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OPTICAL AND DILATOMETRIC MANIFESTATIONS OF PHASE TRANSITIONS IN K_2SeO_4 CRYSTAL

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Temperature dependencies of the characteristic optical paths difference $D(T)$ of K_2SeO_4 crystal in the range of 80–295 K were measured using the Jamen type interferometer. Significant anomalies of $D(T)$ dependencies in the vicinity of incommensurate–paraelectric phase transition ($T_i = 130$ K) are observed. On the basis of $D(T)$ temperature dependencies measured experimentally and linear expansion $l(T)$ known, the temperature derivative of the refractive indices $\mathrm{d}n/\mathrm{d}T$ are found to be negative in the ranges above and below the temperature $T_i = 130$ K.

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1. Introduction

In the past 20 years much experimental activity has been focused on K_2SeO_4 crystal which has the succession of three phases at decreasing temperature: paraelectric *Pnam*, incommensurate (IC) phase in which the wave vector of the incommensurate wave $k_i = (1-\delta)(a^*/3)$ slightly deviates from the value $k_c = (a^*/3)$ and ferroelectric phase $Pna2_1$ in which frozen-in wave is locked at k_c. The phase transition temperatures are: $T_i = 130$ K and $T_c = 93$ K, respectively [1]. The spontaneous polarization in the IC phase is $P_z = 0$ because the averaged symmetry is *mmm* (centrosymmetric phase) [2]. One-dimensional incommensurate–paraelectric (IC–P) phase transition (PT) in K_2SeO_4 near T_i (x-axis is the direction of incommensurate wave displacement) can be characterised by critical exponent $\beta = 0.345 \pm 0.02$ [3].

Many research works concerning the measurements of optical characteristics of crystal with IC phases are performed on the temperature dependencies of birefringence $\Delta n(T)$. It is caused by the comparative simplicity and accuracy of Senarmon method for measurement of temperature induced birefringence. The obtained temperature dependencies $\Delta n(T)$ in the IC phase $T < T_i$ can be presented by the power-like dependence $\Delta n \sim \tau^{2\beta}$, where $\tau = (T_i - T)/T_i$. The parameter

β calculated can be used for the comparison with theoretical critical index in the equation for temperature dependence of order parameter in the thermodynamic Landau theory [4].

It is necessary to note that the optical path difference $D = l\Delta n$ is the parameter which is measured directly in Senarmon method (and in other interferometric methods for measurements of optical characteristics of crystals) instead of birefringence Δn. Thus, to obtain the temperature dependence $\Delta n(T)$ and respective β-value on the basis of $D(T)$ experimental measurements one must possess the temperature dependence of geometric path $l(T)$.

We have investigated the temperature dependencies of the optical paths $D = ln$ of K_2SeO_4 crystal determined by the corresponding (polarized) refractive indices n in the 80–295 K temperature range. Such measurements were not earlier done despite the relatively wide studies of the optical properties of this crystal.

2. Experimental

We measured the temperature dependencies of optical and geometrical sample thickness difference of K_2SeO_4 crystal,

$$D = l(n-1) = l_o - l_g, \tag{1}$$

for the wavelength $\lambda = 632.8$ nm of the He–Ne laser. The measurements were done on the basis of original home-built interferometer of the Jamen type [5] (Fig. 1). The intensity $I(T)$ of output polarized optical beam was periodically changing due to the temperature changing of optical and geometrical thickness of crystal according to the known relation

$$I(T) \sim \cos^2\left(\varphi_0 + \frac{\pi\Delta D}{\lambda}\right), \tag{2}$$

where φ_0 is initial phase and λ is wavelength of light [5]. The temperature dependence $I(T)$ was measured by the photodiode-6, thermocouple-7 and recorder-10 (Fig. 1). Proceeding from the known dependence $I(T)$, the respective temperature dependence $\Delta D(T)$ was calculated. Measurements were performed at the increase in temperature in the 78–295 K range in the temperature scanning mode.

