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Dielectric and Birefringent Properties of $[(CH_3)_2NH_2]_5Cd_2CuCl_{11}$ Solid Solutions in the Region of Their Phase Transitions

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On the basis of the optical and dielectric investigations of $[(CH_3)_2NH_2]_5Cd_2CuCl_{11}$ solid solutions the existence of phase transitions at $T_1 = 175$ K and $T_2 = 117.5$ K was confirmed. Both phase transitions were found to be shifted toward lower temperatures with respect to the corresponding transitions in the "host" $[(CH_3)_2NH_2]_5Cd_3Cl_{11}$ crystals. It was found that the proton conductivity in $[(CH_3)_2NH_2]_5Cd_2CuCl_{11}$ crystals is realized through the Grotthus mechanism. The investigations of the birefringent properties confirmed existence of the structural changes at $T_0 = 320$ K connected with the complex co-operative effect involving weakening of the hydrogen bonds and modification of the Jahn–Teller distortion with temperature.

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1. Introduction

The new solid solution $[(CH_3)_2NH_2]_5Cd_2CuCl_{11}$ (DMACCC) belongs to the family of organic-inorganic crystals containing dimethylammonium cations. The nearest crystal is the "pure" crystalline compound with the composition $[(CH_3)_2NH_2]_5Cd_3Cl_{11}$ (DMACC). The X-ray structural investigations show that at room temperature the DMACC crystal is of orthorhombic symmetry (the space group *Cmcm*) [1]. There are four formula units in the unit cell. The structure is formed by two alternating layers parallel to [001]. One of them consists of the dimethylammonium cations and the other of the complex anions. Hydrogen bonds of the N–H. . .Cl type link the two layers. In the $[Cd_3Cl_{11}]^{5-}$ anion each Cd atom is octahedrally coordinated. The anionic layers are interlinked by two types of DMA cations. Some dimethylammonium cations are disordered and the phase transitions are most probably related to the changes of their reorientational freedom [1]. The Raman scattering spectra of DMACC confirm disordering of the dimethylammonium group [2]. The temperature dependences of the dielectric permittivity of $[(CH_3)_2NH_2]_5Cd_3Cl_{11}$ manifest the strong dielectric anisotropy. A maximal value of the dielectric permittivity was found to be along the c-axis. The dielectric measurements revealed the anomalies at the temperatures $T_1 = 180$ K and $T_2 = 127$ K. These anomalies were supposed to be related to the phase transitions (PTs) [3]. The investigations of the complex dielectric permittivity of DMACC crystal in the frequency range from 20 MHz to 42 GHz revealed the Debye-type dielectric dispersion in the c-cut with the two relaxation times [4].

Unfortunately, the supposed low temperature PTs were not investigated using the X-ray diffraction methods and the information about the corresponding changes of the crystalline structure, especially concerning the metal–halogen sublattice, still is poor. Under such circumstances the solid solutions of $[(CH_3)_2NH_2]_5Cd_2CuCl_{11}$ have been grown and the temperature evolution of their electronic spectra was investigated in detail [5]. The important information concerning the nature of the PTs has been obtained from the analysis of the crystal field (CF) electronic spectra. The nature of PTs was also studied using dielectric and optical methods [6].

The clear anomalies of the spectral parameters [5] were observed at the temperatures close to T_1 and T_2 temperatures for the "host" DMACC crystals. These anomalies were found to be characteristic of the second and the first order PTs, respectively. It has been found that introduction of the copper ions into the structure of the "host" DMACC crystal is followed by shift of the mentioned PTs at T_1 and T_2 by 5 and 3.5 K toward low temperatures, respectively. The structural changes observed around $T_0 = 313$ K in the spectroscopic study were found to be connected with a complex co-operative effect involving weakening of the hydrogen bonds and modification of the Jahn–Teller distortion with temperature. These changes hardly would be considered as an usual phase transition since they are clearly connected only with the distortions of polyhedra within the copper–chlorine sublattice and do not manifest themselves in the "pure" DMACC crystal. Moreover, the above mentioned changes were not observed in the temperature dependences of the optical birefringence and dielectric parameters of DMACCC solid solutions [6].

Under such circumstances one can suppose that the important additional information, especially that concerning the nature of the PTs, should be obtained from the detailed study of the dielectric dispersion and proton conductivity in

DMACCC. It is also expected that the structural changes around T_0 would be detected with application of precise Senarmont's method [7] for the measurements of the increments of the optical birefringence.

