Proceedings of the International Workshop "Oxide Materials for Electronic Engineering" (OMEE-2009), Lviv 2009

Birefringence of Mechanically Stressed Potassium Tetrachlorine Zincanate Crystals

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The spectral and baric dependences of the birefringence Δn_i of K_2ZnCl_4 crystals were studied. It is shown that the dispersion $\Delta n_i(\lambda)$ is normal and sharply increases on approaching the absorption edge. It is established that the uniaxial pressures do not change the character but only the values of the dispersions $\mathrm{d}\Delta n_i/\mathrm{d}\lambda$ and temperature dependences of $\mathrm{d}\Delta n_i/\mathrm{d}T$.

PACS numbers: 77.84.Fa, 78.20.Ci, 77.80.Bh

1. Introduction

K_2ZnCl_4 crystals (TCZP) belong to the known type of ferroelectrics with incommensurate phase (ICP). They undergo successive phase transitions (PTs): a second-order one at $T_i = 553$ K from the paraphase (the space group $Pnam$) into the ICP with the wave vector $q = (1-\delta)\frac{a^*}{3}$, a first-order one at 402 K from the ICP into the ferroelectric commensurate phase (CP) (the space group Pna_12), and a first-order low-temperature one into the ferroelastic phase (the space group $P2_111$) [1–5].

Optical studies of the TCZP dealing with temperature and spectral changes in the refractive indices and the birefringence and temperature dependences of the combined piezooptic coefficients have shown anomalies at the PTs [6–8].

Despite a great interest to the TCZP crystals, the effect of uniaxial pressures on their optical characteristics and behavior of their PT points has not been investigated. Uniaxial pressures generally do not change the crystal symmetry. Instead they affect selectively some groups of bonds and the corresponding structural units. This allows obtaining additional information for analysis of the PT mechanisms. On the other hand, studies of the refractive indices and optical birefringence are very sensitive and thus provide useful information about the structure and physical properties of crystals.

The purpose of the present work is investigation of influence of the uniaxial mechanical pressure acting along the principal directions X, Y and Z and along the bisectors upon spectral and temperature changes in the birefringences Δn_i of TCZP crystals for the light propagation directions X, Y and Z.

2. Experimental procedures

K_2ZnCl_4 crystals were grown by a slow evaporation of a relevant aqueous solution. The crystals grown were of good optical quality and had an orthorhombic-like shape. The spectral dependences of Δn_i were measured using interference technique.

To determine the birefringence, photographic recording of the interference pattern occurring in the focal plane of a DFS-8 spectrograph was used. It ensured a spatial resolution of extrema of various orders, excluded "smearing" patterns, and therefore allowed for their independent registration. The optical transmittance of the polarizing system, composed of crossed polarizers, with a sample in between aligned in a diagonal position, is determined according to the relation

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

where I_0 and I are the intensities of incident and transmitted light beams, respectively, λ is the light wavelength, $n_i - n_j$ is the birefringence, and d — the sample size along the light beam. Spectral positions of the maxima are described as follows:

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

with k being the interference order.

Under variation of temperature, due to $d(T)$ and $n_i(T)$ dependences, the positions of the interference extrema shift. The birefringence may be determined using the expression

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

Upon sample compression or variation of its temperature, the parameters k, d, n_i, n_j and λ exhibit some changes, which are either measured (k and λ) or calculated (d, n_i and n_j). Here the changes in the sample thickness upon

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heating or cooling might be measured following from the known thermal expansion parameters.

3. Experimental results and discussion

We have found that dispersion of the birefringence Δn_i is normal in the whole spectral interval under studies ($\mathrm{d}\Delta n_x/\mathrm{d}\lambda = -4.86 \times 10^{-6}$ nm^{-1}, $\mathrm{d}\Delta n_y/\mathrm{d}\lambda = -4.83 \times 10^{-6}$ nm^{-1}, and $\mathrm{d}\Delta n_z/\mathrm{d}\lambda = -5.11 \times 10^{-6}$ nm^{-1}), so that we have the interrelation $|\mathrm{d}n_z/\mathrm{d}\lambda| > |\mathrm{d}n_x/\mathrm{d}\lambda| > |\mathrm{d}n_z/\mathrm{d}\lambda|$.

Temperature dependences of the birefringence Δn_i in the range of PTs paraphase–ICP–CP are shown in Fig. 1.

