Crystallooptical Properties of Ferroics with the Dimethylammonium Cation (DMA-MeCl$_4$, Me=Cu, Zn; DMA-MnCl$_3$) in the Region of their Phase Transitions

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Abstract

The results of investigations of the crystallooptical effects in the ferroics with dimethylammonium-cation performed in vicinity of phase transitions using Senarmont's method are presented in the paper. The existence of incommensurate phase in DMA-CuCl$_4$ crystals was confirmed within the framework of 279.5-296 K. Besides, the phase sequence for DMA-ZnCl$_4$ and DMA-MnCl$_3$ compounds has been amended.

Key words: ferroics, incommensurate phase, piezooptic, electrooptic, dimethylammonium.

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Introduction

This work is devoted to the study the phase transitions (PTs) in crystals with dimethylammonium cation: $(NH_2(CH_3)_2)_2MeCl_4$ (DMA-MeCl$_4$, Me=Cu, Zn) and $NH_2(CH_3)_2MnCl_3 \times 2\ H_2O$ (DMA-MnCl$_3$). DMA-CuCl$_4$ undergoes a complicate sequence of PTs including ferroelectric (T_c=279.5 K) and ferroelastic (T_l=253 K) ones (in a cooling run) [1, 2]. The specific optical and spectral properties, observed in the previous experiments, allowed to suggest the existence of the incommensurate (IC) phase within the temperature region 279.5-296 K [2]. At room temperature DMA-CuCl$_4$ belongs to the space group of symmetry *Pnam* [3]. DMA-ZnCl$_4$ is characterised by the symmetry $P2_1/n$ at T=296 K. As it follows from the data of previous optical, dielectric and spectral investigations, this crystal undergoes phase transitions at T_1=310 K, T_3=272 K, T_4=252 K, T_6=215 K and T_7=201 K [4].

It was suggested that DMA-MnCl$_3$ belongs to the space group of symmetry *Cmca* at room temperature [5]. Nevertheless, in more recent investigations it has been shown that this crystal possesses the *C/*2*c* group of symmetry at room temperature [6] and undergoes a second order phase transitions at T_1=300 K, T_2=235 K and T_3=180 K that manifest themselves in the temperature dependences of the dielectric parameters and thermal expansion coefficients [7]. In the same time, similarly to the case of DMA-ZnCl$_4$ the nature of these PTs is not clear enough at this moment.

Experimental

Good quality crystal samples were grown by slow evaporation of water from an aqueous solution of dimethylammonium and metal chlorides taken in the stoichimetric ratio.

The increments of optical birefringence were measured using Senarmont's method. The electric field was applied to the sample through the transparent tin oxide electrodes.

Results and discussion

The changes of slope in the temperature dependences of the optical birefringence of DMA-$MnCl_3$ at T_1=302 K, T_2=230 K i T_3=180 K (Fig.1) would be related to the phase transitions of a second order. Due to the continuous nature of these PTs the corresponding anomalies of the optical birefringence become clearly seen only when to take into account the data of thermal expansion [7].

The corresponding anomalies were found in the temperature dependences of the effective piezooptic coefficients of DMA-$MnCl_3$ (Fig.2) it would be presented as $\pi^0_{ij}=d(\delta(\Delta n)_i)/\sigma_j$, where $\delta(\Delta n)_i$ is the optical birefringence induced by applied mechanical stress σ_j. These parameters are expressed through the coefficients π_{jl} of true piezooptic effect: $\pi^0_{il}=1/2\ (n^3_j\pi_{jl} - n^3_k\pi_{kl})$, where n_j and n_k are the refractive indices.

It is interesting to note that the low temperature anomaly of π^0_{21} is observed at higher temperature (T_3^*=198 K) than those for other coefficients and optical birefringence

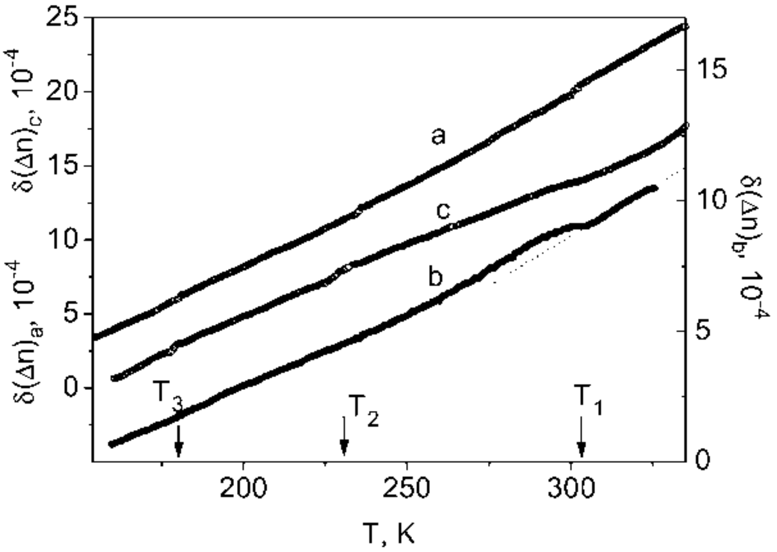

Fig.1. Temperature dependences of the optical birefringence for the principal cuts, perpendicular to the *a*-, *b*- and *c*- crystallographic axes of DMA-$MnCl_3$ crystal respectively.

