
STUDY OF INCOMMENSURATE PHASE OF K_2ZnCl_4 CRYSTALS UNDER UNIAXIAL STRESSES
V.YO. STADNYK,¹ Z.O. KOHUT,² R.S. BREZVIN,¹ V.M. GABA,² I.M. MATVIISHYN¹
¹**Ivan Franko Lviv National University**
(8, Kyrylo and Mefodii Str., Lviv 79005, Ukraine; e-mail: vasylstadnyk@ukr.net)
²**National University "Lviv Politechnika"**
(13, Bandery Str., Lviv 79066, Ukraine)

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The influence of uniaxial stresses applied along the main crystallophysical directions of K_2ZnCl_4 crystals on the temperature dependences of birefringence Δn_i and refractive indices n_i of the crystals in the range of their phase transitions that includes the incommensurate phase has been studied. Both parameters, Δn_i and n_i , were found to be sensitive to the action of the uniaxial pressure. Considerable pressure-induced shifts of phase transition points toward different temperature regions at the paraphase–incommensurate and incommensurate–commensurate ferroelectric phase transitions were observed. The displacements were found to depend on the uniaxial stress direction, which can be explained by the influence of the applied pressure on the structure of K_2ZnCl_4 crystals.

1. Introduction

Crystals of potassium tetrachlorozincate (PTCZ), K_2ZnCl_4 , are typical representatives of one-dimensionally modulated incommensurate structures of the A_2BX_4 type. They undergo a sequence of phase transitions, which is standard for such crystals: a paraphase (PP, mmm , $Z = 4$, $T_i = 555$ K) \rightarrow an incommensurate phase (IP, $T_c = 403$ K) \rightarrow a commensurate ferroelectric phase (CP, $P2_1cn(mm2)$, $\mathbf{q} = \mathbf{c}^*/3$, $Z = 12$) [1, 2]. High-temperature phase I of PTCZ crystal is paraelectric with the spatial group $Pm\bar{c}n$, similar to the crystals of β - K_2SO_4 group. Intermediate phase II ($T_c < T < T_i$) is incommensurately modulated in the c -direction by the wave vector $\mathbf{q} = (1 - \delta)\mathbf{c}^*/3$. Low-temperature phase III ($T < T_c$) is a non-intrinsic ferroelectric with a spontaneous polarization directed

along the b -axis and a triple elementary cell parameter along the pseudohexagonal c -axis.

The IP of PTCZ crystal was identified by the position of satellite peaks in the X-ray reflection spectra and using the neutron diffraction method [3, 4]. The authors found that the atomic displacements caused by modulation waves are rather large for chlorine atoms. This originates from the fact that, at the phase transition phase I–phase II, a substantial bending of a tetrahedron $ZnCl_4$ is observed.

The phase transition PP–IP in PTCZ crystals is associated with the phonon condensation at the point q of the Brillouin zone, and this mode has a relaxation character in this case. In K_2ZnCl_4 crystals, the temperature of the existence of the IP is rather high, which weakens long-range correlations between atomic displacements. That is why the temperature dependence of the order parameter, $\delta(T)$, is very weak here. In crystals with some disordering, long-range correlations between ionic displacements are small. Therefore, the structure ordering weakly affects the character of the region distribution in space, until the ordering level becomes high enough [5–7].

This work aimed at studying the behavior of phase transitions in PTCZ crystals subjected to the uniaxial stress by examining the temperature dependences of the birefringence and refractive indices.

