Condensed Matter Physics, 1999, Vol. 2, No. 4(20), pp. 693–702

Anisotropy of critical indices of ferroelectric phase transition in TGS crystals by the optical interference investigation

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Received January 13, 1999, in final form September 14, 1999

Temperature dependences of the optical path difference, variable part of the refractive index and thickness of triglycine sulphate crystal for three crystallophysic directions are studied in the temperature range of 39–70 °C, including the ferroelectric phase transition at T_c=49 °C, using the Jamen type optical interferometer. Temperature dependences of the spontaneous changes of the characteristics studied in the range of 39–49 °C are fitted by the power-like low $Y \sim \tau^{2\beta}$ with doubled averaged effective critical indices 2β=0.87–0.95. The 2β values being different from the unity is explained by the essential temperature dependence of the coefficients of electrooptic, inverse piezoelectric and electrostriction effects in the range close to the phase transition point.

Key words: *ferroelectrics, phase transition, optical properties, critical indices*

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

1. Introduction

It is known, that the critical behaviour of the spontaneous polarization P_s at the 2nd order phase transition (PT) in a crystal can be described by the critical index β,

$$P_s \sim (T_c - T)^\beta, \tag{1}$$

where T_c is the PT temperature [1]. Here, index β can be treated as asymptotic or effective one [2]. The effective critical index β_{eff} is determined to be the derivative

$$\beta_{\text{eff}}(\tau) = \mathrm{d}[\ln(P_s)]/\mathrm{d}[\ln \tau], \tag{2}$$

taken at some temperature $T < T_c$. Here, $\tau = (T_c - T)/T_c$. The effective critical index β_{eff} is becoming the asymptotic one, when the value τ is approaching zero

($\tau < 10^{-3}$) [2].

On the other hand, experimental temperature dependences of crystal parameters in the range of PT can be also presented with the help of coefficients of thermodynamic potential expansion. According to the Landau theory, the elastic Gibbs energy G_1 in the case of uniaxial ferroelectric can be expressed in the polynomial form

$$G_1 = \frac{1}{2}AD^2 + \frac{1}{4}BD^4 + \frac{1}{6}CD^6, \tag{3}$$

where D is electric displacement, A, B and C are coefficients [3]. Here, the energy is measured from the non-polar phase and the polynomial is arbitrarily terminated at D^6. Dielectric state equation $E = \partial G_1/\partial D$ takes the following form

$$E = AD + BD^3 + CD^5, \tag{4}$$

where E is electric field. In the first approximation, which is in many cases satisfying, we assume:

$$A = A_0(T - T_c). \tag{5}$$

Coefficient A_0 is usually determined from the measurements of dielectric constant as a function of temperature in the paraelectric (PE) phase. In the ferroelectric (FE) phase the coefficients B and C can be determined from the temperature dependence of P_s (E=0, D=P_s). The equation of dielectric state (3) can be now written as follows

$$P_s^2 = (B/2C)\left\{\left[1 + 4A_0(T_c - T)C/B^2\right]^{(1/2)} - 1\right\}. \tag{6}$$

To characterize the order of PT, the parameter $V = B^2/A_0C$ can be used [3]. The physical sense of this parameter is clearly visible in the description of the first-order PT. The polarized state becomes stable at the temperature $T_0 = T_c + 3/16(B^2/A_0C)$, whereas the upper limit of a superheating is $T_1 = T_c + B^2/4A_0C$. When the first-order PT comes near the second-order PT, the absolute value of V decreases at the tricritical point $T_0 = T_1 = T_c$.

Both sets of parameters, index 2β in formulae (1), and coefficients A, B, and C in formulae (6), can be used for the approximation of temperature dependences of spontaneous polarization of ferroelectrics near the PT point. In the first five columns of table 1 the parameter V as well as the parameters A_0, B, C of the equation of state for some ferroelectric crystals are presented [3].

Based on the values of coefficients A, B and C presented in table 1, we have calculated the temperature dependences of spontaneous polarization $P_s(T)$ by the formula (6) in the range of 312–322 K. Then, using the dependence $P_s(T)$ obtained, we have calculated the corresponding effective critical index β_{eff} averaged in this temperature range using the formula (2).