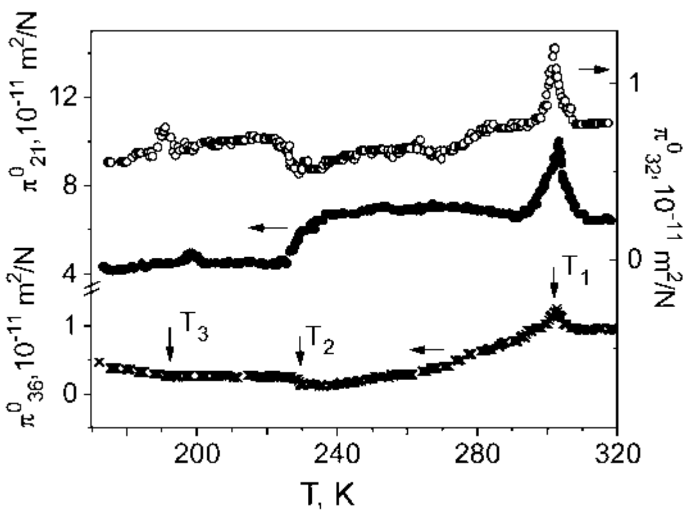

Fig.2. Temperature dependences of the piezooptic coefficients π^0_{32}, π^0_{36} and π^0_{21} for DMA-$MnCl_3$ crystals.

(T_3=180 K). Such a situation, obviously, is connected with the shift of the corresponding phase transition temperature under the influence of the applied stress σ_j. One can note a large anisotropy of these parameters. Indeed, the π^0_{21} coefficient value appeared to be one order of magnitude larger than the value of π^0_{32}. This phenomenon is connected with a layered structure of the crystal (the layers are parallel to the (100) planes [6]). The nonzero value of the π^0_{36} coefficient correlate with the conclusion [6] about the monoclinic symmetry of the room temperature phase.

The thermooptic memory effect (TOM) was investigated in DMA-$CuCl_4$ crystals in the temperature range of 279.5-296 K to confirm the existence of the IC modulation. Indeed, it has been found that after continued keeping of the sample at the constant temperature T_{st}=285,2 K within the mentioned region one can observe the characteristic anomaly on the $\delta(\Delta n)$ temperature dependence (Fig.3). Its magnitude and shape similarly to the isomorphous TMA-$MeCl_4$ (Me = Zn, Co, Fe) crystals depend on the time of temperature stabilisation. It should be noted that in comparison with the mentioned compounds the DMA-$CuCl_4$ crystal is characterised by the largest magnitude and the most wide region of the TOM effect existence at close values of time and temperature of stabilisation [9]. In comparison Fig.3 presents the corresponding anomaly in TMA-$ZnCl_4$ crystals, that possess the IC modulation almost in the same temperature region (280-296 K). Such a difference in the TOM effect magnitude, first of all, would be caused by more pronounced contribution of the nonequilibrium electrons arising at the optical excitation. In this case one can note, that DMA-$CuCl_4$ crystals are characterised by considerable intraionic absorption at the wavelength of the probing laser radiation (λ=633 nм) unlike to the TMA-$ZnCl_4$.

To confirm the supposition concerning existence in DMA-$CuCl_4$ of the IC structure within the temperature range of 279,5-296 K we investigated in details the electrooptic effect in vicinity of the incommensurate and ferroelectric phase transitions.

The effective electrooptic coefficient r^0_{ij} is connected with induced birefringence $d(\delta(\Delta n)_i)$ and electric field E_j by relation [8]: $r^0_{ij}=d(\delta(\Delta n)_i)/dE_j$. Fig.4 depicts the temperature dependence of the r^0_{11} coefficient (the direction of applied electric field coincides with the direction of spontaneous polarisation below T_c)