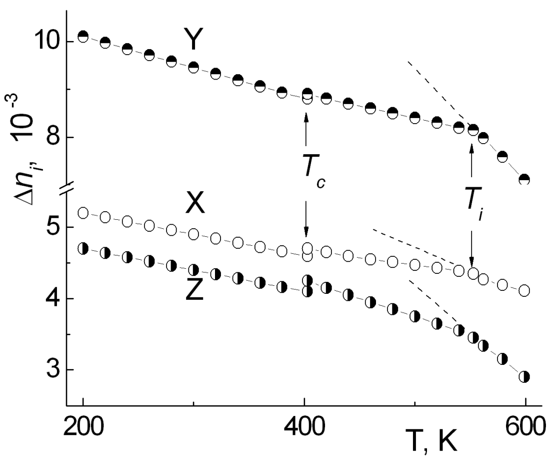

Fig. 1. Temperature dependence of optical birefringence for K_2ZnCl_4 crystals at $\lambda = 500$ nm.

It is revealed that the dependences $\Delta n_i(T)$ are almost linear for all the phases. In the paraphase the temperature changes of $\Delta n_i(T)$ are significant: $\mathrm{d}\Delta n_x/\mathrm{d}T = 5.1 \times 10^{-6}$ K^{-1}, $\mathrm{d}\Delta n_y/\mathrm{d}T = 9.0 \times 10^{-6}$ K^{-1} and $\mathrm{d}\Delta n_z/\mathrm{d}T = 8.2 \times 10^{-6}$ K^{-1}; In the ICP we have $\mathrm{d}\Delta n_x/\mathrm{d}T = 1.5 \times 10^{-6}$ K^{-1}, $\mathrm{d}\Delta n_y/\mathrm{d}T = 6.0 \times 10^{-6}$ K^{-1}, and $\mathrm{d}\Delta n_z/\mathrm{d}T = 5.1 \times 10^{-6}$ K^{-1}. At the PT ICP–CP step-like changes in Δn_i have been observed: $\delta\Delta n_a = -3.9 \times 10^{-5}$, $\delta\Delta n_b = 5.2 \times 10^{-5}$, and $\delta\Delta n_a = 9.1 \times 10^{-5}$ [9, 10]. These results refer to the samples annealed at $T \approx 380$ K for 10 h.

For the as-prepared samples, only insignificant increase of the PT hysteresis is observed (about 4.1 K). The minimal annealing time that provides complete reproducibility of experimental results observed for the TCZP crystals amounts to 10 h.

The as-grown crystals involve a significant number of defects of "crystallization water" type. Their existence leads to smearing and displacement of the PT. The hysteresis takes place at the ICP–CP PT, which is probably due to additional fixation of phase solitons at those defects. At the same time, annealing of crystals stabilizes the defects. The time needed for total reproducibility of the PT temperatures could be considered as a minimal one required for stabilizing those defects completely.

The spectral dependences of Δn_i for the TCZP obtained at the room temperature and different directions of mechanical pressures are shown in Fig. 2. It has been established that the birefringence is sensitive to uniaxial stresses along the principal directions and is less sensitive to stresses directed along the bisectors. The changes in Δn_i are almost linear with the stress variations. At the room temperature we have $\delta(\Delta n_x) = +3.5 \times 10^{-4}$ and -1.8×10^{-4} (for σ_z and $\sigma_y = 200$ bar, respectively), $\delta(\Delta n_y) = +4.8 \times 10^{-4}$, -4.3×10^{-4} (for σ_x and $\sigma_z = 200$ bar), and $\delta(\Delta n_z) = +1.6 \times 10^{-4}$, -2.1×10^{-4} (for σ_y and $\sigma_x = 200$ bar, respectively).