Earlier, the influence of the hydrostatic pressure on the PP–IP–CP phase transition in a K_2ZnCl_4 crystal was studied, by using the differential thermal analysis [8]. The PP–IP phase transition point was found to shift toward higher temperatures with increase in the pres-

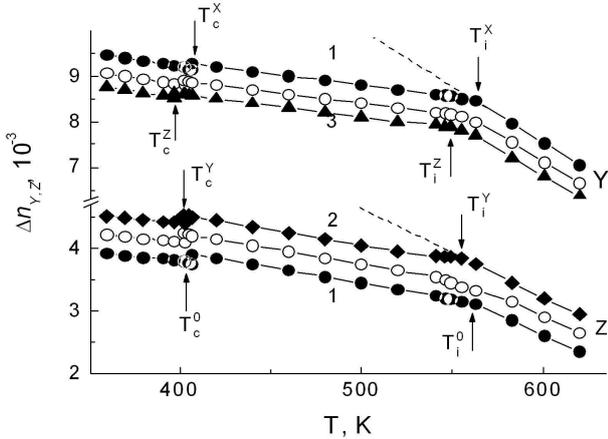


Fig. 1. Temperature dependences of birefringence in K_2ZnCl_4 crystals at $\lambda = 500$ nm for various uniaxial squeezings. Hollow symbols correspond to a mechanically free crystal, solid symbols to a mechanically gripped crystal with $\sigma_x = 200$ bar (1), $\sigma_y = 200$ bar (2), and $\sigma_z = 200$ bar (3)

sure ($dT_i/dp = 110$ K/GPa), whereas the IP-CP one toward lower temperatures ($dT_c/dp = -86.2$ K/GPa). The authors established the following baric dependence of the temperature T_c : $T_c = T_c^0 + Kp + \gamma p^2$, where $T_c^0 = (400 \pm 0.2)$ K, $K = -(86.2 \pm 0.9)$ K/GPa, and $\gamma = (37 \pm 1)$ K/(GPa)². The baric coefficient of -86.2 K/GPa obtained in this work for the K_2ZnCl_4 crystal is similar to its counterpart for Rb_2ZnCl_4 crystals (-48 K/GPa) [9].

Earlier [10, 11], we studied the influence of the uniaxial pressure on the spectral and temperature dependences of the birefringence and refractive indices in a number of crystals that are isomorphic to PTCZ ones. We established a substantial baric sensitivity of the electron subsystem of those crystals, which manifested itself in a significant displacement of effective bands of ultra-violet and infra-red oscillators in their energy spectrum.

2. Experimental Technique

The crystals of PTCZ were grown up from an aqueous solution using the slow cooling method. The grown crystals looked like rhombic prisms with a large number of crystal faces.

The temperature variations of the birefringence were studied by analyzing changes in the interference pattern of polarized beams which was registered with the help of a KSVU-23 spectral system. A specimen to be studied was mounted in an electric furnace into the diagonal position between crossed nicols. The passage of a white

light beam through this system was accompanied by an emergence of an interference pattern in the focal plane of a spectrograph. A condition for the interference extrema to appear in the spectrum is the relation

$$d(n_i - n_j) = k\lambda,$$

where k is the order of interference maximum; d is the specimen thickness along the beam direction; and n_i and n_j are the refractive indices in crystallophysical directions i and j , respectively.

In the case of the uniaxial squeezing of a specimen—it was carried out with a special device—the spectral shift of interference bands related to a change of the birefringence was observed. In this case, the pressure dependence of Δn_i is determined by the relation

$$\Delta n_i(\lambda, \sigma_i) = \frac{k\lambda}{d(\sigma)}$$

The measurements were carried out up to pressures $\sigma_i \sim 200$ bar. The measurement error for the birefringence was $\delta\Delta n_i = \pm 2 \times 10^{-5}$.

3. Results of Researches and Their Discussion

3.1. Baric changes of birefringence

We found that the birefringence in PTCZ crystals is sensitive to the action of uniaxial pressures oriented along the main crystallophysical directions, being less sensitive if the pressure is applied along bisectors between them. We found that the stresses σ_m give rise to different, by sign, changes of the birefringence Δn_i . In particular, the uniaxial squeezing σ_y increases Δn_z and decreases Δn_x ; whereas σ_z increases the birefringence in the X -direction and decreases it in the Y -direction.