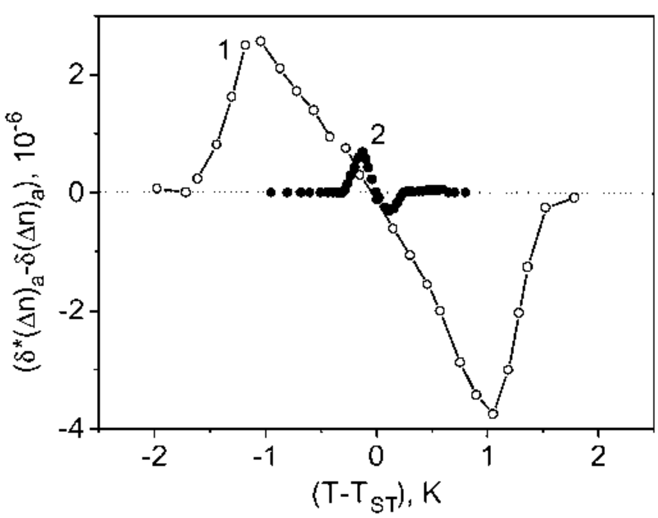

Fig.3. The anomalies of the thermooptic memory effect: 1 – in DMA-$CuCl_4$ crystal (time of stabilisation within the IC phase: t=25 h; T_{st}=285.2 K); 2 – in TMA-$ZnCl_4$ (t=25 h; T_{st}=283.4 K).

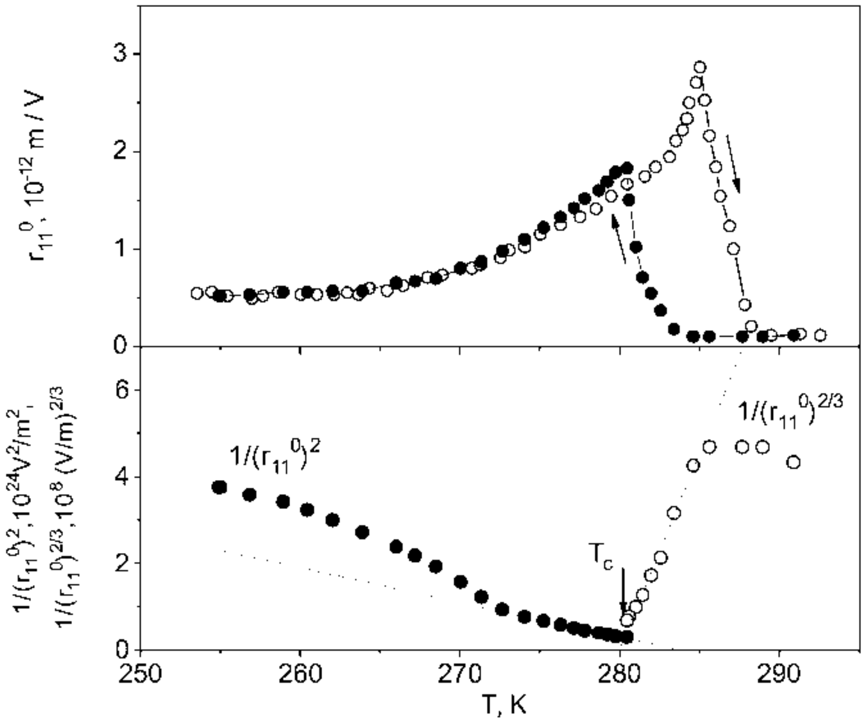

Fig.4. The temperature dependences of the effective electrooptic coefficient $r_{11}^0 = \bar{n}^3 (r_{21}-r_{31})$ [2] and inverse values for DMA-$CuCl_4$ crystal.

in cooling and heating run [2]. The electrooptic coefficient shows at T_c the anomalies characteristic of I order improper ferroelectric phase transition with the clear temperature hysteresis ($\Delta T_C \cong 5$ K). Moreover, this coefficient stays nonzero even within the comparatively wide range in the framework of the IC phase. Such a situation is explained in terms of polarizability of the soliton structure under the applied static electric field.

The presence of the linear EOE at $T>T_c$ as well as specific behaviour of the optical birefringence [2] including the thermooptic memory effect would be related to the existence of the IC structure. The global hysteresis in the temperature dependences of $\delta(\Delta n)_i$ for example is explained by the appearance of the structural solitons that would exist not only in the IC phase but also in the neighbouring commensurate phases [9]. The linear EOE in the IC phases does not occur [10] in the crystal sample without application of polarising static electric field E_1^{dc} (in the ferroelectric phase this field is used for the transformation of the sample into the single domain state). Under the influence of E_1^{dc} there would arise the linear EOE which should be quadratic by its nature. Its value depends on the external field, which induces polarisation of the soliton structure [11]. Moreover, this polarisation P_s^{dc} stays nonzero even after removing the external field E_1^{dc} due to the defect-induced pinning of solitons. Under such circumstances the sample stays unipolar and would be characterised by nonzero value of r_{11}^0 in the low temperature part of the IC phase (soliton regime).

