

## Influence of the growing conditions on thermochromic properties of $[\text{NH}_2(\text{C}_2\text{H}_5)_2]_2\text{Cu}_x\text{Zn}_{1-x}\text{Cl}_4$ crystals

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The absorption spectra of  $[\text{NH}_2(\text{C}_2\text{H}_5)_2]_2\text{CuCl}_4$  crystals grown from ethanol solution as well as of  $[\text{NH}_2(\text{C}_2\text{H}_5)_2]_2\text{ZnCl}_4 \cdot n\text{H}_2\text{O}$ ,  $[\text{NH}_2(\text{C}_2\text{H}_5)_2]_2\text{Cu}_{0.25}\text{Zn}_{0.75}\text{Cl}_4$  crystals grown from water solutions have been investigated in the visible spectral region. The influence of ionizing irradiation on these spectra has been studied as well. The  $[\text{NH}_2(\text{C}_2\text{H}_5)_2]_2\text{CuCl}_4$  crystal grown from the ethanol solution has been shown to undergo the thermochromic phase transition at a higher temperature ( $T_T^h = 324.5$  K) and to manifest a higher sensitivity to ionizing irradiation influence as compared to the similar crystal grown from water solution. 75 % substitution of copper ions by zinc at the Transition to  $[\text{NH}_2(\text{C}_2\text{H}_5)_2]_2\text{Cu}_{0.25}\text{Zn}_{0.75}\text{Cl}_4$  solid solution results in the change of the thermochromic phase transition character from the discontinuous to continuous one. The high sensitivity of the exciton absorption band long-wave edge location to low doses of ionizing radiation in  $[\text{NH}_2(\text{C}_2\text{H}_5)_2]_2\text{ZnCl}_4 \cdot n\text{H}_2\text{O}$  hydrated crystal has been revealed.

Исследованы спектры поглощения кристаллов  $[\text{NH}_2(\text{C}_2\text{H}_5)_2]_2\text{CuCl}_4$ , выращенных из спиртового раствора, и  $[\text{NH}_2(\text{C}_2\text{H}_5)_2]_2\text{ZnCl}_4 \cdot n\text{H}_2\text{O}$ ,  $[\text{NH}_2(\text{C}_2\text{H}_5)_2]_2\text{Cu}_{0.25}\text{Zn}_{0.75}\text{Cl}_4$  выращенных из водных растворов, в видимой области спектра, а также влияние на них ионизирующего облучения. Показано, что кристалл  $[\text{NH}_2(\text{C}_2\text{H}_5)_2]_2\text{CuCl}_4$ , выращенный из спиртового раствора, претерпевает термохромный фазовый переход при более высокой температуре ( $T_T^h = 324.5$  K) в сравнении с аналогичным кристаллом, выращенным из водного раствора, а также имеет более высокую чувствительность к ионизирующему облучению. 75 %-ное замещение ионов меди ионами цинка при переходе к твердому раствору  $[\text{NH}_2(\text{C}_2\text{H}_5)_2]_2\text{Cu}_{0.25}\text{Zn}_{0.75}\text{Cl}_4$  сопровождается изменением характера термохромного фазового перехода со скачкообразного на непрерывный. Обнаружено высокую чувствительность положения длинноволнового края экситонной полосы поглощения в кристаллогидрате  $[\text{NH}_2(\text{C}_2\text{H}_5)_2]_2\text{ZnCl}_4 \cdot n\text{H}_2\text{O}$  к малым дозам ионизирующего излучения.

Recently, thermochromism phenomenon draws a considerable interest of numerous scientists dealing with the solid state physics. Thermochromic crystals are sensitive materials of good promise for sensor technique, in particular, for thermography and for optical data storage. The compounds of  $\text{A}_2\text{MeCl}_4$  and  $\text{AMeCl}_3$  types (Me = Cu, Co) with an alkylammonium cation [1–5] could be considered as a new class of the thermochromic materials. The diethylammonium tetrachlorocuprate  $[\text{NH}_2(\text{C}_2\text{H}_5)_2]_2\text{CuCl}_4$  (DEACC) crystals undergo a first order thermochromic phase transition (PT) accompanied

by an abrupt change of the sample color from green to yellow under heating. The hydrogen bonds play an essential part in the distortion of the metal-halogen complexes which is clearly reflected in the changes of the absorption spectra. The thermochromic PT temperature in the investigated crystals depends considerably on the technological factors such as growing conditions, the samples thermal history and purity, atmospheric humidity, etc. In particular, the previous study of the crystals grown from water solution (from here on, DEACC-II) has revealed the

thermochromic PT at  $T_T = 311$  K (in the heating mode) [2, 4].