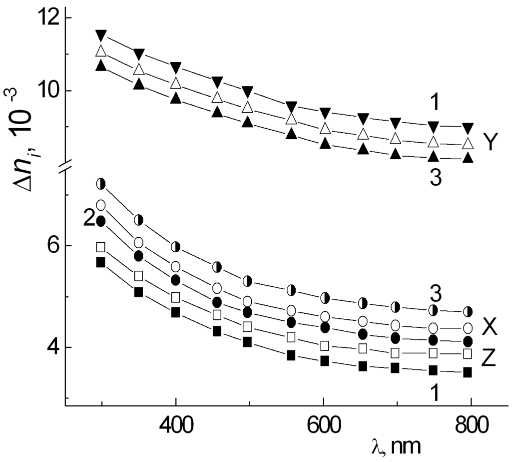

Fig. 2. Spectral dependences of optical birefringence for K_2ZnCl_4 crystals at the room temperature. Open symbols correspond to unstressed sample, whereas half-opened and solid ones to mechanically stressed one: 1 — $\sigma_x = 200$, 2 — $\sigma_y = 200$, 3 — $\sigma_z = 200$ bar.

If the uniaxial stress is directed along the Y axis, then Δn_x decreases and Δn_z increases. They become equal to each other at $\sigma_y \approx 355$ bar: $\Delta n_x = \Delta n_z = 4.58 \times 10^{-3}$ ($\Delta n_x = 4.91 \times 10^{-3}$ and $\Delta n_z = 4.32 \times 10^{-3}$ for the room temperature). Since the relation $n_x > n_y > n_z$ for the refractive indices of TCZP crystals has been revealed, the equality $\Delta n_x(\sigma_y) = \Delta n_z(\sigma_y)$ would be valid for the following relation for n_i of the stressed TCZP: $n_x - n_y = n_y - n_z$ or $n_x + n_z = 2n_y$. This means that application of the uniaxial pressure σ_y results in averaging of one of the refractive indices.

According to Fig. 2, we observe the intersection at $\lambda = 500$ nm if the stress $\sigma_y \approx 355$ bar is applied. In other words, increasing stress shifts the "pseudo-isotropic" point towards shorter wavelengths (the rate $\mathrm{d}\lambda_0/\mathrm{d}\sigma = 0.85$ nm/bar). The latter rate corresponds to baric modifications of the isotropic state in $LiRbSO_4$ crystals occurring under the stress [11]. The stress σ_y shifts the "isotropic point" towards the long-wave region with the rate of $\mathrm{d}\lambda_0/\mathrm{d}\sigma = 0.048$ nm/bar, while the stress σ_z gives rise to the opposite shift ($\mathrm{d}\lambda_0/\mathrm{d}\sigma = -3.4$ nm/bar).

In general, although mechanical stresses affect the Δn_i values, they do not change substantially their dispersion.

For example, we have $\mathrm{d}\Delta n_x/\mathrm{d}\lambda = -4.89 \times 10^{-6}$ and -4.87×10^{-6} nm^{-1} (at σ_y, and $\sigma_z = 200$ bar).

It is also found that the uniaxial stresses do not change the temperature behaviour of Δn_i in essence, i.e. the profiles of the curves $\Delta n_i(T)$ and the PT patterns are practically reproducible in every phase. On the contrary, the Δn_i values, the positions of PT points, and the jumps $\delta\Delta n_i$ are revealed to be substantially affected.

References

[1] F. Milia, R. Kind, J. Slak, *Phys. Rev. B* **27**, 6662 (1983).

[2] K. Gesi, M. Iizumi, *J. Phys. Soc. Japan* **53**, 4271 (1984).

[3] K. Itoh, T. Kataoka, H. Natsunaga, *J. Phys. Soc. Japan* **48**, 1039 (1980).

[4] T. Sakata, K. Hamano, K. Ema, *J. Phys. Soc. Japan* **57**, 4242 (1988).

[5] F. Milia, *Phys. Lett.* **102A**, 317 (1984).

[6] G. Znang, S.L. Qiu, M. Dutta, *J. Phys. Soc. Japan* **55**, 275 (1985).

[7] V.M. Gaba, N.A. Romanyuk, V.Y. Stadnyk, *Ukr. J. Phys.* **35**, 659 (1990).

[8] N.A. Romanyuk, V.M. Gaba, V.Y. Stadnyk, *Kristallografiya* **35**, 1292 (1990).

[9] N.A. Romanyuk, V.M. Gaba, V.Y. Stadnyk, *Fiz. Tverd. Tela* **32**, 1233 (1990).

[10] N.A. Romanyuk, V.Y. Stadnyk, R.S. Brezvin, *Ukr. J. Phys.* **40**, 1068 (1995).

[11] V.Y. Stadnyk, N.A. Romanyuk, L.T. Karplyuk, *Ukr. J. Phys.* **49**, 805 (2004).