

EFFECT OF UNIAXIAL PRESSURE ON BIREFRINGENCE OF TRIGLYCINE SULFATE CRYSTALS WITH *L*-VALINE ADMIXTURE

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PACS 61.72.JJ
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The temperature and baric dependences of the birefringence Δn_i of triglycine sulphate (TGS) crystals with *L*-valine admixture are investigated. It is established that the introduction of the *L*-valine admixture results in the weakening of the temperature dependence of the birefringence of TGS crystals. It is shown that Δn_i is rather sensitive to the action of uniaxial pressures. The baric shift coefficients of the point of phase transition $\partial T_c/\partial \sigma_m$ are determined.

1. Introduction

The introduction of impurities into a ferroelectric TGS crystal results in a change of its optical properties. For example, it is shown that the insertion of the admixtures of alanine [1] and *L*-threonine [2] influences the refractive indices n_i and Δn_i of TGS crystals.

The given work is devoted to the investigation of the influence of the *L*-valine admixture and a uniaxial mechanical pressure on the dispersion and temperature variations of Δn_i in TGS crystals.

L-valine is an amino acid differing from glycine in the C-(CH₃)₂ group [3]. It is established that the domain structure of impurity TGS crystals changes, by depending on the time of spontaneous ageing [4]. All impurity TGS crystals are characterized by the displacement fields, whose influence is similar to that of an external field, so that a sample becomes single-domain, and the domain structure gets fixed [5].

2. Measurement Results and Discussion

Figure 1 shows the dispersion Δn_i of pure and impurity TGS crystals measured by the interference method using the technique described in [6]. One can see that the introduction of an impurity substantially changes the absolute value of Δn_i without affecting the character of the dispersion $|\partial \Delta n_z/\partial \lambda| > |\partial \Delta n_x/\partial \lambda| > |\partial \Delta n_y/\partial \lambda|$. The birefringence of the impurity crystal decreases in the *Z*- and *Y*-directions: $\Delta n_z^p - \Delta n_z^L = 7.87 \times 10^{-3}$ and 7.58×10^{-3} , $\Delta n_y^p - \Delta n_y^L = 4.42 \times 10^{-3}$ and 7.6×10^{-3} for

$\lambda = 300$ and 700 nm, respectively. In the *X*-direction, we revealed a change of sign of the birefringence as compared to the pure TGS crystal: $\delta(\Delta n_x) = \Delta n_x^p - \Delta n_x^L = -1.88 \times 10^{-3}$ and $+1.31 \times 10^{-3}$ for $\lambda = 300$ and 700 nm, respectively.

It is discovered that, at room temperature and $\lambda \sim 349$ nm, Δn_i of pure and impurity TGS crystals become equal $\Delta n_x^p = \Delta n_x^L = 0.07861$. As Δn_x of the impurity crystal decreases with temperature much slower than that of the pure one, a decrease of the temperature will result in a shift of the point $\Delta n_x^p = \Delta n_x^L$ toward larger wavelengths. A similar situation was observed in the TGS crystal with *L*-threonine admixture. It is clear that the introduction of impurities of different weight compositions into a TGS crystal will result in quantita-

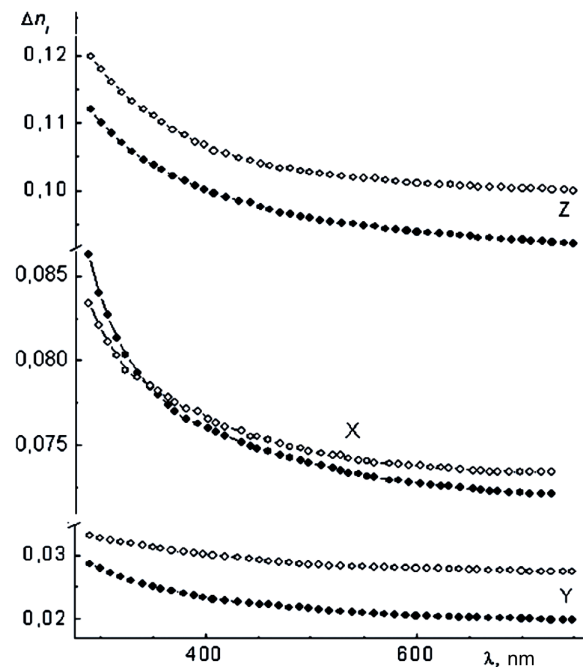


Fig. 1. Birefringence of pure TGS crystals (light points) and those with *L*-valine admixture (LVTGS) (dark point)