In connection with the thermochromic nature of the above-mentioned PT, it is just the absorption spectroscopy that appeared to be an effective method to study its nature [4]. The investigations have shown that this PT is connected with the changes in the copper ion coordination associated with redistribution of 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 coordination forms are coexistent (each environment provides two absorption bands). The abrupt change of the anion configuration causes a considerable shift of the spectral "transparency window" which is followed by change of the sample color from deep green to yellow (during heating).

On the other hand, due to the essential role of hydrogen bonds in the nature of the mentioned PT, a higher sensitivity of DEACC-II spectral properties to rather low doses of ionizing radiation was revealed. The observed radiochromic effect [2, 4] opens a wide possibility for application of the materials under study as sensitive materials in the ionizing radiation sensors [6]. Besides, it is just the DEACC-II crystals grown from water solution that have been proposed for the application in sensor technique and for data storage [7]. Unfortunately, their technical application is complicated because of the crystal hygroscopicity and instability of their spectral parameters after repeated thermal cycling near the PT. From this point of view, the crystals grown from ethanol solution (DEACC-I) appear to be much more perspective, since they are characterised by a higher stability.

Another way to modify the thermochromic properties of the crystals under consideration is connected with the partial isomorphous substitution of  $\text{Cu}^{2+}$  by  $\text{Zn}^{2+}$  ions. The  $[\text{NH}_2(\text{C}_2\text{H}_5)_2]_2\text{Cu}_x\text{Zn}_{1-x}\text{Cl}_4$  (DEACZC) solid solution crystals are also expected to manifest thermochromic properties and at the same time to be less hygroscopic in comparison with the DEACC-II crystals grown from the water solution. It is necessary to note that the pure  $[\text{NH}_2(\text{C}_2\text{H}_5)_2]_2\text{ZnCl}_4 \cdot n\text{H}_2\text{O}$  (DEAZC) crystals contain crystallization water in their structure [8]. They are transparent in the visible region and thus cannot be considered as thermochromic materials. In [8], the hydration ratio for this crystals has been found to decrease from  $n = 0.75$  to  $n =$

$0.33$  after passing the heating-cooling cycle near the PT. This process is followed by decreasing of the PT temperature from  $333$  K to  $308$  K. The DEAZC crystal possesses  $Pn$  symmetry in the low-temperature phase with  $n = 0.75$  and  $P2_1nm$  in the high-temperature phase ( $n = 0.33$ ) [8]. Taking into account poor information concerning the nature of the thermochromic PT in DEACC-I crystals and the novelty of the DEAZC solid solutions, the temperature evolution of the absorption spectra in the PT vicinity in the mentioned materials (including the spectra variations under ionizing irradiation) have been studied in detail.

The samples of DEACC-II, DEAZC, DEACZC, and DEACC-I crystals were grown respectively from aqueous and ethanol solutions of  $\text{CuCl}_2$ ,  $\text{ZnCl}_2$  and  $[(\text{C}_2\text{H}_5)_2\text{NH}_2]\text{Cl}$  taken in the stoichiometric ratio using slow evaporation at room temperature. The samples were cut perpendicularly to the  $z$  axis in the shape of thin ( $0.1$  to  $0.3$  mm) plates. The absorption spectra were recorded in the range of  $350$  to  $800$  nm using an SF-26 spectrophotometer and ZMR-3 monochromator. The absorption coefficients were calculated by the traditional two-thickness method of [9]. The photon energies were measured to within  $\pm 0.0005$  eV. The relative error of the measurements did not exceed  $1\%$ . A special nitrogen cryostat together with an "UTREKS" temperature controller [10] (produced by the Institute of Physics, National Academy of Sciences of Ukraine) provided the necessary precision of temperature measurements and stabilization ( $\Delta T = \pm 0.05$  K). A copper-constantan thermocouple was used as a temperature sensor. The samples were irradiated by  $^{226}\text{Ra}$  isotope at the  $2.238$  mR/h power in the point of irradiation.

Fig. 1 presents the temperature dependences of the absorption coefficient obtained for DEACC-I (Fig. 1a) and DEACC-II (Fig. 1b) crystals at  $633$  nm wavelength. In the case of DEACC-I crystal, the stepwise absorption change at  $T_T = 324.5$  K (in the heating mode, Fig. 1a) corresponds to the abrupt change of the sample color from green to yellow. To clarify the nature of this effect, the absorption spectra of DEACC-I and DEACC-II crystals were compared. The complex absorption bands were resolved into elementary contours using the method described in [11]. The main criterion of the correct approximation is the minimal number of the contours at the maximal coincidence of their resultant

