystal.

The displacement of the IR BSI point under the influence of uniaxial stresses has been studied, which enabled us to describe a wide range of the spectrum by varying the amplitude and the direction of the specimen squeezing. The anomalies of  $\Delta n_i$  at  $T \approx 200 \text{ K}$  have been

revealed, and the nonidentity of non-polar RS phases, as well as the possibility of antiferroelectric ordering in the low-temperature phase, has been confirmed.

1. *Mason W.P.* Piezoelectric Crystals and Their Applications to Ultrasonics. — Princeton, New Jersey: D. Van Nostrand, 1950.
2. *Zheludev I.S., Romanyuk N.A.* // *Kristallogr.* — 1959. — **4**, N 5. — P. 710–717.
3. *Zheludev I.S., Romanyuk N.A.* // *Ibid.* — 1966. — **11**, N 4. — P. 610–613.
4. *Mori K., Hayashi M.* // *J. Phys. Soc. Jap.* — 1974. — **33**, N 5. — P. 1396–1400.
5. *Levitskii R.R., Zachek I.R., Verkholyak T.M., Moina A.P.* // *Cond. Matter Phys.* — 2003. — **6**, N 2(34). — P. 261–270.
6. *Levitskii R.R., Zachek I.R., Moina A.P., Andrusyk A.Ya.* // *Ibid.* — 2004. — **7**, N 1(37). — P. 111 – 139.
7. *Levitskii R.R., Zachek I.R., Verkholyak T.M., Moina A.P.* // *Phys. Rev. B.* — 2003. — **67**. — P. 174112-1 – 174112-12.
8. *Slivka A.G., Kedyulich V.M., Levitskii R.R. et al.* // *Cond. Matter Phys.* — 2005. — **8**, N 3. — P. 623–638.
9. *Stadnyk V.Yo., Romanyuk M.O., Vakhulovych V.F.* // *Ukr. Fiz. Zh.* — 1997. — **42**, N 10. — P. 1245–1251.
10. *Gaba V.M., Kostetskii A.M., Romanyuk N.A.* // *Kristallogr.* — 1989. — **34**, N 4. — P. 1041 – 1043.
11. *Romanyuk N.A., Kostetskii A.M.* // *Fiz. Tverd. Tela.* — 1976. — **18**. — P. 206–209.
12. ???
13. *Moss T.S.* Optical Properties of Semiconductors. — New York: Academic Press, 1959.
14. *Romanyuk A.M., Viblyi I.F.* // *Opt. Spekr.* — 1976. — **41**, N 6. — P. 1011–1014.
15. *Gaba V.M., Romanyuk N.A., Franiv A.V.* // *Ukr. Fiz. Zh.* — 1982. — **27**, N 3. — P. 333–338.
16. *Poplavko Yu.M., Slesarenko N.V., Pasechnik L.A.* // *Fiz. Tverd. Tela.* — 1985. — **27**. — P. 1248.
17. *Dey P.K., Som K.K., Chowdhury K.R. et al.* // *Phys. Rev. B.* — 1993. — **47**, N 6. — P. 3001–3004.
18. *Romanyuk M.O., Stadnyk V.Y.* // *Ferroelectrics.* — 1997. — **192**, N 1–4. — P. 235–241.

Received 07.12.05.

Translated from Ukrainian by O.I. Voitenko

#### БАРИЧНІ ЗМІНИ ОПТИЧНИХ ВЛАСТИВОСТЕЙ КРИСТАЛІВ СЕГНЕТОВОЇ СОЛІ

*М.О. Романюк, В.Й. Стадник*

#### Резюме

Досліджено вплив одновісного механічного тиску  $\sigma_m \leq 200$  бар на спектральну (300–800 нм) і температурну (77–320 К) залежності показників заломлення  $n_i$  і точку інверсії знака двопронезаломлення (ІЗД)  $\Delta n_i$  кристалів сегнетової

солі в близькій інфрачервоній ділянці спектра. Розраховано електронні поляризованості  $\alpha_i$ , рефракції  $R$  та параметри ультрафіолетових осциляторів ( $\lambda_{0i}$ ,  $B_{1i}$ ) механічно затиснутих кристалів. Побудовано температурно-спектрально-баричну діаграму ІЗД кристалів сегнетової солі. Виявлено аномалію  $\Delta n_i$  в околі 200 К та відмінності  $\Delta n_i(T)$  у

неполярних фазах, що свідчать про їх неідентичність та пов'язуються з наявністю антиполяризації. Показано, що баричні зміни  $n_i(\sigma)$  зумовлені змінами концентрації осциляторів (на 30%), зміщенням краю поглинання і максимуму ефективної смуги та збільшенням сили осцилятора (на 70%).