Experimental temperature changes of the optical path difference determined by birefringence, $D = l\Delta n$, are frequentely identified in practice with the changes of the birefringence Δn. But the thickness l and birefringence Δn can have different temperature dependences. The temperature dependences of $D(T)$ and $l(T)$ are usually investigated in different experiments. This restricts the accuracy of determining

Table 1. Coefficients A, B and C of the equation of dielectric state (6), coefficient V [3], and the corresponding averaged effective critical index $\beta_{\rm eff}$ for some ferroelectrics calculated in the temperature range of $(T_c - T)$=10 K
Here: TGS – $(NH_2CH_2COOH)_3{\cdot}H_2SO_4$; TGSe – $(NH_2CH_2COOH)_3{\cdot}H_2SeO_4$; $DTGS_{47\%}$ – 47% deuterated TGS crystal ; DGN – $(NH_2CH_2COOH)_2{\cdot}HNO_3$; DMAAS – $(CH_3)_2NH_2Al(SO_4)_2{\cdot}6H_2O$; MAPBB – $(CH_3NH_3)_5Bi_2Br_{11}$; MAPCB – $(CH_3NH_3)_5Bi_2Cl_{11}$; TAAP – $|Te(OH)_6|{\cdot}2|NH_4H_2PO_4|{\cdot}|(NH_4)_2HPO_4|$; CDP – CsH_2PO_4.

Crystal	A_0 [Vm/K]	B [Vm^5/C^3]	C [Vm^9/C^5]	$V = B^2/A_0C$	$\beta_{\rm eff}$
TGS	$3.7 \cdot 10^7$	$7.5 \cdot 10^{11}$	$5 \cdot 10^{15}$	3.03	0.38
TGSe	$2.63 \cdot 10^7$	$3.97 \cdot 10^{10}$	$3 \cdot 10^{14}$	0.20	0.30
$DTGS_47\%$	$3.4 \cdot 10^8$	$3.1 \cdot 10^{11}$	$1 \cdot 10^{15}$	2.76	0.30
DGN	$1.26 \cdot 10^7$	$6.1 \cdot 10^{13}$	$9.5 \cdot 10^{15}$	$3 \cdot 10^3$	0.50
DMAAS	$3.69 \cdot 10^7$	$3.5 \cdot 10^{11}$	$4.2 \cdot 10^{15}$	0.79	0.33
MAPBB	$5.57 \cdot 10^7$	$1.64 \cdot 10^{12}$	$2.6 \cdot 10^{16}$	1.88	0.36
MAPCB	$11.56 \cdot 10^7$	$7.2 \cdot 10^{12}$	$2.4 \cdot 10^{17}$	1.88	0.37
TAAP	$2.97 \cdot 10^7$	$6.9 \cdot 10^{11}$	$1.5 \cdot 10^{15}$	10.38	0.44
CDP	$1.56 \cdot 10^6$	$1.32 \cdot 10^9$	$1.5 \cdot 10^{13}$	0.07	0.28

the corresponding dependence of $\Delta n(T)$ and $l(T)$, and makes it complicated to compare these different parameters of crystal in the region of PT. We have suggested the techniques of simultaneous determination of temperature dependences of the variable part of the refractive index $(n-1)$ and the thickness l of a sample.

Temperature dependences of the refractive indices and the linear thermal expansion of TGS in the range of PT have already been studied [4–6], but the corresponding critical indices have not been determined. The goals of the present investigation were the precise measurements of the temperature dependences of optical path difference (OPD) determined by the refractive index for TGS crystal in the range of 2nd order PT at 322 K, calculating the temperature dependences of refractive indices and linear thermal expansion for the principal crystallophysic directions, as well as the study of these dependences using the corresponding effective critical indices $2\beta_{\rm eff}$.

2. Experimental

Temperature dependences of OPD, $D = l(n-1)$, determeined by the variable part of refractive index (VPRI), $(n-1) = \eta$, for two interfering beams, one of which has passed through a sample studied, and the other one through the air, were measured using the Jamen type home built interferometer (figure 1). In this case, the OPD D and its temperature dependence $D(T)$ can be written as follows

$$D = l(n-1) = l\eta, \quad D(T) = l(T)\eta(T), \tag{7}$$

where l is thickness of a sample. The laser light of the wavelength λ=632.8 nm was used in the experiment.

