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BIREFRINGENT AND DIELECTRIC PROPERTIES OF $[N(C_2H_5)_4]_2ZnBr_4$ AND $[N(C_2H_5)_4]_2CdBr_4$ CRYSTALS

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Dielectric and birefringent properties of $[N(C_2H_5)_4]_2ZnBr_4$ and $[N(C_2H_5)_4]_2CdBr_4$ crystals were investigated. It has been ascertained that two phase transitions manifest themselves in the temperature dependencies $\varepsilon(T)$ for $[N(C_2H_5)_4]_2CdBr_4$ crystal — a second-order transition at T_1 = 311 K and a first-order one — at T_2 = 39 K (ΔT_2 = 11 K). Besides two earlier known phase transitions in $[N(C_2H_5)_4]_2ZnBr_4$ at T_1 = 350 K and T_2^{cool} = 282.8 K ($\Delta T_2 \approx 2.3$ K), the additional one was found at T_2^* = 287.0 K, both on the cooling and heating runs. On the basis of the data about the peculiarities of dielectric and optical properties in the vicinity of T_2 one can made the conclusion about the ferroelectric character of the phase, situated between T_2^* and T_2^{cool}.

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1. Introduction

At room temperature $[N(C_2H_5)_4]_2ZnBr_4$ crystals belong to the tetragonal symmetry group $P4_2/n$–C_{4h}^4 with parameters $a = b = 9.047(5)$ Å, $c = 15.946(5)$ Å, $z = 2$. Their structure consists of complex $[ZnBr_4]^{2-}$ anions with distorted tetrahedral co-ordination of central atoms and molecular $[N(C_2H_5)_4]^+$ cations, in which methylen and methyl groups are disordered [1]. The alignment of a structural unit is very close to the one of $[N(C_2H_5)_4]_2NiCl_4$ crystals (space group

$P4_2/nmc - D_{4h}^{15}$) [2]. However, the absence of vertical ($\parallel c$) mirror planes leads to the lowering of the cation symmetry to $\bar{4}$–S_4 and to the disordering of C atoms in $[N(C_2H_5)_4]^+$ complex. Thus, in $[N(C_2H_5)_4]_2ZnBr_4$ crystals, the following sequence of phases is realised [1]:

$$2/m\ (?)\ \underset{\text{1st order}}{\xrightarrow{T_2\,=\,281.5\text{ K}}}\ 4/m\ (P4_2/n)\ \underset{\text{2nd order}}{\xrightarrow{T_1\,=\,350\text{ K}}}\ 4/mmm\ (P4_2/nmc).$$

The $[N(C_2H_5)_4]_2CdBr_4$ crystals were studied by light absorption [3] methods. It is revealed that the following sequence of phase transitions is characteristic of these crystals:

$$2/m\ (?)\ \underset{?}{\xrightarrow{T_2\,=\,72\pm5\text{ K}}}\ 4/m\ (P4_2/n)\ \underset{\text{2nd order}}{\xrightarrow{T_1\,=\,311\text{ K}}}\ 4/mmm\ (P4_2/nmc).$$

The $[N(C_2H_5)_4]_2CdBr_4$ crystals were studied also by dilatometric methods [4], but the obtained phase transition temperatures differ significantly from the mentioned values.

Therefore, a significant dynamics of organic complex and a distortion of $[ZnBr_4]^{2-}$ tetrahedron in the $[N(C_2H_5)_4]_2ZnBr_4$ in comparison with $[N(CH_3)_4]_2MeBr_4$ (Me = Cd, Co, Mn, Zn) must cause more complicated sequence of phase transitions. A discrepancy in phase transition points for $[N(C_2H_5)_4]_2CdBr_4$ crystals needs more detailed investigation of their physical properties. The investigations of birefringent and dielectric properties of $[N(C_2H_5)_4]_2ZnBr_4$ and $[N(C_2H_5)_4]_2CdBr_4$ in the temperature region of their phase transitions were performed.

The samples were grown at room temperature from aqueous solution of the $N(C_2H_5)_4Br$, $ZnBr_2$, and $CdBr_2$ salts taken in the stoichiometric ratio. Orientation of the samples was performed according to data [1]. The birefringent properties of the crystals were investigated by Senarmont's method at the wavelength $\lambda = 632.8$ nm. Electric permittivity and dielectric losses tangent $\tan\delta$ were measured using the Hewlett–Packard 4275A-MULTI-FREQUENCY LCR METER. The specimen square was about 15–25 mm^2 and the thickness was equal to 0.5–1.0 mm. After polishing, conducting silver paste electrodes to the samples were applied. The sample holder was inserted into a Leybold flow liquid helium cryostat. The temperature of samples was measured by the silicon DT-470 Lake Shore Cryotronics temperature sensor.