In Fig. 1, the temperature dependences of birefringence Δn_i in PTCZ crystals in the range of PP-IP-CP phase transitions are depicted for various values of uniaxial squeezing.

The uniaxial pressures in PTCZ crystals were found to affect the phase transition points and the temperature dependence of birefringence. It was established that the uniaxial squeezing does not change the character of temperature dependences $\Delta n_i(T)$, but modifies the quantity $d\Delta n_i/dT$ only. The dependence $\Delta n_i(T)$ was determined to be almost linear for all phases. The paraphase demonstrates the most substantial variations of $\Delta n_i(T)$: $d\Delta n_x/dT = 5.1 \times 10^{-6}$ K⁻¹, $d\Delta n_y/dT = 9.0 \times 10^{-6}$ K⁻¹, and $d\Delta n_z/dT = 8.2 \times 10^{-6}$ K⁻¹ for mechanically free crystals. For PTCZ crystals undergone

uniaxial stresses, the corresponding values do not differ considerably (see Table 1). For the IP, the following coefficients were determined: $d\Delta n_x/dT = 1.5 \times 10^{-6} \text{ K}^{-1}$, $d\Delta n_y/dT = 6.0 \times 10^{-6} \text{ K}^{-1}$, and $d\Delta n_z/dT = 5.1 \times 10^{-6} \text{ K}^{-1}$. Temperature differences in the behavior of $\Delta n_i(\sigma)$ -dependence for mechanically free and squeezed specimens were observed only in the IP (see Table 1). It is evident that the uniaxial squeezing in the IP enhances the temperature sensitivity of birefringence. Jump-like variations of Δn_i are observed at the IP-CP phase transition: $\delta\Delta n_x = 2.9 \times 10^{-4}$, $\delta\Delta n_y = 1.2 \times 10^{-4}$, and $\delta\Delta n_z = 1.1 \times 10^{-4}$. In the case of uniaxial squeezing, the amplitudes of corresponding jumps became a little smaller: $\delta\Delta n_x = 2.2 \times 10^{-4}$ for $\sigma_y = 200$ bar and 2.5×10^{-4} for $\sigma_z = 200$ bar; $\delta\Delta n_y = 1.0 \times 10^{-4}$ for $\sigma_z = 200$ bar and 0.9×10^{-4} for $\sigma_x = 200$ bar; $\delta\Delta n_z = 0.9 \times 10^{-4}$ for $\sigma_y = 200$ bar and 0.8×10^{-4} for $\sigma_x = 200$ bar.

3.2. Baric changes of the refractive indices

The uniaxial squeezing was found not to change the character of curves $n_i(\lambda)$. Only the dispersions $dn_i/d\lambda$ change: in the spectral range near $\lambda = 500$ nm, $dn_x/d\lambda = 7.6 \times 10^{-4}$ and 7.3×10^{-4} , $dn_y/d\lambda = 7.5 \times 10^{-4}$ and 7.1×10^{-4} , and $dn_z/d\lambda = 7.3 \times 10^{-4}$ and 7.0×10^{-4} for mechanically free and uniaxially squeezed ($\sigma_m = 200$ bar), respectively, specimens. The uniaxial squeezing was revealed to increase the refractive indices by $dn_i/d\sigma \approx 2 \times 10^{-6} \text{ bar}^{-1}$ on the average. In Fig. 2, the temperature-induced variations of the refractive in-