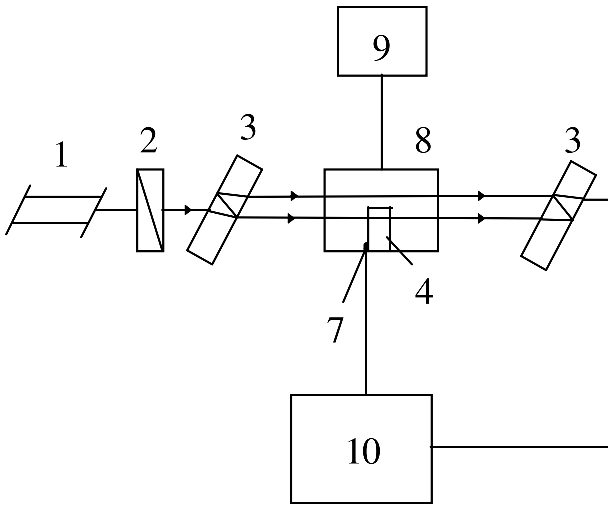

Figure 1. Scheme of the experiment: 1 – He-Ne laser; 2 – polarizer; 3 – glass plates of Jamen type interferometer; 4 – sample; 5 – diaphragms; 6 – photodiodes; 7 – thermocouple; 8 – thermostat (furnace); 9 – electrical supply block; 10 – recording block

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Proceeding from the relation (6), the temperature changes of relative OPD $\Delta D/D$ along three crystallophysic directions can be written in the form of a system of linear equations

$$\frac{\Delta D_{ij}}{D_{ij}} = \frac{\Delta l_i}{l_i} + \frac{\Delta \eta_j}{\eta_j}, \qquad (i, j = 1, 2, 3; \quad i \neq j), \tag{8}$$

where index i denotes the direction of light propagation, index j denotes the direction of light polarization. Based on the six temperature dependences $\Delta D_{ij}/D_{ij}$ measured we have determined the relative temperature changes of the thickness $\Delta l_i/l_i$ and VPRI $\Delta\eta_j/\eta_j$ [7]. The results of the corresponding computer calculations have shown that the relative errors of the temperature changes determination of thickness $\delta l_i/l_i$ and VPRI $\delta\eta_j/\eta_j$ caused by solving the system (8) did not exceed 5% of the respective maximum magnitudes $\Delta l_i/l_i$ and $\Delta\eta_j/\eta_j$ for the case of TGS crystal. The initial l_i and η_j values were measured independently at the initial temperature T_0. In our case ($l \approx 5$ mm and $n \approx 1.5$) the error of determining the interference order was $\delta m(T) \leqslant 1/4$, which corresponds to the errors of $\delta D/D \sim \delta l/l \sim \delta\eta/\eta \sim 10^{-5}$.

3. Results and discussion

Temperature dependences of the relative changes of OPD $\Delta D_{ij}/D_{ij}$ for TGS crystal are shown in figure 2. Refractive indices $n_j(T_0)$ of TGS crystal were taken from the paper [6]. The forms of temperature dependences of the thickness $\Delta l_i/l_i$

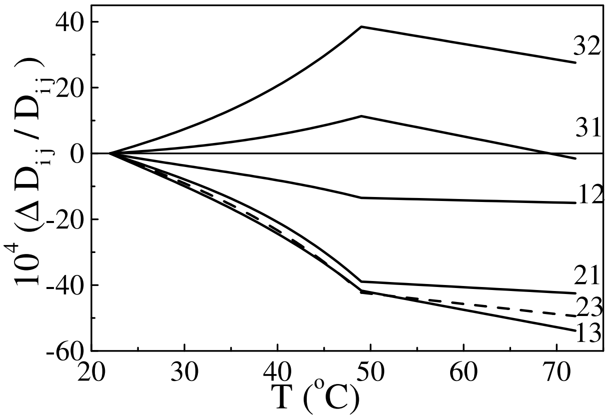

Figure 2. Experimental temperature dependences of the relative changes of the optical path difference $\Delta D_{ij}/D_{ij}$ of TGS crystal (indices ij indicate the corresponding curves)

and VPRI $\delta\eta_j/\eta_j$ calculated from the system of equations (8) are characterized by the similar anomalies at PT temperature. Based on the known relation for the temperature changes of the order parameter $p = P_s$ for 2nd order PT in the range of $T < T_c$,

$$\Delta Y_s \sim P_s^2 \sim \tau^{2\beta} = \left(\frac{T_c - T}{T_c - T_{\min}}\right)^{2\beta}, \qquad (9)$$

we have calculated the double effective critical indices 2β averaged in the range of 39–49 °C, replacing P_s^2 value by the spontaneous increases of $\Delta Y_s(T)/\Delta Y_s(T_{\min})$ (Y=D, l and η). Here T_c=49 °C is the temperature of PT, $T_{\min}$ is the lower edge of the temperature range studied ($T_{\min}$=39 °C in our case), $\Delta Y_s(T)$ and $\Delta Y_s(T_{\min})$ are spontaneous increments corresponding to the T_c and $T_{\min}$ temperatures. The double critical indices 2β of TGS in the range of 39–49 °C are shown in table 2.

