IMPACT OF SIZE EFFECTS ON THE THERMOCHROMIC PROPERTIES OF NANO- AND MICROCOMPOSITES BASED ON $(NH_2(C_2H_5)_2)_2CUCL_4$ CRYSTALS

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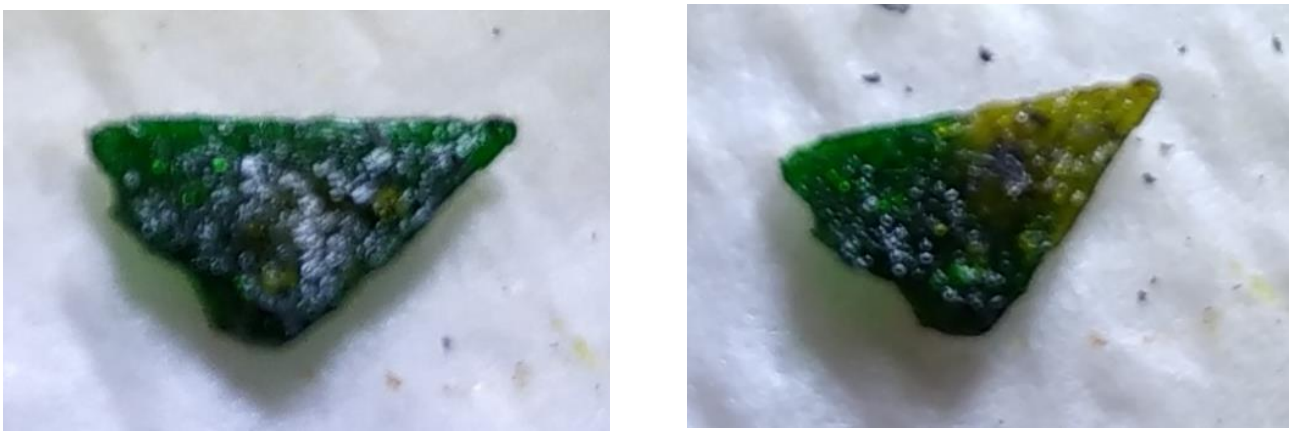
The crystal structure diethylammonium tetrachlorocuprate $[NH_2(C_2H_5)_2]_2CuCl_4$ (DEACC) consists of DEA^+ cations and metal-halogen complexes (MHC) connected by the hydrogen bonds. The high-temperature phase is characterized by a distorted tetrahedral environment of the copper ion, whereas in the case of the low-temperature phase, the tetrahedral and planar square coordinations coexist [1, 2]. In the room temperature phase crystal belongs to the space group $P2_1/n$. The parameters of the unit cell are: a = 7.362 Å, b = 15.025 Å, c = 45.193 Å, β = 89.94°, and z = 12. One asymmetrical structural group includes three tetrahedral and nine square planar $[CuCl_4]^{2-}$ ions in an abnormally large cell. In a first approximation, they can be considered to possess the D_{2d} symmetry. The crystal system in the high-temperature phase is also monoclinic with the space group $P2_1/c$ (a = 25.055 Å, b = 10.531 Å, c = 15.455 Å, β = 100.6°, and z = 8) [1, 3]. In this phase, two independent crystallographic $[CuCl_4]^{2-}$ ions have the shape of a distorted tetrahedron.

DEACC crystals undergo the clear discontinuous thermochromic phase transition (PT) at 311 K (at heating) accompanied by the sharp change of sample color from deep green to pale yellow connected with the change of the copper ion coordination (Fig. 1). Such a change manifest itself in the shift of the principal spectral bands corresponding to the internal transition of Cu^{2+} ion by about 50 nm (Fig. 2).



a) **b)**

Figure 1. DEACC crystal at different temperature:

a) – “green” phase; b) – “yellow” phase.