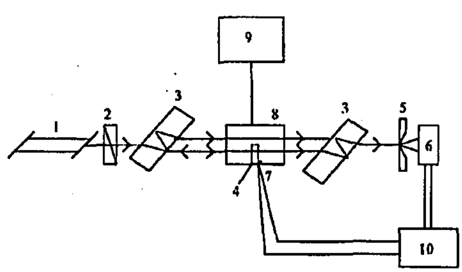

Fig. 1. Scheme of the experimental setup: 1 — He–Ne laser; 2 — polarizer; 3 — glass plates of Jamen type inteferometer; 4 — sample; 5 — diaphragms; 6 — photodiodes; 7 — thermocouple; 8 — thermostate (furnace); 9 — electrical supply block; 10 — X–Y recorders.

Determination of crystallographic directions in K_2SeO_4 samples was performed using a supervision of conoscopic interferometric figures and known main refractive indices $n_a = n_g = 1.549$, $n_b = n_p = 1.539$, $n_c = n_m = 1.543$ ($a \equiv x$, $b \equiv y$, $c \equiv z$) for the wavelength $\lambda = 514.5$ nm [1]. On the basis of these data and results of conoscopic interferometric investigations the orientation of the c-axis and the directions of other two crystallographic axes were established. Small sizes of K_2SeO_4 sample have allowed to perform temperature-and-interferometric measurement in the $[110] \equiv XY$ direction of light propagation only for two its polarizations, $\boldsymbol{E}_1 \parallel [1\bar{1}0] \equiv YX$ and $\boldsymbol{E}_2 \parallel [001] \equiv Z$.

3. Results and discussion

Our investigation showed that ferroelectric PT in K_2SeO_4 crystal at the temperature $T_c = 93$ K is almost not displayed on the temperature dependencies of difference of optical and geometrical thickness $D(T)$ (Fig. 2). The IC–P PT in the vicinity of $T_i = 130$ K is displayed distinctly in the form which is characteristic of the continuous 2nd order PT (Fig. 2). The temperature dependence of optical

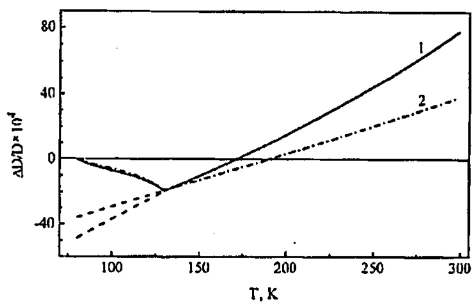

Fig. 2. Temperature dependencies of the relative changes of optical thickness $\Delta D/D$ of K_2SeO_4 single crystal along the [110] direction for light polarization $\boldsymbol{E} \parallel [1\bar{1}0]$ (1) and $\boldsymbol{E} \parallel [001]$ (2).

paths difference $D(T)$ in the $T > T_i$ range is almost linear, and in the $T < T_i$ range it is nonlinear. An approximation of the mentioned above linear dependence $D(T)$ to the $T < T_i$ range has allowed to obtain the temperature dependence of the difference $\Delta D_s(T) = D_{ic}(T) - D_p(T)$, corresponding to the spontaneous increases caused by PT only. Assuming that the ΔD_s value is proportional to characteristic order parameter, we constructed the dependence of normalised spontaneous change $\Delta D_s(T)/\Delta D_s(T_0)$ upon the normalised temperature $(T_i - T)/(T_i - T_0)$ in logarithmic coordinates and defined the respective critical index β according to the relation

$$\Delta D_s(T)/\Delta D_s(T_0) = (T_i - T)/(T_i - T_0)^{2\beta}. \tag{3}$$

These dependencies are close to the linear one for both light polarizations in the temperature range $T_i - T \approx 20$ K (Fig. 3), and the equalities $2\beta_{xy}^{(yx)} = 0.803$ and $2\beta_{xy}^{(z)} = 0.760$ take place. Here, the bottom index corresponds to the direction of