2. Experimental results

The birefringence ($\delta(\Delta n)$) temperature dependencies for $[N(C_2H_5)_4]_2ZnBr_4$ and $[N(C_2H_5)_4]_2CdBr_4$ crystals are shown in Figs. 1, 2. Upon cooling the following phase transitions were observed: at $T_1 \approx 350$ K, $T_1 \approx 311$ K and $T_2 \approx 281.5$ K, $T_2 \approx 72 \pm 5$ K for $[N(C_2H_5)_4]_2ZnBr_4$ and $[N(C_2H_5)_4]_2CdBr_4$ crystals respectively. The phase transition at $T_2 = 72 \pm 5$ K is not approached, since the measurements were performed up to liquid nitrogen temperature (77 K). The T_2 value was obtained as a result of extrapolation. The jumps of $\delta(\Delta n_c)$ and $\delta(\Delta n_b)$ (Fig. 1), observed in $[N(C_2H_5)_4]_2ZnBr_4$ crystals at $T_2 = 281.5$ K, testify to the possibility of a first-order phase transition. The temperature hysteresis of $\delta(\Delta n_c)$ at this

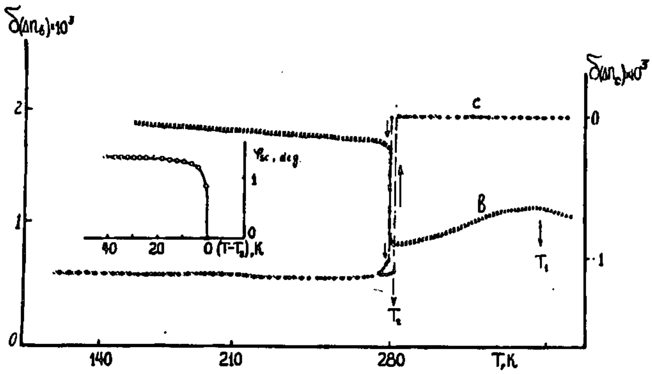

Fig. 1. Temperature dependence of the optical birefringence for $[N(C_2H_5)_4]_2ZnBr_4$ crystal. Insert — temperature dependence of neighbouring domain indicatrix spontaneous rotation angle.

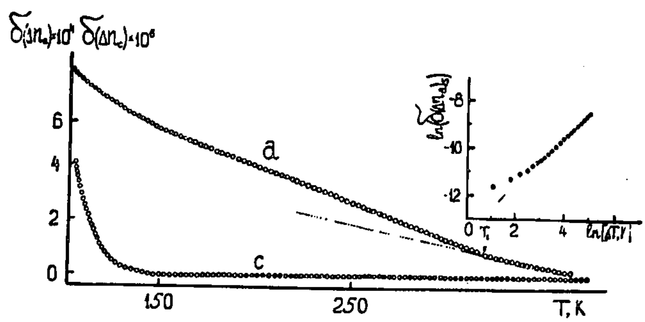

Fig. 2. Temperature dependence of the optical birefringence for $[N(C_2H_5)_4]_2CdBr_4$ crystal. Insert — temperature dependence of the optical birefringence in the double logarithmic scale.

transition is $\Delta T = 2$ K. The dependence $\delta(\Delta n_a) = f(T)$ undergoes the kink at $T_1 = 311$ K (Fig. 2), characteristic of a second-order phase transition, which is confirmed also by piezooptic measurements. The critical index β in this case is equal to 0.49 ± 0.01 (insert in Fig. 2) which corresponds to the Landau theory concerning phase transitions of second order [5]. For c-cut of $[N(C_2H_5)_4]_2CdBr_4$ crystals, as it would be expected, $\delta(\Delta n_c) = 0$ for $T \geq 150$ K. Starting from $T = 150$ K, $\delta(\Delta n_c)$ increases. The appearance of optical biaxiality is evidently connected with arising of stresses and testifies to one more phase transition at low temperatures. The anomalous growth of π^0_{66} value in this temperature interval was also observed. The spontaneous increment $\delta(\Delta n_b)$ below T_1 is described by the index $\beta = 0.48 \pm 0.02$ for $[N(C_2H_5)_4]_2CdBr_4$ crystals.