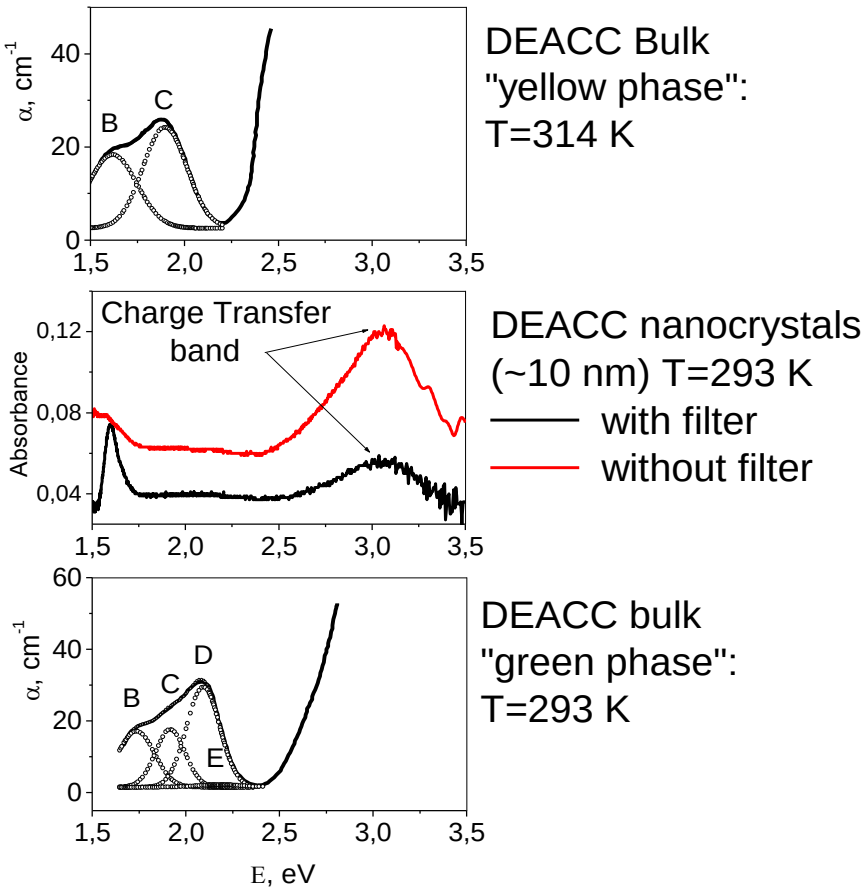


Figure 2. Absorption spectra of DEACC crystals at different temperature and NCs of DEACC.

The low temperature “green” phase is characterized by coexistence of the tetrahedral and square planar coordinations of the copper ion, whereas the structure of the high temperature “yellow” phase contains only the tetrahedral copper-halogen complexes [1, 2].

The absorption spectra of DEACC bulk crystals and nanocrystals in the visible and near infrared region are presented in Fig. 1 for comparison. It has been found that contrary to the case of the initial bulk crystals undergoing the first order thermochromic phase transition the composite with the nanocrystals of average size 160 nm are characterized only by continuous change of color.

As it follows from Fig. 3 b, c the microcomposites with a latex matrix also are characterized by the change of the absorption spectra very similar to those in the bulk crystals. As it follows from Fig. 4 b, c the microcomposites with latex matrix also are characterized by the hysteresis loops, but they look more broad and diffused than in the case of DEACC bulk crystal. Nevertheless, one can conclude that the these microcomposites undergo clear but a little diffused thermochromic PT of the first order in vicinity of 316 K (at heating) accompanied by a considerable change of the sample colour from deep green to pale yellow.