2. Experimental

The crystals of $[(CH_3)_2NH_2]_5Cd_2CuCl_{11}$ were grown at 304 K from the saturated aqueous solution of stoichiometric quantities of $CdCl_2 \cdot 4H_2O$, $CuCl_2 \cdot 2H_2O$ and $(CH_3)_2NH_2Cl$ with small excess of HCl.

For the dielectric measurements the crystalline platelets of *b*- and *c*-cut with a thickness of 0.5–1 mm were used. After polishing the two opposite sides of the plate were covered by the conducting silver paste electrodes. To avoid the influence of water absorption the samples were previously annealed at the temperature $T =$ 350 K. The dielectric parameters were measured with an accuracy of nearly 1% at different frequencies of the measuring electric field (from 1 kHz up to 1 MHz) using a precision LCR-meter Hewlett-Packard 4284A. The applied ac electric field did not exceed 1 V/cm.

The increments of the optical birefringence were measured using the Senarmont method on the *c*-cut of DMACCC crystal.

For the temperature investigations the samples were placed in a liquid nitrogen cryostat. The rate of the temperature change was 0.5 K/min.

3. Results and discussion

The strongly anisotropic structure of DMACCC and presence of the organic molecules with a dipole moment would assume interesting dielectric properties. The temperature dependences of the real part of the dielectric permittivity measured on *c*- and *b*-cuts in the temperature range of 135−350 K are presented in Fig. 1. The second order PT, which has been clearly detected in the spectral investigations [5], manifests itself only as a weak but noticeable change of slope of above mentioned dependences around $T_1 = 175$ K (Fig. 1b). The peak-like anomalies of the $\mathrm{d}\varepsilon_i'/\mathrm{d}T$ derivatives clearly show the temperature points of the PT.

The second anomaly observed in the temperature dependences of the dielectric permittivity at $T_2 = 117.5$ K is characteristic of the first order PT (Fig. 1a, inset). The measurements of the linear birefringence also revealed existence of the PT at 175 K [6]. The low temperature PT was not investigated since below 120 K the sample became opaque due to appearance of microcracks at these temperatures obviously connected with the spontaneous strains [6] that frequently appear at the ferroelastic PT.

The wide maximum of dielectric permittivity is observed around 260 K for all investigated frequencies of the measuring field. The similar maxima in the same temperature region were observed in the "pure" DMACC crystals [3]. Moreover, they manifested clear frequency shift at much higher frequencies of measuring field (20 MHz–3.5 GHz). Similarly to the case of DMACC the wide maxima of the

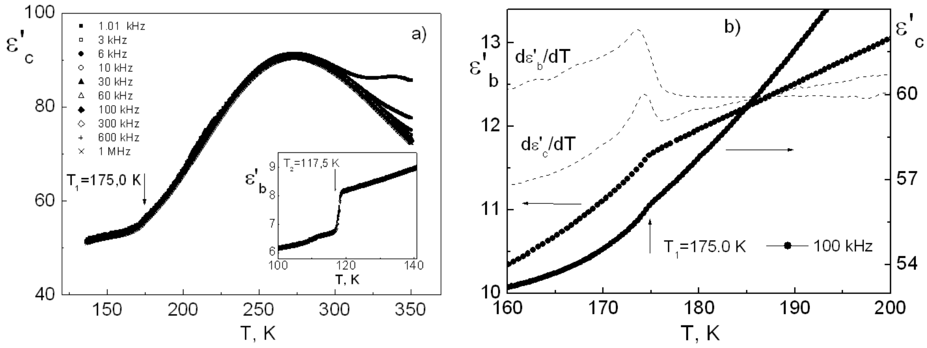

Fig. 1. (a) Temperature dependence of ε_c' for DMACCC crystals obtained at different frequencies of measuring field; (b) temperature dependences of ε_c', ε_b' and their derivatives in the vicinity of PT at T_1. The inset in part (a) presents the temperature dependence of ε_b' around the first-order phase transition at lower temperatures.

dielectric permittivity should be related to the thermal dipole relaxation connected with ordering of one of the two possible types of the DMA groups.