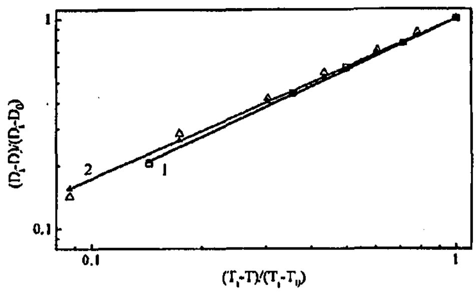

Fig. 3. Dependencies of the normalized spontaneous change of the optical thickness $(D_i - D)/(D_i - D_0)$ upon the normalized temperature $(T_i - T)/(T_i - T_0)$ of K_2SeO_4 single crystal along the [110] direction for light polarization $\boldsymbol{E} \parallel [1\bar{1}0]$ (square, 1) and $\boldsymbol{E} \parallel [001]$ (triangle, 2) in the range of $T < T_i = 130$ K. T_0 value is the starting temperature $(T_0^{(1)} = 116$ K, $T_0^{(2)} = 107$ K).

light propagation and the top one corresponds to the direction of light polarization. The β-value received in this work appreciably exceeds the similar parameter $\beta = 0.345$ obtained from the birefringence study of K_2SeO_4 [3]. This discrepancy is probably connected with different values of temperature ranges, on which the β-parameters were determined. However, if the size of actual temperature ranges does not influence essentially on the β-value calculated, then the reason of the mentioned above difference can be explained by different β-values for various temperature dependent parameters of crystals. The optical thickness $l_o = ln$ and the difference of optical and geometrical thickness $D = ln - l$ of crystal is a combination of its different physical characteristics. Refractive indices characterise the susceptibility of electron and phonon subsystems of crystal to the electromagnetic radiation, but the geometrical thickness is connected directly to the sizes of its unit cell. Therefore, the mentioned above different $2\beta_{xy}^{(yx)}$ and $2\beta_{xy}^{(z)}$ values show the different rates of temperature changes for the refractive indices $n^{(yx)}$ and $n^{(z)}$. Taking into account the definition of optical path difference measured, $D = ln - l$, and the relation $2\beta_{xy}^{(yx)} \neq 2\beta_{xy}^{(z)}$, one can assume different rates of temperature changes for refractive indices $n^{(yx)}$, $n^{(z)}$ and geometric thickness l_{xy}, too.

If η is order parameter of crystal with PT, then the relation $\eta^2 = c_1\tau$ fulfils, where c_1 is constant (see, for example, perfect quadratic temperature dependence of spontaneous polarization for triglycine sulphate (TGS) crystal [6]). The relation $\Delta X/X = a\eta^2 = ac\tau$ can appear as a definition of quadratic dependence of spontaneous change of physical parameter (in our case $X = D,\ l$, or n) upon the order parameter η. If the relation $\Delta X/X = c_2\tau^{2\beta}$ describes an experimental dependence upon the relative temperature τ, then the nonequality $2\beta \neq 1$ is displayed in the temperature dependence of a-coefficient, $\Delta X/X = a(\tau)c_1\tau$.

It is interesting to compare the temperature changes of geometric thickness and refractive indices separately in the temperature range of IC–P PT in the K_2SeO_4 crystal. Proceeding from the definition of difference of optical and geometrical thickness $D = ln - l$, it is possible to write its relative temperature change

$\mathrm{d}(\ln D)/\mathrm{d}T$ in the form

$$\frac{\mathrm{d}(\ln D)}{\mathrm{d}T}=\frac{\mathrm{d}D}{D\mathrm{d}T}=\frac{\mathrm{d}[l(n-1)]}{l(n-1)\mathrm{d}T}=\frac{\mathrm{d}l}{l\mathrm{d}T}+\frac{\mathrm{d}n}{(n-1)\mathrm{d}T}. \tag{4}$$

The relation (4) permits to calculate the parameter $\mathrm{d}n/((n-1)\mathrm{d}T)$ proceeding from the known dependencies $D(T)$ and $l(T)$. On the basis of $D(T)$ dependencies measured by us and dependencies of unit cell parameters $a(T)$, $b(T)$ and $c(T)$ of K_2SeO_4 taken from [1], we have calculated the parameters $\mathrm{d}n/((n-1)\mathrm{d}T)$ in the temperature ranges above and below the IC–P PT temperature (T_i = 130 K). The results of these calculations for different temperature ranges and light polarizations are listed in Table. Proceeding from Table, one can see the decrease in

TABLE

Refractive and dilatometric parameters of K_2SeO_4 crystal in the vicinity of PT at $T_\mathrm{i} = 130$ K.