Table 2. Effective critical indices 2β, corresponding to the temperature dependences of spontaneous increments of $\Delta D_s/D$, $\Delta l_s/l$ and $\Delta\eta_s/\eta$ for different crystallophysic direction of TGS crystal

$2\beta_{12}^{(D)}$	$2\beta_{13}^{(D)}$	$2\beta_{21}^{(D)}$	$2\beta_{23}^{(D)}$	$2\beta_{31}^{(D)}$	$2\beta_{32}^{(D)}$
0.90	0.90	0.89	0.89	0.95	0.92
$2\beta_1^{(l)}$	$2\beta_2^{(l)}$	$2\beta_3^{(l)}$	$2\beta_1^{\eta}$	$2\beta_2^{\eta}$	$2\beta_3^{\eta}$
0.91	0.90	0.92	0.88	0.93	0.88

The results obtained testify to an inexact fulfilment of the functional dependences for quadratic electrooptic effect

$$\Delta n_s \sim P_s^2 \qquad (10)$$

and electrostriction

$$\Delta l_{\mathrm{s}} \sim P_{\mathrm{s}}^2. \tag{11}$$

If these effects were displayed in the form indicated, the double critical index 2β would be equal to unity, 2β=1. Let us try to explain the experimental facts obtained.

Analytical relation of the observed temperature dependence of OPD $\Delta D_{\mathrm{s}}/D$ induced by spontaneous polarization can be presented in the most common form

$$\Delta D_{\mathrm{s}}/D(\tau) = a(\tau)P_{\mathrm{s}}^2(\tau) = a(\tau)\tau, \tag{12}$$

where $a(\tau)$ is the temperature dependent coefficient. It follows from the character of experimental dependences of spontaneous increases of $\Delta D_{\mathrm{s}}/D$, $\Delta l_{\mathrm{s}}/l$, and $\Delta\eta_{\mathrm{s}}/\eta$, that the corresponding coefficients $a(\tau)$ are maximal in the region of PT (figure 3).

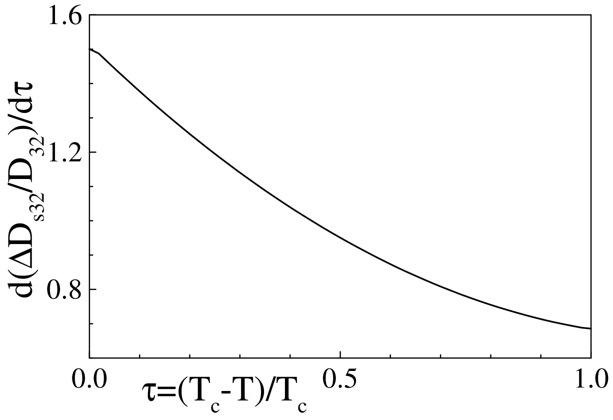

Figure 3. Temperature dependence of the derivative $\mathrm{d}(\Delta D_{s32}/D_{32})/\mathrm{d}\tau$ in the ferroelectric phase of TGS crystal

To obtain the additional proofs of the validity of this viewpoint, we have performed experimental study of the artificially induced electrooptic effect in TGS crystal in the temperature range of 30–65 °C. This investigation was carried out using the same optical scheme. The external electric field of the magnitude $E \approx 3.5\,\mathrm{kV/cm}$ was applied to the sample of TGS crystal at different temperatures along the [010]-direction of spontaneous polarization P_{s}, and the corresponding induced increments of the OPD $\Delta D_e/D$ were measured. The maximum-like temperature dependence of $\Delta D_e/D$ value (figure 4) correlates well with the temperature dependence of $a(\tau)$ in the ferroelectric phase. This maximum-like character of the coefficient mentioned is connected with the inequality $2\beta < 1$.

Taking into account that the temperature dependences of spontaneous increments of $\Delta Y_{\mathrm{s}}/Y$ parameters can be presented in two forms, $Y(\tau) = \tau^{2\beta}$, and $Y(\tau) = a(\tau)\tau$, one can obtain the relation for the temperature dependence of $a(\tau)$ coefficient

$$a(\tau) = \tau^{2\beta-1}. \tag{13}$$

In the cases of $2\beta \neq 1$ and $\tau \neq 1$, the decreasing temperature dependence of the coefficient $a(\tau)$ takes place in the ferroelectric phase at the removal from the PT point $\tau = 0$ (figure 3).