Temperature variation coefficients for the birefringence ($-d\Delta n_i/dT$, $\times 10^{-6} \text{ K}^{-1}$) and the refractive indices ($-dn_i/dT$, $\times 10^{-5} \text{ K}^{-1}$) in K_2ZnCl_4 crystals at $\lambda = 500$ nm for various directions of the uniaxial squeezing

| Light/pressure | $\sigma = 0$ | | $\sigma_x = 200$ bar | | $\sigma_y = 200$ bar | | $\sigma_z = 200$ bar | |
|----------------------|--------------|-------|----------------------|-------|----------------------|-------|----------------------|-------|
| | Δn_i | n_i | Δn_i | n_i | Δn_i | n_i | Δn_i | n_i |
| paraphase | | | | | | | | |
| X | 5.1 | 10.9 | - | - | 4.9 | 10.5 | 5.1 | 10.3 |
| Y | 9.0 | 10.7 | 9.1 | 10.4 | - | - | 8.8 | 10.0 |
| Z | 8.2 | 9.8 | 8.1 | 9.9 | 8.0 | 9.5 | - | - |
| incommensurate phase | | | | | | | | |
| X | 1.5 | 11.8 | - | - | 1.8 | 11.5 | 1.9 | 11.7 |
| Y | 6.0 | 11.1 | 6.1 | 11.0 | - | - | 6.2 | 10.8 |
| Z | 5.1 | 10.0 | 5.0 | 10.1 | 5.2 | 9.7 | - | - |
| ferroelectric phase | | | | | | | | |
| X | 1.8 | 7.5 | - | - | 1.6 | 7.3 | 1.7 | 7.4 |
| Y | 6.4 | 5.1 | 6.1 | 5.0 | - | - | 6.3 | 5.0 |
| Z | 3.2 | 5.0 | 3.0 | 4.5 | 3.0 | 4.7 | - | - |

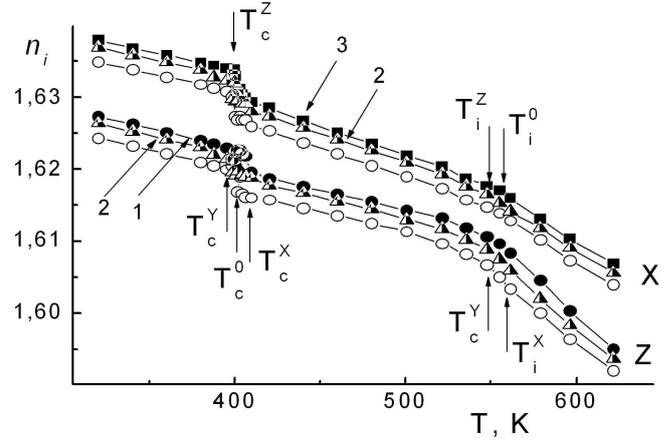


Fig. 2. The same as in Fig. 1, but for the refractive indices

indices for K_2ZnCl_4 crystals at $\lambda = 500$ nm are shown for various uniaxial stresses.

The crystals of PTCZ are characterized by a nonlinear dependence $n_i(T)$. Moreover, the nonlinearity increases with the specimen temperature growth, and it is higher in the IP as compared with that in the CP (see Table 1).

At the phase transition IP-CP which occurs at $T = 403$ K, the following jumps of the refractive indices were revealed: $\delta n_x = 7.7 \times 10^{-4}$, $\delta n_y = 7.8 \times 10^{-4}$, and $\delta n_z = 5.2 \times 10^{-4}$. A uniaxial squeezing reduces the magnitudes of those jumps to some extent: $\delta n_x = 7.1 \times 10^{-4}$ at $\sigma_y = 200$ bar and 7.0×10^{-4} at $\sigma_z = 200$ bar, $\delta n_y = 7.2 \times 10^{-4}$ at $\sigma_x = 200$ bar and 7.1×10^{-4} at $\sigma_z = 200$ bar, $\delta n_z = 4.4 \times 10^{-4}$ at $\sigma_x = 200$ bar and 4.7×10^{-4} at $\sigma_y = 200$ bar.

The specimens were annealed at a temperature of 380 K for 10 h. All measurements were carried out in the temperature decrease regime. At the heating of a specimen, the temperature hysteresis of 2.5 K was found. The phase transition IP-CP in a mechanically free crystal occurred at $T_c = 406$ K (Fig. 3).