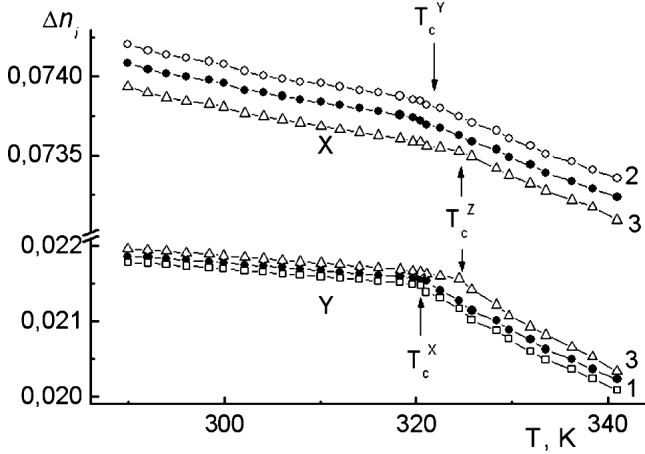


Fig. 2. Temperature behavior of the birefringence of TGS crystals with 5% admixture of *L*-valine for different directions of the uniaxial pressure for $\lambda = 500$ nm: dark points – mechanically free crystal, 1 – σ_x , 2 – σ_y , 3 – $\sigma_z = 200$ bar, respectively

tive variations of n_i and Δn_i . Therefore, the existence of the point of equality of Δn_i in certain directions for pure and impurity crystals can be used for the optical investigation of the impurity distribution.

Figure 2 shows the temperature variations of the principal values of Δn_i of the LVTGS crystals for loaded samples. The general peculiarities are as follows: Δn_i changes proportionally with temperature; the value of the derivative $\partial \Delta n_i / \partial T$ changes at the transition through the Curie point; the uniaxial pressures do not essentially influence the temperature behavior of Δn_i , though they change its absolute value; the phase transition (PT) point shifts under the action of the pressure. With decreasing temperature, Δn_i falls in all the three crystallophysical directions. It is established that changes of Δn_i in the paraphase are linear in all directions of the impurity TGS crystal: $d\Delta n_y/dT = 6.54 \times 10^{-5}$, $d\Delta n_z/dT = 12.44 \times 10^{-5}$, and $d\Delta n_x/dT = 2.41 \times 10^{-5} \text{ K}^{-1}$. In the ferrophase, there exists an inessential nonlinearity of variations of Δn_i . In the *Z*- and *Y*-directions, we observed pronounced changes of $\Delta n_i(T)$ at the Curie point, whereas these changes were inessential in the *X*-direction. In the ferrophase, Δn_i of the impurity crystal changes with temperature very weakly: $d\Delta n_y/dT = 0.85 \times 10^{-5}$, $d\Delta n_z/dT = 1.86 \times 10^{-5}$, and $d\Delta n_x/dT = 1.85 \times 10^{-5} \text{ K}^{-1}$.

It is established that Δn_i increases linearly up to the pressures $\sigma_i \sim 200$ bar. The pressures σ_x and σ_y result in variations of Δn_z of different magnitudes and unlike signs: $\delta \Delta n_z = 8.1 \times 10^{-5}$ ($\sigma_x = 200$ bar) and -7.2×10^{-5} ($\sigma_y = 200$ bar). Similar dependences were obtained for

Δn_x and Δn_y : $\delta \Delta n_y = -6.2 \times 10^{-5}$ and 9.8×10^{-5} for σ_x and $\sigma_z = 200$ bar, $\delta \Delta n_x = 10.1 \times 10^{-5}$ and -12.3×10^{-5} for σ_y and $\sigma_z = 200$ bar. In whole, one of the pressures normal to the direction of observation always gives an increase of Δn_i , and the other one – a decrease; in addition, these increments are different in absolute value, and for the LVTGS crystal $\delta \Delta n_x > \delta \Delta n_y \geq \delta \Delta n_z$.