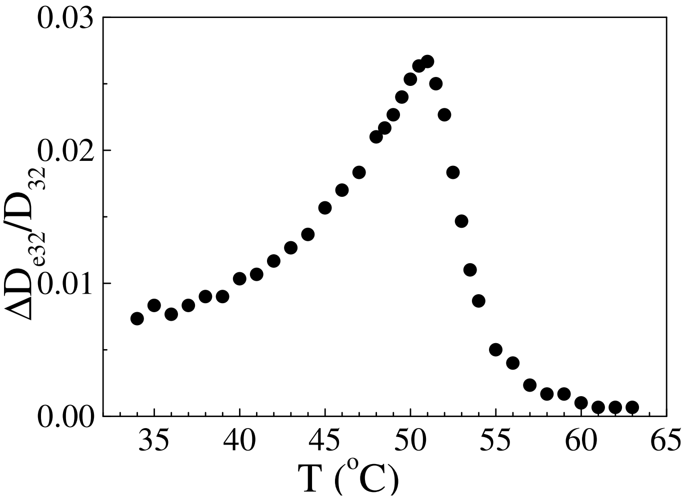

Figure 4. Temperature dependence of the relative optical path difference $\Delta D_{e32}/D_{32}$ of TGS crystal induced by the constant electric field of 3.5 kV/cm along the [010]-direction

Taking into account all the results obtained, we can summarize that the temperature dependences of the coefficients of quadratic electrooptic and electrostriction effects for TGS crystals take place (see relations (10) and (11)). The analysis of table 1 testifies to some segregation of the [010]-direction of spontaneous polarization. Really, among the temperature changes of spontaneous increments Δl_i and $\Delta\eta_j\,(i,j = 1,2,3)$, the dependence $\Delta l_2(\tau)$ is characterised by the least index 2β while the dependence $\Delta n_2(\tau)$ is characterised by the greatest index (see table 2). On the other hand, a proximity of the values $2\beta_2^{(l)} \approx 2\beta_2^{\eta}$ is observed (see table 1), whereas obvious inequalities of similar characteristics for the other two crystallophysic directions $2\beta_{1,3}^{(l)} > 2\beta_{1,3}^{\eta}$ take place (see table 2 and figure 4).

The latter features can be interpreted as a different rate of the ordering of two subsystems. One subsystem relates to the electrons forming the refractive index n while the other is connected with geometric parameters of the crystal unit cell for the directions [100] and [001]. The equality $2\beta_2^{(l)} \approx 2\beta_2^{\eta}$ for the direction of spontaneous polarization [010] can be interpreted as good correlation of the subsystems in TGS crystal mentioned above. From such a viewpoint, the observable inequalities of the indices $2\beta_{1,3}^{(l)} > 2\beta_{1,3}^{\eta}$ testify to various rates of the temperature changes of the corresponding subsystems of the crystal in the temperature range ($\Delta T \sim 10$ °C) below PT point. It is seen in figure 5, in case of z-direction of the crystal studied. A crossing of the curves on figure 6 corresponds to two different indices $\beta_3^{(l)}$ and β_3^{η}. Such a crossing will take place in all cases if the experimental temperature dependence of the parameters studied ($V = \Delta D_{\mathrm{s}}/D$, $\Delta l_{\mathrm{s}}/l$, $\Delta\eta_{\mathrm{s}}/\eta$) is described by different indices β.

We suppose that such a peculiarity in the temperature dependence of different parameters can be characteristic of the ordering of the other ferroelectric crystals.