For as-fabricated specimens, the hysteresis magnitude was 4 K. It is worth noting that the growth of the annealing time brought about a reduction of the hysteresis magnitude. However, the specimen annealing for more than 10 h did not result in a further decrease of the hysteresis. One may assume that the annealing of PTCZ crystals for 10 h leads to a complete elimination of defects of the "crystallization water" type, because they are the major defects in PTCZ crystals [12].

The application of uniaxial pressures σ_x and σ_z was found to diminish the hysteresis by $\Delta T = 0.5$ and 0.1 K, respectively. The uniaxial pressure effect is similar to that of the thermal annealing, because reductions of tem-

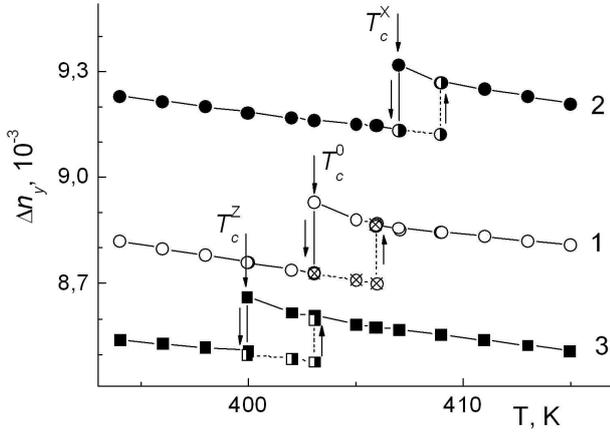


Fig. 3. Temperature dependences of the birefringence Δn_y in a mechanically free K_2ZnCl_4 crystal specimen (1) and a specimen gripped by uniaxial pressures σ_x (2) and σ_z (3) crystals $K ZnCl$ at $\lambda = 500$ nm in a vicinity of the incommensurate–commensurate phase transition in the cooling and heating regimes

perature hysteresis magnitudes and jump-like changes at phase transition points were observed in both cases.

A deformation of the soliton structure or a reduction of potential barriers at defect localization sites can be probable mechanisms of the influence of a mechanical loading on the hysteresis. The application of an external mechanical pressure to a crystal in the metastable state changes its stability and accelerates or decelerated the relaxation of the crystal to its equilibrium state.

3.3. Baric shifts of phase transition points

The phase transitions in the crystals concerned were found to be rather sensitive to the action of uniaxial stresses. In this case, a substantial displacement of the phase transition points in different directions on the temperature scale, depending on the squeezing direction, was revealed. For instance, it was found that, at the pressures $\sigma_m = 200$ bar, the phase transition PP–IP occurs at $T_i^X = 557.8$ K, $T_i^Y = 552.0$ K, and $T_i^Z = 550.4$ K, whereas $T_i = 553.0$ K for a mechanically free crystal. At the same pressures, the phase transition IP–CP occurs at $T_c^X = 406.6$ K, $T_c^Y = 399.8$ K, and $T_c^Z = 401.4$ K, whereas $T_c = 403.0$ K for a mechanically free crystal.

In general, the following baric displacement coefficients for PP–IP–CP phase transition points in PTCZ crystals were determined: $dT_i/d\sigma_x = +0.023$ K/bar, $dT_c/d\sigma_x = +0.018$ K/bar, $dT_i/d\sigma_y = -0.005$ K/bar, $dT_c/d\sigma_y = -0.016$ K/bar, $dT_i/d\sigma_z = -0.013$ K/bar, and $dT_c/d\sigma_z = -0.008$ K/bar. Hence, the uniaxial

squeezing along the X -axis shifts the phase transitions in PTCZ crystals toward higher temperatures, whereas the uniaxial squeezing along the Y - and Z -axes do it in the lower-temperature direction.