This model was developed for the description of the linear EOE around T_c point in the related materials of the A_2BX_4 family with an IC phase [11]. According to this model:

$$r_{11}^0 = 2\varepsilon_0(\varepsilon_a^{'}-1)\, R_{11}^* P_0 n_s p^s E_1\,, \qquad (1)$$

where $\varepsilon_a^{'}$ is the dielectric permittivity; $R_{11}^* = R_{2211} - (n_3/n_2)^3 R_{3311}$ is the effective coefficient of the quadratic EOE; P_0 is the amplitude of the spontaneous polarisation wave in the IC structure, n_s is the soliton density, p^s describes the polarizability of the soliton lattice; E_1 – is the electric field used at measurements of the r_{11}^0 coefficient ($E_1 < E_1^{dc}$).

Taking into account that R_{11}^* and P_0 practically do not depend on the temperature at least for the crystals of the A_2BX_4 family [11, 12], the anomalous behaviour of r_{11}^0 at T_c would be connected with the changes of n_s, p^s and ε_a' values whereas the hysteresis should be related to the processes of nucleation and annihilation of the solitons and their pinning on defects. It has been found [13] that the dielectric permittivity in the framework of the IC phase in vicinity of T_c follows the Curie-Weiss law: $\varepsilon_a' \sim (T-T_c)^{-1}$. Assuming that other parameters show the temperature behaviour similar to those in the related crystals of A_2BX_4 family, such as Rb_2ZnBr_4 [14], for estimation of r_{11}^0 one can use the relations $p^s \sim (T-T_c)^{-1}$ and $n_s \sim (T-T_c)^{1/2}$. In the framework of this model for the IC phase the r_{11}^0 coefficient should be written as $r_{11}^0 \sim (T-T_c)^{3/2}$, whereas for the ferroelectric phase: $r_{11}^0 \sim (T_c-T)^{-1/2}$. It has been found that these relations approximate the experimental data within the temperature regions 5.5 K above T_c (the soliton regime) and 8 K below T_c respectively (see Fig.4). Therefore, one can conclude that electrooptic measurements confirm the supposition concerning the phase sequence in $DMA\text{-}CuCl_4$.

The study of the optical birefringence [14] and piezooptic effect confirms the presence of the PTs in $DMA\text{-}ZnCl_4$ at T_1=310 K, T_2=295 K, T_3=272 K, T_4=250 K, T_5=238 K and T_6=217 K (Fig.5). The observed strong anisotropy of the effective piezooptic coefficients (the π_{23}^0 coefficient [14] appeared to be two order of magnitude larger than π_{31}^0) in this crystal as well as in $DMA\text{-}MnCl_3$ reflect the two-dimensional character of the crystalline structure arrangement.

Conclusion

As it follows from the data of the birefringent, electro- and piezooptic measurements, the investigated crystals possess the following sequences of phase transitions*:

$DMA\text{-}MnCl_3$: T_3=180 K, T_2=235 K, T_1=302 K;

$DMA\text{-}CuCl_4$: T_L=253 K, T_c=279,5 K, T_i=296 K;

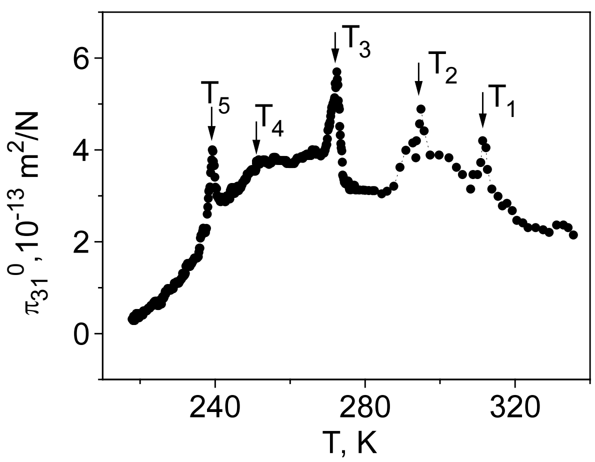

Fig.5. Temperature dependence of π_{31}^0 effective piezooptic coefficient for $DMA\text{-}ZnCl_4$ crystal.

DMA-$ZnCl_4$: T_7=201 K, $T_{6(L)}$=217 K, T_5=238 K, T_4=250 K, T_3=272 K,T_2=295 K, T_1=310 K;

Performed investigations confirmed that the room temperature phase in DMA-$MnCl_3$ possesses the space group of symmetry *C/2c*. The large values of the effective piezooptic coefficients make the DMA-$MnCl_3$ crystals very attractive for application in the stress sensors.

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*Assignment of phase transitions:

c – ferroelectric,

L – ferroelastic;

i – incommensurate.