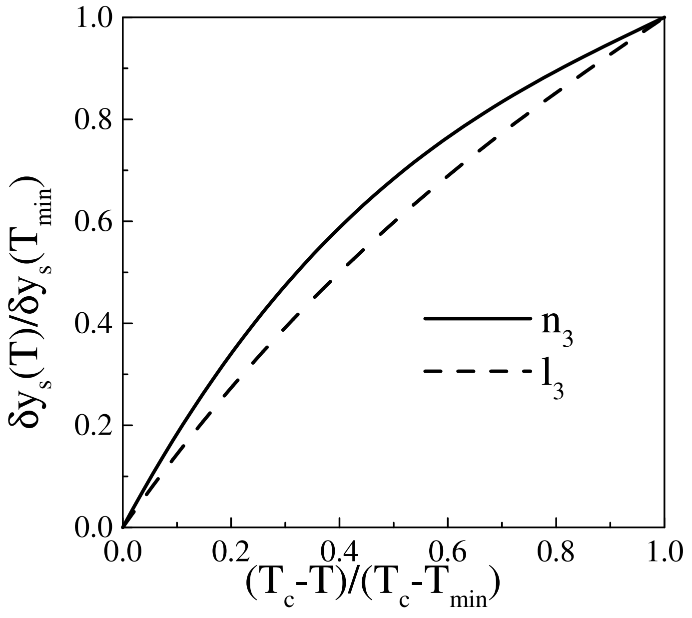

Figure 5. Dependences of the normalized spontaneous changes of thickness (l_3) and changes of the variable part of refractive index (η_3) of TGS for [001]-direction on the normalised temperature $(T_c - T)/(T_c - T_{min})$ in the range of 39–49 °C

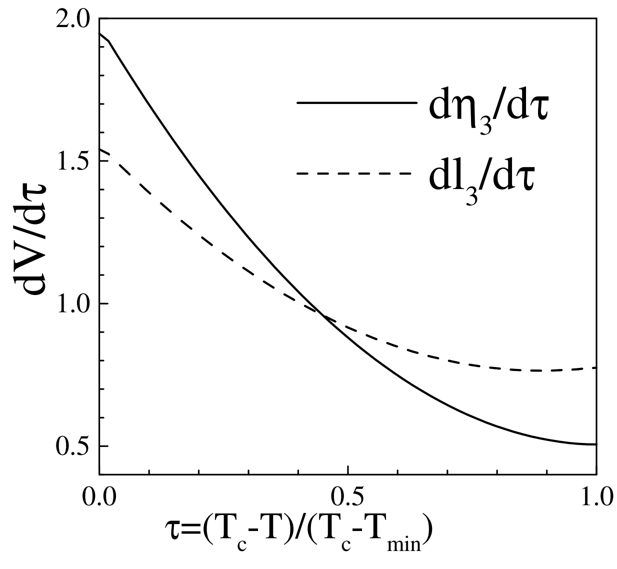

Figure 6. Temperature derivatives of the dependences from figure 5

4. Conclusion

1. The original laser interferometer techniques of Jamen type for measuring the temperature change of the optical path difference of a transparent sample is offered. The techniques makes it possible to define the temperature dependences of thickness $l(T)$ and the variable part of refractive index $[n(T) - 1]$ of the crystal based on the measurements of temperature dependences of the optical path difference $D(T) = l(T)[n(T) - 1]$ for different directions of light propagation and polarization.

2. Deviation from the unity of the double effective critical index 2β for the temperature dependence of the optical path difference induced by a spontaneous polarization in TGS sample is explained by a significant temperature dependence of the maximum-like character of the coefficient of electrooptic, inverse piezooptic, and electrostriction effects.

3. An anisotropy of the critical indices $2\beta_i^{(l)}$ and $2\beta_i^{(\eta)}$, and nonequality $2\beta_i^{(l)} \neq 2\beta_i^{(\eta)}$ testify to different rates of temperature changes of different crystal subsystems taking place at the ferroelectric ordering in the range of $\Delta T \sim 10$ °C below T_c.

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Анізотропія критичних індексів сегнетоелектричного фазового переходу в кристалах ТГС визначена з оптико-інтерференційних досліджень

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Отримано 13 січня 1999 р., в остаточному вигляді –
14 вересня 1999 р.

Досліджено температурні залежності оптичної різниці ходу, змінної частини показника заломлення і товщини кристала тригліцинсульфату для трьох кристалофізичних напрямів в області температур 39–70 °C, що містить температуру T_c=49 °C сегнетоелектричного фазового переходу, використовуючи оптичний інтерферометр типу Жамена. Температурні залежності спонтанних змін досліджуваних характеристик в області 39–49 °C апроксимовані степеневими залежностями $Y \sim \tau^{2\beta}$ з подвоєними засередненими ефективними критичними індексами $2\beta = 0.87 - 0.95$. Відмінність 2β від одиниці пояснюється суттєвою температурною залежністю поблизу точки фазового переходу коефіцієнтів електрооптичного, оберненого п'єзоелектричного ефектів та електрострикції.

Ключові слова: *сегнетоелектрики, фазові переходи, оптичні властивості, критичні індекси*

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