Parameter	$T \leq T_\mathrm{i}$	$T \geq T_\mathrm{i}$
$(\mathrm{d}l/(l\mathrm{d}T))_x$ [K^{-1}] [1]	3.76×10^{-5}	3.0×10^{-5}
$(\mathrm{d}l/(l\mathrm{d}T))_y$ [K^{-1}] [1]	8.95×10^{-5}	4.12×10^{-5}
$(\mathrm{d}l/(l\mathrm{d}T))_z$ [K^{-1}] [1]	-19.2×10^{-5}	2.88×10^{-5}
$\mathrm{d}(\ln \Delta_{xy}^{(yx)})/\mathrm{d}T$ [K^{-1}]	-9.50×10^{-5}	2.78×10^{-5}
$\mathrm{d}(\ln \Delta_{xy}^{(z)})/\mathrm{d}T$ [K^{-1}]	-6.58×10^{-5}	3.29×10^{-5}
$(\mathrm{d}l/(l\mathrm{d}T))_{xy}$ [K^{-1}]	-6.4×10^{-5}	3.7×10^{-5}
$[\mathrm{d}n/((n-1)\mathrm{d}T)]^{(yx)}$ [K^{-1}]	-15.9×10^{-5}	-0.92×10^{-5}
$[\mathrm{d}n/((n-1)\mathrm{d}T)]^{(z)}$ [K^{-1}]	-12.98×10^{-5}	-0.41×10^{-5}

refractive indices $n^{(z)}$ and $n^{(yx)}$ with an increase in temperature above and below the IC–P PT. The reduction of refractive indices in the $T \leq T_\mathrm{i}$ range exceeds similar reduction in the $T \geq T_\mathrm{i}$ range more than one order of magnitude.

4. Summary

1. Temperature dependencies of the difference of optical and geometrical thickness $D(T)$ of K_2SeO_4 in the range of 80–295 K are measured and these significant anomalies in the vicinity of $T_\mathrm{i} = 130$ K were observed. No appreciable anomalies of such dependencies in the vicinity of ferroelectric 1st order PT at $T_\mathrm{c} = 93$ K were observed.
2. The values of critical indices $b_{xy}^{(yx)} = 0.401$, $b_{xy}^{(z)} = 0.380$ for the IC–P PT at $T_\mathrm{i} = 130$ K are calculated proceeding from the representation of temperature dependence of difference of optical and geometrical thickness $D(T)$ in the form $D(T) \sim ((T_\mathrm{i} - T)/T_\mathrm{i})^{2\beta}$.
3. On the basis of temperature dependencies $D(T)$ measured experimentally and temperature dependencies of linear expansion $l(T)$ known, the temperature derivatives of K_2SeO_4 refractive indices $\mathrm{d}n/((n-1)\mathrm{d}T)$ are found to be negative for temperatures above and below the IC–P PT at $T_\mathrm{i} = 130$ K.

The value $dn/((n-1)dT)$ in the range of $T < T_i$ ($[dn/((n-1)dT)]^{(xy)} = -15.9 \times 10^{-5}$ K^{-1}, $[dn/((n-1)dT)]^{(z)} = -12.98 \times 10^{-5}$ K^{-1}) exceeds analogous ones in the $T > T_i$ range ($[dn/((n-1)dT)]^{(yx)} = -0.92 \times 10^{-5}$ K^{-1}, $[dn/((n-1)dT)]^{(z)} = -0.41 \times 10^{-5}$ K^{-1}) by more than one order of magnitude.

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