The crystal of $[N(C_2H_5)_4]_2ZnBr_4$ becomes optically biaxial in the phase taking place below T_2. The domains arising in this case have two orientational states, which are well observed on the c-cut in polarized light. They move under the influence of mechanical stress. This testifies to the ferroelastic nature of the noted phase. The temperature dependence of neighbouring domain indicatrix spontaneous rotation angle is shown in the insert of Fig. 1. Taking into account all noted above, according to [6], the appearance of two orientational states of domains is possible when low-temperature phase is monoclinic and has point group of $2/m$.

The dependence $\delta(\Delta n_c) = f(T)$ for different values of σ_6 is shown in Fig. 3. It may be noted that with increase in σ_6 value, the minimum at T_2 at first is

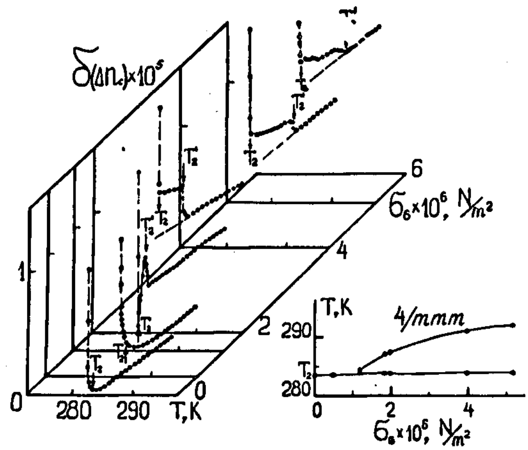

Fig. 3. Temperature dependence of the optical birefringence at different values of σ_6. Insert — dependence of $T = f(\sigma_6)$.

eroded and for $\sigma_6 = 1.2 \times 10^6$ N/m^2 the additional phase transition manifests itself. Further increase in σ_6 is followed by the broadening of intermediate phase existence region (insert of Fig. 3). Splitting of the phase transition at T_2 under the influence of σ_6 in $[N(C_2H_5)_4]_2ZnBr_4$ is impossible to be explained only by change of $ZnBr_4^{2-}$ tetrahedron size as it was supposed in the case of hydrostatic measurements of $[N(CH_3)_4]_2MeCl_4$ group crystals [7]. It may be also noted that such changes are not observed under the influence of σ_1. Probably, σ_6 stress causes also particular ordering of $[N(C_2H_5)_4]^+$ groups.

The temperature dependence of electric permittivity ε'_c of $[N(C_2H_5)_4]_2ZnBr_4$ crystals along c—axis upon cooling run are shown in Fig. 4a for three frequencies. At room temperature the value of electric permittivity presented for $\nu =$ 10 kHz was $\varepsilon'_c = 4.7 \pm 0.2$. The value of ε'_c decreases slightly with cooling, and the sharp increase in ε'_c value from $\varepsilon'_c = 4.5$ to $\varepsilon'_{c\,\max} = 17.2$ is observed at $T_2^{\rm cool} = 282.8$ K. Then ε'_c decreases slightly down to helium temperature ($\varepsilon'_c = 2.1$ at $T = 4.2$ K). The temperature dependence of dielectric losses tangent for c-cut of crystal (Fig. 4b) also has a peak $\tan\delta_{\max} = 0.63$ at $T_2^{\rm cool}$. Besides, an anomalous behaviour of ε'_c and $\tan\delta$ (Fig. 4a,b) is observed in the vicinity of $T = 265$ K. A similar temperature dependence is characteristic also of ε' and $\tan\delta$ along b-axis

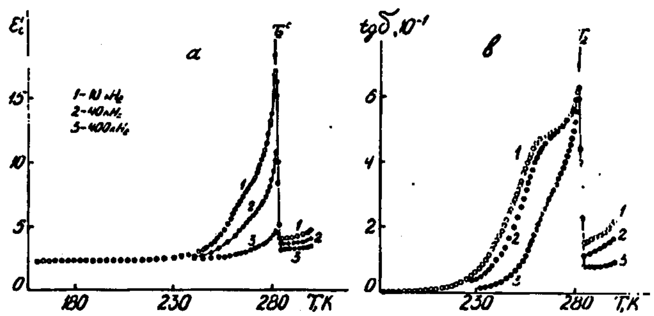

Fig. 4. The temperature dependencies of ε_c' (a) and $\tan\delta$ (b) for $[N(C_2H_5)_4]_2ZnBr_4$ crystal.