One can also see from Fig. 2 that, under the action of the pressures σ_x and σ_y , the PT point shifts toward lower temperatures: $T_c^x = 320.5$ K and $T_c^y = 320.2$ K, while the pressure σ_z shifts the latter toward higher temperatures $T_c^z = 325.2$ K ($T_c^0 = 321.8$ K). In this case, the temperature coefficients of a shift of the PT point amount to $\partial T_c / \partial \sigma_x = -0.0064$, $\partial T_c / \partial \sigma_y = -0.008$, and $\partial T_c / \partial \sigma_z = +0.0171 \text{ K/bar}$. The total (hydrostatic) shift coefficient of the PT point under the action of the uniaxial pressures is equal to:

$$\partial T_c / \partial p = \sum_{i=1}^3 \partial T_c / \partial \sigma_i = +0.0027 \text{ K/bar}.$$

On the one hand, these results are in good agreement with the corresponding data for a pure TGS crystal obtained in [7]: $\partial T_c / \partial \sigma_x = -7$, $\partial T_c / \partial \sigma_y = -8.5$, and $\partial T_c / \partial \sigma_z = 20 \text{ K/bar}$. Our coefficients are somewhat lower, which confirms an increase of the hardness of TGS crystals due to the introduction of admixtures.

On the other hand, similar results were obtained for LiKSO_4 , RbNH_4SO_4 , and $(\text{NH}_4)_2\text{BeF}_4$ crystals, as well as Rochelle salt and KDP [10–13], where one observed a shift of T_c toward higher or lower temperatures depending on the pressure direction; moreover, the total shift coefficient was negative. These shifts of the PT points were explained by the influence of the temperature and pressure on the shift of structural elements characteristic of a given PT.

Figure 3 shows the baric dependences of the birefringence of TGS crystals with 5% admixture of *L*-valine at room temperature at $\lambda = 500$ nm. It is seen that the quantity Δn_i increases linearly to pressures $\sigma_i \sim 200$ bar. Pressures σ_x and σ_y causes changes in Δn_z different in values and signs: $\delta \Delta n_z = 8.1 \cdot 10^{-5}$ ($\sigma_x = 200$ bar) and $-7.2 \cdot 10^{-5}$ ($\sigma_y = 200$ bar).

Thus, we have investigated the temperature and baric dependences of Δn_i of triglycine sulphate crystals with *L*-valine admixture. It is established that the introduction of the *L*-valine admixture results in the weakening of the temperature dependence of Δn_i , which is caused by an increase of the hardness of impurity crystals and a reduction of the spontaneous polarization. It is discovered that Δn_i is rather sensitive to the action of uniaxial

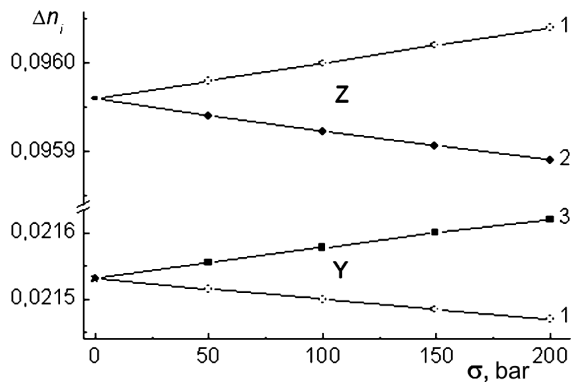


Fig. 3. Baric dependence of the birefringence of TGS crystals with 5% admixture of *L*-valine at room temperature at $\lambda = 500$ nm: 1 – σ_x ; 2 – σ_y ; 3 – σ_z

pressures. Moreover, one of the pressures normal to the direction of observation always results in an increase of Δn_i , while the other one does in its decrease, and these increments are different in absolute values. The temperature coefficients of the shift of the PT point $\partial T_c / \partial \sigma_m$ determined in the work appeared to be somewhat lower than those in pure TGS crystals.

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Received 07.10.09.

Translated from Ukrainian by H.G. Kalyuzhna

ВПЛИВ ОДНОВІСНОГО ТИСКУ
НА ДВОПРОМЕНЕЗАЛОМЛЕННЯ
КРИСТАЛІВ ТГС З ДОМІШКОЮ *L*-ВАЛІНУ

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Резюме

Досліджено температурні й баричні залежності двоприменезаломлення Δn_i кристалів тригліцинусульфату (ТГС) з домішкою *L*-валіну. Встановлено, що внесення домішки *L*-валіну приводить до послаблення температурної залежності Δn_i кристалів ТГС. Встановлено, що Δn_i достатньо чутливе до дії одновісних тисків. Визначено баричні коефіцієнти зміщення точки фазового переходу $\partial T_c / \partial \sigma_m$.