The coefficients of total displacements of phase transition points under the influence of all uniaxial pressures along the main crystallophysical directions (an analog of hydrostatic pressure) are

$$dT_i/d\sigma_m = dT_i/d\sigma_x + dT_i/d\sigma_y + dT_i/d\sigma_z =$$

$$= +0,005 \text{ K} \cdot \text{bar}^{-1},$$

$$dT_c/d\sigma_m = dT_c/d\sigma_x + dT_c/d\sigma_y + dT_c/d\sigma_z =$$

$$= -0,006 \text{ K} \cdot \text{bar}^{-1}.$$

The results obtained agree with the character of the hydrostatic pressure influence on phase transitions [8].

Since the baric coefficients of a phase transition point displacement are different ($dT_c/d\sigma_x > dT_i/d\sigma_z$), one may expect that the incommensurate phase of a PTCZ crystal will narrow under the influence of the stress σ_z . Really, by extrapolating the curves $T_c(\sigma_z)$ and $T_i(\sigma_z)$, we found that, at the pressure $\sigma_z \approx 29.5$ kbar and the temperature $T \approx 163$ K, the IP will disappear, and the phase transition “paraphase–ferroelectric phase” will take place, without entering into the incommensurate phase; i.e. there emerges a “triple point”. The uniaxial squeezings σ_x and σ_y , in turn, result in an expansion of the IP existence range toward both higher and lower temperatures (Fig. 4).

The baric displacements of the phase transition points that were found in PTCZ crystals can be explained as a result of the K_2ZnCl_4 crystal structure modification. It is known that, in the initial paraphase, one of the vertices in every T-group is directed along $\pm Z$, the other three vertices of a $ZnCl_4$ -tetrahedron lie in the plane $00Z$. In addition, the orientations of T-group bases in the plane (001) are identical in every layer of cation polyhedra, being directed oppositely in the neighbor layers, so that $Z = 4$ in K_2ZnCl_4 . At the same time, the vertex of a certain tetrahedron in every layer is directed along the $+Z$ -direction, and that of another one along the $-Z$ -one. Therefore, the numbers of T-groups in a cell oriented along the $+Z$ - and $-Z$ -directions are identical [13].

Considering every T-group as an integer, the main modifications in the IP structure in comparison with the initial one comprise the shift waves of atoms K(1)

and $K(2)$, as well as tetrahedral groups $ZnCl_4$, predominately along the Z -axis (the future polar axis), and the rotations of T -groups around all three axes: X , Y , and Z [1, 15]. In this case, the rotations around the Z -axis are identical for all groups translationally shifted with respect to one another along the Z -axis, being not connected with the modulation wave.

It is clear that, if the direction of an uniaxial squeezing coincides with the direction of the tetrahedron $ZnCl_4$ rotation, the phase transition will take place at higher temperatures. However, if the tetrahedron rotation direction is opposite to the direction of the uniaxial stress, the phase transition will occur at lower temperatures. Since the tetrahedron $ZnCl_4$ rotates in the XY -plane, it is evident that the phase transition point shifts toward higher temperatures in the case of a σ_x -stress and toward lower temperatures in the case of σ_y -stress.

The displacement of the phase transition points under the action of σ_z toward lower temperatures is driven by the rotation of a tetrahedron around the Z -axis. This looks like the pressure σ_z grips the tetrahedron and, hence, hamper its transition into a new thermodynamic state.

Concerning the commensurate ferroelectric phase, we found that, for the structure to be reconstructed from $Pm\bar{c}n$ to $P2_1cn$, two main bendings must be done. The first of them includes rotations of T -groups around an axis close to Z -one, and the second is related to the displacement of K and Zn atoms along the polar axis. The corresponding reasoning on the influence of an uniaxial pressure on the rotations of T -groups can be applied as well to the displacements of the IP–CP phase transition points. The shift of points of a phase transition from the incommensurate into the commensurate phase is also governed by the fact that the action of an external mechanical stress on a crystal in the metastable state changes its stability, which gives rise to a deformation of the soliton structure.