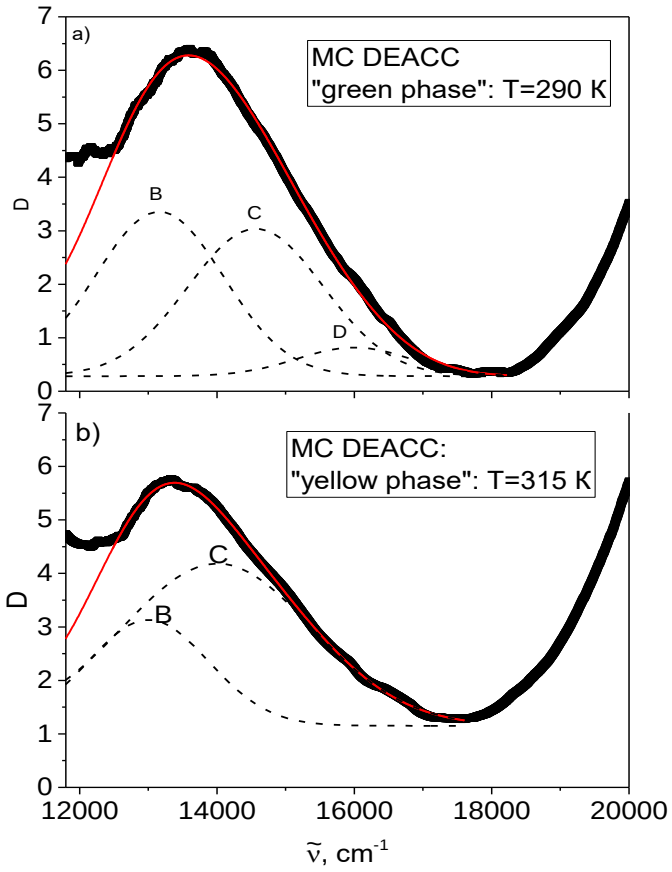


Figure 3. The absorption spectra of DEACC + polymer microcomposite (latex matrix) approximated with Gaussians (dashed lines) at: a) 294 K; b) 318 K.

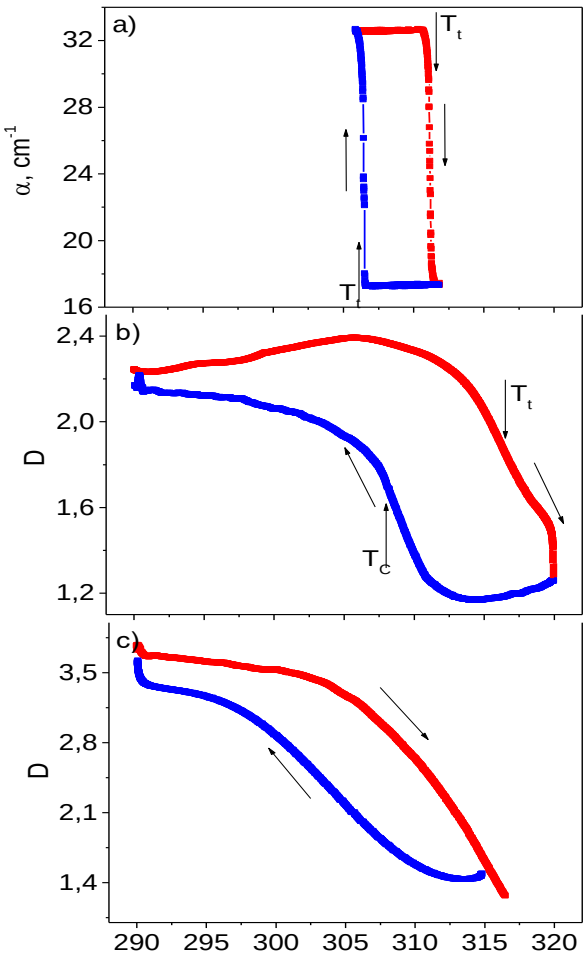


Figure 4. The temperature dependences of the absorption coefficient of DEACC bulk crystal (a) and of the optical density of MCs with latex matrix (b, c) at λ = 633 nm (15800 cm^{-1}) (a, c) and λ = 530 nm (18870 cm^{-1}) (b).