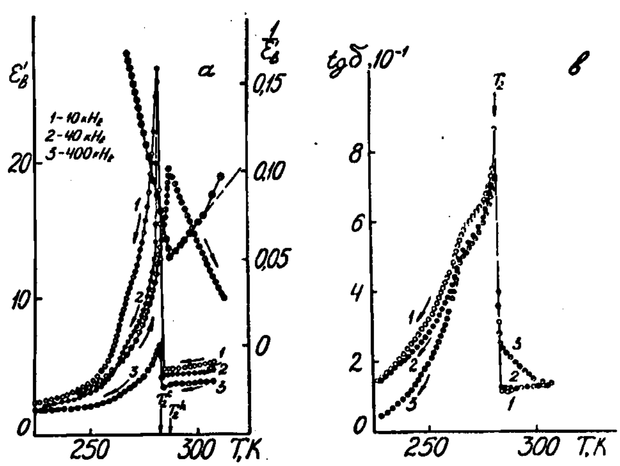

Fig. 5. The temperature dependencies of ε_b', $1/\varepsilon_b'$ (a) and $\tan\delta$ (b) for the $[N(C_2H_5)_4]_2ZnBr_4$ crystal.

of the $[II(C_2H_5)_4]_2ZnBr_4$ crystals (Fig. 5a,b). However, the maxima of ε' and $\tan\delta$ values are equal to 26.8 and 0.87, respectively. The insignificant dispersion of ε_c', ε_b' and $\tan\delta$ occurs above T_2. An essential decrease in ε' and $\tan\delta$ with increasing frequency is observed together with a sharp increase in ε' at phase transition point. The frequency dependence of ε' and $\tan\delta$ at lower temperatures is less essential. The ε' and $\tan\delta$ values become practically independent on frequency in the temperature region of 4.2–220 K.

The temperature dependencies of ε_c' and ε_b' for $[N(C_2H_5)_4]_2ZnBr_4$ crystal are depicted in Fig. 5a and Fig. 6 for cooling and heating run. The temperature of phase transition on the cooling run is $T_2 = 282.8$ K. Upon heating it is shifted to the higher temperatures, the value of the hysteresis is $\Delta T = 4$ K. Moreover,

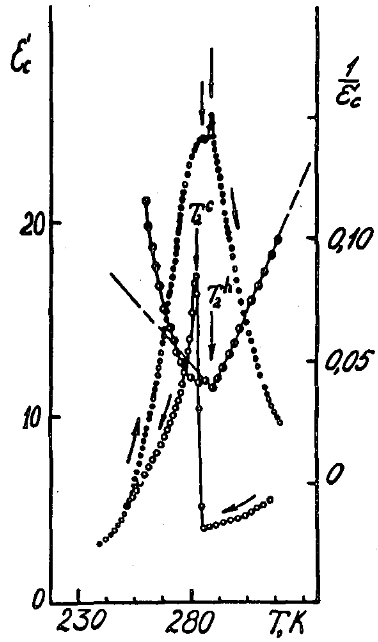

Fig. 6. The temperature dependencies of ε_c' and $1/\varepsilon_c'$ for the $[N(C_2H_5)_4]_2ZnBr_4$ crystal on heating (*) and cooling (o) runs at the frequency of the measuring electric field $\nu = 10$ kHz.

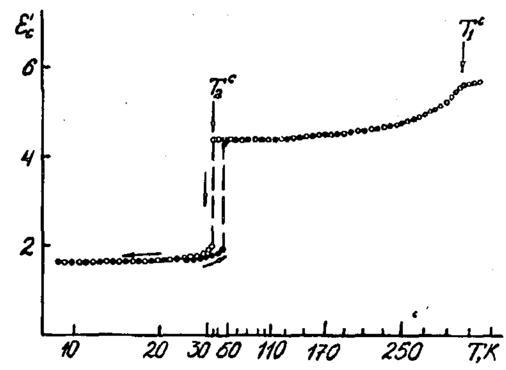

Fig. 7. The temperature changes of ε_c' for the $[N(C_2H_5)_4]_2CdBr_4$ crystal.

a phase transition at T_2^{heat} is splitted into two transitions at $T_2^{\text{heat}} = 285.1$ K and $T_2^{*\text{heat}} = 287.0$ K upon heating of the c-cut.

Contrary to the $[N(C_2H_5)_4]_2ZnBr_4$ crystals a dispersion of the dependence of ε_c' and tanδ for $[N(C_2H_5)_4]_2CdBr_4$ crystals is insignificant at room temperature ($\varepsilon'_{c\,\text{room}} = 5$). A phase transition of the second order at $T_1 = 311$ K is observed for these crystals on cooling run (Fig. 7), as well as a first-order one at $T_2^{cool} = 39$ K ($\Delta\varepsilon'_c = 2.4$) with the hysteresis $\Delta T = 11$ K. The former phase transition was observed by birefringence method.