4. Conclusions

To summarize, in this work, the influence of the uniaxial squeezing applied along the main crystallophysical directions on the temperature-induced variations of the birefringence Δn_i and the refractive indices n_i in K_2ZnCl_4 crystals, which possess the incommensurate phase in a wide temperature range, has been studied. It is found that Δn_i is rather sensitive to the action of an uniaxial squeezing. It is determined that the pressure does not change the character of the temperature dependences of

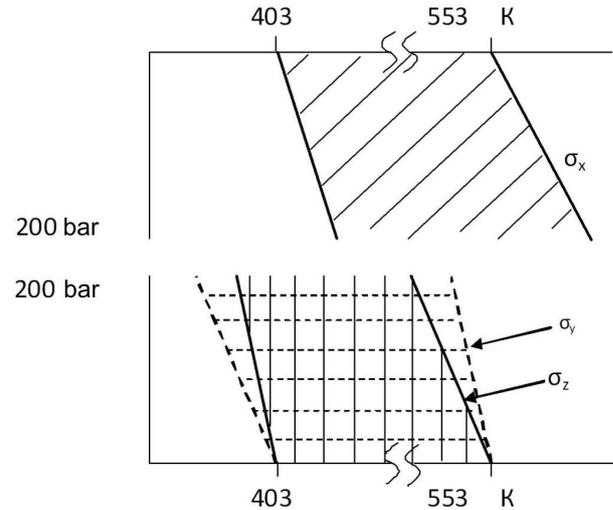


Fig. 4. Schematic temperature–pressure phase diagram for K_2ZnCl_4 crystals. Dashed curves denote a possible expansion (or narrowing) of the existence range for the incommensurate phase under the influence of uniaxial pressures applied along the main crystallophysical axes

the birefringence and the refractive indices, modifying only the quantities $d\Delta n_i/dT$ and dn_i/dT .

It is established that the temperature hysteresis at the IP–CP phase transition decreases after the thermal annealing and the application of an uniaxial pressure to the crystal. The latter phenomenon is driven by a deformation of the soliton structure and a variation of its stability.

It is found that the phase transitions of the crystals concerned are rather sensitive to the action of an uniaxial squeezing which is accompanied by considerable displacements of the phase transition points in different directions on the temperature scale which depend on the squeezing direction. It is demonstrated that, at the pressure $\sigma_z \approx 29.5$ kbar and the temperature $T \approx 163$ K, the incommensurate phase disappears, and the phase transition “paraphase–ferroelectric phase” takes place, without entering the incommensurate phase; i.e. there emerges a “triple point”. The uniaxial pressures σ_x and σ_y stimulate, in turn, an expansion of the incommensurate phase toward both higher and lower temperatures. Such baric displacements of the phase transition points can be explained by the influence of an uniaxial squeezing on the structure of a PTCZ crystal, namely on the rotation of $ZnCl_4$ tetrahedra.

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НЕСУМІРНА ФАЗА КРИСТАЛІВ K_2ZnCl_4 В УМОВАХ
ОДНОВІСНИХ ТИСКІВ

*В.Й. Стадник, З.О. Козут, Р.С. Брезвін, В.М. Габа,
І.М. Матвійшин*

Р е з ю м е

Досліджено вплив одновісного тиску вздовж головних кристалофізичних напрямів на температурні зміни двопронезаломлення Δn_i та показників заломлення n_i кристалів K_2ZnCl_4 в області фазових переходів, що охоплюють несумірну фазу. Встановлено, що Δn_i та n_i достатньо чутливі до дії одновісних тисків. Виявлено значне баричне зміщення точок фазових переходів парафаза–несумірна–сумірна сегнетофаза в різні температурні області залежно від напрямку прикладання тиску, що зумовлено впливом одновісних тисків на структуру кристала K_2ZnCl_4 .