The high temperature region ($T > 300$ K) is characterized by considerable increase in the dielectric losses (Fig. 2) and pronounced dispersion of the dielectric permittivity, especially for the low frequencies of measuring field. Such a behaviour is connected with the proton conductivity which should be considered as a feature characteristic of the compounds with an alkylammonium cation [8]. It is quite possible that the pronounced low frequency conductivity in this case masks the anomalies that could be expected around T_0.

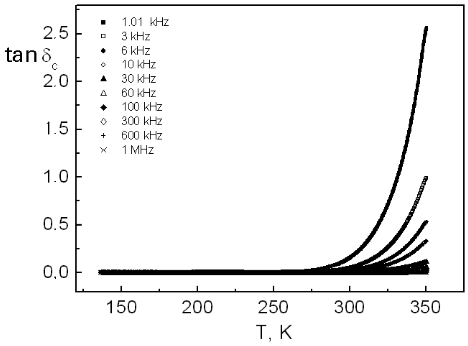

Fig. 2. Temperature dependence of $\tan\delta_c$ for DMACCC crystals obtained at different frequencies of measuring field.

It is clearly seen that the frequency dependence of the real part of the dielectric permittivity at $T = 350$ K (Fig. 3) consists of the two different parts connected with the high frequency relaxation processes and low frequency proton conductivity, respectively.

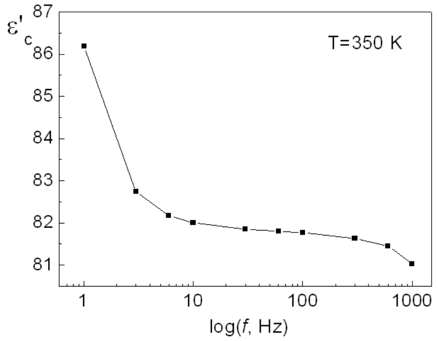

Fig. 3. Frequency dependence of ε'_c in the semi-logarithmic scale at $T = 350$ K.

The mentioned conductivity is determined from the relation [9]:

$$\sigma = \varepsilon_{\mathrm{v}}\omega\varepsilon'', \tag{3.1}$$

where ε_{v} is the dielectric permittivity of vacuum, ε'' is the imaginary part of the dielectric permittivity. The temperature dependence of the electric conductivity measured at the frequency 100 kHz in regime of cooling is depicted in Fig. 4.

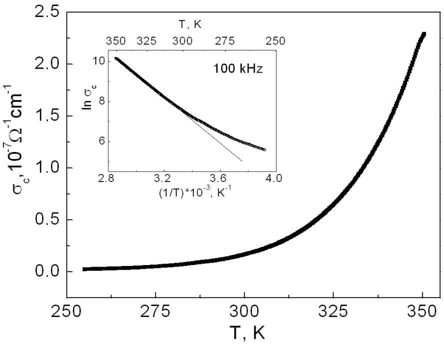

Fig. 4. Temperature dependence of σ_c conductivity measured at the frequency of electric field 100 kHz. The inset shows inverse temperature dependence of $\ln \sigma_c$.

It is clearly seen that σ depends exponentially on temperature (Fig. 4, inset) that is characteristic of the hopping conductivity. This type of conductivity is described by equation [10]:

$$\sigma = \sigma_0 \exp\left(-\frac{E_{\mathrm{a}}}{kT}\right), \tag{3.2}$$

where σ_0 is a pre-exponential factor and E_{a} is the activation energy of the conductivity. According to (3.2) the dependences of $\ln \sigma_c$ on the inversed temperature should be linear that is observed in the experiment (Fig. 4, inset).

The activation energy of the conductivity should be calculated from the dependence of $\ln \sigma_c = f(1/T)$. In our case $E_{\mathrm{a}} = 0.48$ V. The obtained experimental data testify that the considerable deviation from the Debye type relaxation observed in the high temperature phases of DMACCC is connected with contribution of proton conductivity. Similarly to the case of other crystals with an alkylammonium cation its nature should be related to the so-called "Grotthus" mechanism involving correlated jumps of the bare proton between the different hydrogen bonds and correlated reorientation of the host molecules (in this case — the DMA groups) [11]. The nature of proton conductivity in such a type of materials is described in detail on the example of trimethylammonium trichlorocadmate [12]. The "Grotthus" mechanism implies a lack of protons on some of the hydrogen bonds [11]. Besides, the latter should be comparatively weak. Unfortunately, there are no structural data concerning DMACCC but corresponding data for the "pure" DMACC crystal [1] testify that the N–H. . .Cl bonds are comparatively long (3.288–3.576 Å) and therefore would be considered as weak ones.