3. Discussion and conclusions

It must be noted that $[N(C_2H_5)_4]_2MeCl_4$ crystals may exist in three phases [2]. According to the studies of NMR spectra of $[N(C_2H_5)_4]_2MeCl_4$ crystals [2], their high-temperature phase is characterized by high dynamics of tetrahedron of both types, high symmetry and intrinsic disordering of $[N(C_2H_5)_4]^+$ molecule. A phase transition of "displacive" type occurs near 225 K in these crystals, which manifests itself in a sharp increase in dielectric permittivity. This transition is shifted to higher temperature region with the increase in MeX_4^{2-} tetrahedron size. A dynamics of organic complexes is less in the intermediate phase, but disorder of $[N(C_2H_5)_4]^+$ molecule is still kept. It is possible that this phase is ferroelectric one.

Another phase transition is connected with the order of $[N(C_2H_5)_4]^+$ ions. This transition is shifted to lower temperature region with the increase in MeX_4^{2-} tetrahedron size. A large temperature hysteresis is characteristic of this phase transition. The obtained phase diagram (a dependence of a phase transition temperatures versus MeX_4 tetrahedron size) is in good agreement with the data of [8], where one phase transition at $T_2 = 220$ K is revealed in $[N(C_2H_5)_4]_2CoCl_4$ crystals only.

The $[N(C_2H_5)_4]_2MeBr_4$ (Me = Mn, Co) crystals were investigated in detail. The phase transitions at 270 K and 280 K for $[N(C_2H_5)_4]_2MnBr_4$ crystals were observed [2, 8] and a relaxation behaviour of ε' in the vicinity of 200 K for $[N(C_2H_5)_4]_2CoCl_4$ crystals was detected.

The results described above for the electric permittivity ε' of the $[N(C_2H_5)_4]_2ZnBr_4$ crystals showed only one phase transition on the cooling run $T_2^{cool} = 282.8$ K and two phase transitions on the heating run $T_2^{heat} = 285.1$ K and $T_2^{*heat} = 287.0$ K. The electric permittivities ε'_c and ε'_b achieve significant values at T_2, as it may be seen from Figs. 6 and 5. Moreover, the ε'_c value in the initial phase is described by the Curie–Weiss law

$$\varepsilon' = \frac{C}{T - 275},$$

where $C = 350$ K. Thus, it may be suggested that an intermediate ferroelectric phase appears below T_2. In this phase the crystals must belong to a point symmetry element action.

The presence of the additional phase transition is also confirmed by optical studies. The temperature dependence of $\delta(\Delta n_b)$ (Fig. 8) shows the existence of two phase transitions at $T_2^{*cool} = 287$ K and $T_2^{cool} = 282 \pm 5$ K. The temperature dependence of the piezooptic coefficient π_{66}^0 also has anomalies at these temperatures. Thus, an intermediate phase exists in the narrow temperature region near T_2. The additional phase transition at T_2^{heat} revealed in $\delta(\Delta n)$ data at the cooling run.

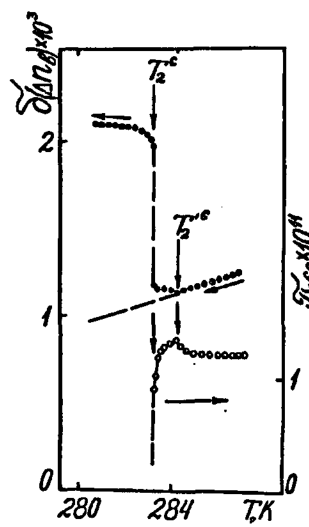

Fig. 8. The temperature changes of birefringence $\delta(\Delta n_b)$ (*) and reduced piezooptic coefficient π_{66} (o) for the $[N(C_2H_5)_4]_2ZnBr_4$ crystal.

According to the results of the temperature investigation of the electric permittivity of the $[N(C_2H_5)_4]_2CdBr_4$ crystal the low-temperature phase transition occurs at $T_2 = 39$ K. The absence of ε_c' and $\tan\delta$ dispersion, as well as the characteristic behaviour of ε_c' at $T_2 = 39$ K may be a confirmation of the conclusion made in [9] about ferroelastic nature of the phase below T_2. The obtained phase transition temperatures for $[N(C_2H_5)_4]_2CdBr_4$ are in good agreement with those in [2].

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