Microcomposites with polystyrene matrix also are characterized by the hysteresis loops and very similar to those in DEACC bulk crystal (Fig. 5). These microcomposites undergo the thermochromic PT of the first order in vicinity of 337 K (at heating) accompanied by a drastic change of the sample colour from deep green to pale yellow. It is clear from the temperature dependence of the optical density of the microcomposite measured at λ = 590 nm (18870 cm^{-1}). Shift of the phase transition temperature is associated with influence of the PS matrix. The clear hysteresis loop observed in this case looks the most attractive for the practical application of this microcomposite.

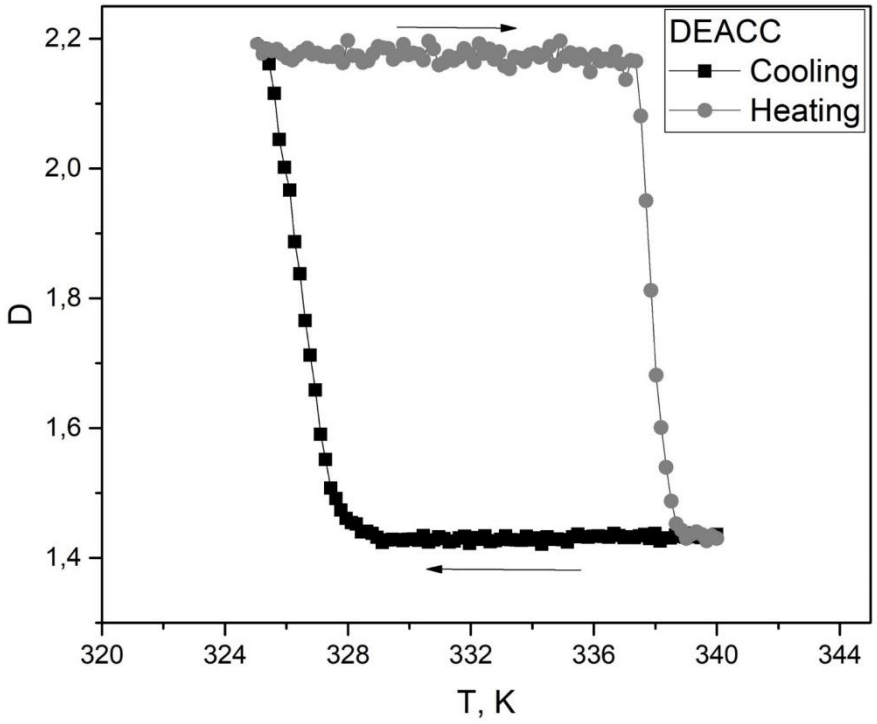


Figure 4. The temperature dependences of the optical density of DEACC microcrystals in PS matrix at λ = 590 nm

Summary

- The detailed study of the size effects manifestation in the spectral properties of the nano- and microcrystals of DEACC embedded into the polymer matrices were performed.
- The microcomposites with a latex matrix were found to possess the thermochromic properties very similar to those in a bulk crystal. They undergo clear but a little diffused thermochromic PT of the first order in vicinity of 316 K (at heating) accompanied by a considerable change of sample color from deep green to pale yellow. The observed shift of the PT temperature in the MCs in respect to the case of the bulk crystal as well as the distorted shape of the hysteresis loop observed in the temperature dependence of the absorption coefficient at the constant wavelength would be explained by influence both of the polymer matrix and surface phenomena that still are important in the microcomposite.
- The microcomposites based on PS matrix possess properties similar to a bulk crystals DEACC. Temperature of phase transition is shifted from 311 K for the bulk crystal to 337 K for the microcomposite (at heating). However, the color is changed drastically at the phase transition contrary to the case of the microcomposites based on the latex matrix.
- The discovered thermochromic properties of the microcomposites based on DEACC look very attractive for the practical application. This material appeared to be no hygroscopic, mechanically stable and very technological. One can produce this material of a large area and various shapes that is suitable for the thermography. On the other hand, the observed hysteresis loops of absorbance look very attractive for the optical storage of information.

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