One can note that the determined value of E_a is higher than those in related compounds with alkylammonium cation ($E_\mathrm{a} = 0.340$ eV for $[NH_2(CH_3)_2]_2CoCl_4$ [9] and $E_\mathrm{a} = 0.355$ eV for $NH_2(CH_3)_2MnCl_3 \cdot 2H_2O$ [8]), first of all, due to the larger energy barrier between two different H bonds [2].

The previous investigations of the temperature dependences of the linear birefringence performed using the rotating-analyzer method [6] have not supplied any new information about the changes around T_0. At the same time, as it has been found in the spectral study [5], the behaviour of the crystal's properties at high temperatures, first of all the position of the anomalies at T_0, strongly depend on the previous thermal history of the sample. Besides, the spectral parameters showed a considerable global hysteresis in the vicinity of the mentioned temperature. This is connected with the supposed influence of the spatial modulation of the crystalline lattice arising due to the some periodic distribution of the copper–chlorine complexes among the cadmium–chlorine polyhedra in the solid solution. That is why the increments of birefringence were measured on the sample previ-

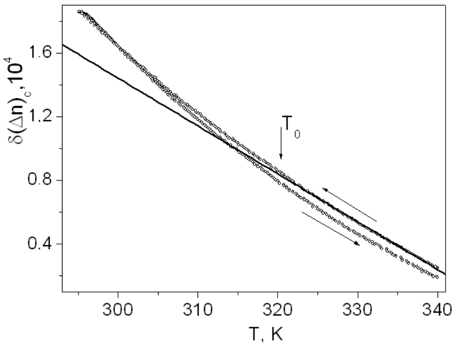

Fig. 5. Temperature dependence of the optical birefringence increment measured both in heating and cooling run on the sample previously annealed at $T = 350$ K. The directions of temperature change are shown by arrows.

ously annealed at $T = 350$ K. The annealing was performed till the stabilization of its optical birefringence. This allows to diminish the global hysteresis. Under such circumstances one could observe the clear change of a slope at $T_0 = 320$ K (both at cooling and heating; see Fig. 5). It is necessary to note that the high temperature region lying above T_0 is characterized by nearly straight-line temperature dependences of $\delta(\Delta n)_c$, whereas below this temperature the dependence becomes considerably nonlinear. Although the T_0 temperature is somewhat shifted with respect to those obtained from the spectral investigations one can conclude that the origin of this anomaly is also connected with the change of the tetragonal distortion of the copper–chloride octahedra within the complex metal–halogen anions.

4. Conclusion

As it follows from the dielectric investigations, the crystals of $[(CH_3)_2NH_2]_5Cd_2CuCl_{11}$ undergo the second-order phase transition at the temperature $T_1 = 175$ K and the first-order phase transition at the temperature $T_2^h = 117.5$ K. Taking into account the data of the optical study [6] one can suppose that the low temperature PT is a transition into ferroelastic phases. The temperatures of PTs are very close to those obtained from the spectral investigations (with accounting of the ΔT_2 hysteresis). Both PTs were found to be shifted toward lower temperatures with respect to the corresponding transitions in the "host" $[(CH_3)_2NH_2]_5Cd_3Cl_{11}$ crystals. The thermal dipole relaxations of quasi-Debye type were observed at the temperatures higher than T_1. However, the considerable proton conductivity strongly complicates determination of the relaxation process parameters. At the same time the dielectric dispersion was found to be very similar to those in the "host" DMACC crystals that allows to relate it to the reorientation of the DMA groups of two different types [4]. Complex approximation of the dielectric spectra in the high temperature phase allowed to define the value of the activation energy of conductivity: $E_\mathrm{a} = 0.483$ eV. One can suggest that the proton conductivity in $[(CH_3)_2NH_2]_5Cd_2CuCl_{11}$ crystals is realized through the Grotthus mechanism. The investigations of the birefringent properties confirmed existence at $T_0 = 320$ K of the structural changes connected with the tetragonal distortion of the copper–chloride octahedra within the complex metal–halogen anions.

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