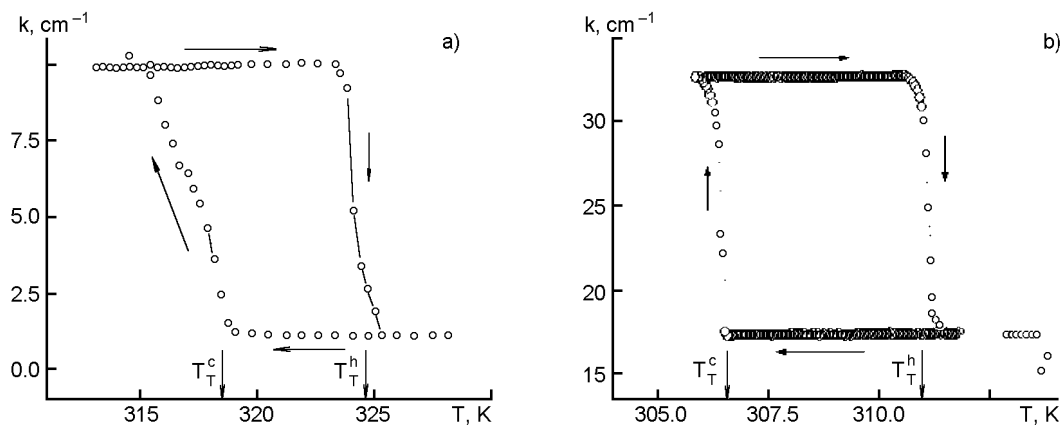


Fig. 1. Temperature dependences of absorption coefficient for DEACC-I (a) and DEACC-II (b) crystals at  $\lambda = 633$  nm.  $T_T^h$ , temperature of the thermochromic PT obtained under heating;  $T_T^c$ , that under cooling.

curve with the experimental spectrum. In order to attain the maximum objectiveness of the resolution process, the so-called derivative spectroscopy [12] was employed.

The analysis testifies that the DEACC-I crystals are characterized by a distorted tetrahedral symmetry of the copper ion environment in the high-temperature phase, and by coexistence of the tetrahedral and planar square environments in the low-temperature one. These conclusions agree well with the X-ray structure analysis data [1]. In spite of the similarity with DEACC-II, it is almost evident that DEACC-I crystal structure is formed *a priori* by the network of stronger hydrogen bonds. This fact is confirmed not only by the higher PT temperature but also by a higher extent of the tetrahedron distortion in the high-temperature phase. The last conclusion follows from the fact that in the case of DEACC-I crystals, the absorption spectra consist of three A, B and C bands (Fig. 2a) instead of two ones observed in DEACC-II [4]. At the same time, at transition into the low-temperature phase, the number of bands in the absorption spectra of DEACC-I corresponding to the tetrahedrally coordinated copper ion decreases down to two ones, A and C (Fig. 2,b), that corresponds to a change of the crystal field strength (most likely to its increasing). The comparison of the oscillator strength for different bands, which is proportional to the area limited by the contours of Gaussian shape, testifies that the ratio of the number of tetrahedral anions to that of square ones is higher for the DEACC-I crystals. Thus, in the case of DEACC-II crystals, water molecules adsorbed during the growth process favor the formation of the quadratic anions

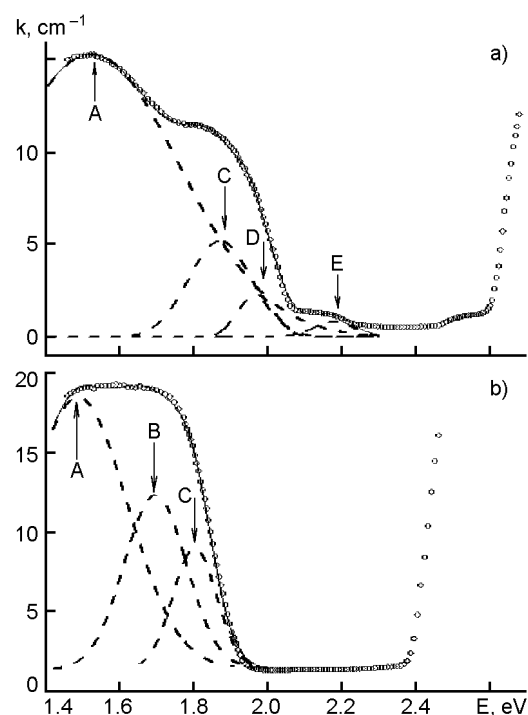


Fig. 2. Absorption spectra of DEACC-I obtained at  $T = 293$  K (a); and at  $T = 326$  K (b). Solid lines show the fitting curves resulting from the Gaussian contours shown by dotted lines.

that results in a more intense absorption in the visible region (see Figs. 1, 2).

It has been shown that irradiation of the samples in the real time results mainly in lowering of the thermochromic phase transition temperature. In particular,  $^{226}\text{Ra}$  irradiation of the DEACC-I sample during 180 s initiates the PT at the temperature lower by 0.9 K (at heating) in comparison with those for the nonirradiated sample (at heating). Besides, the steepness of the PT shift vs.

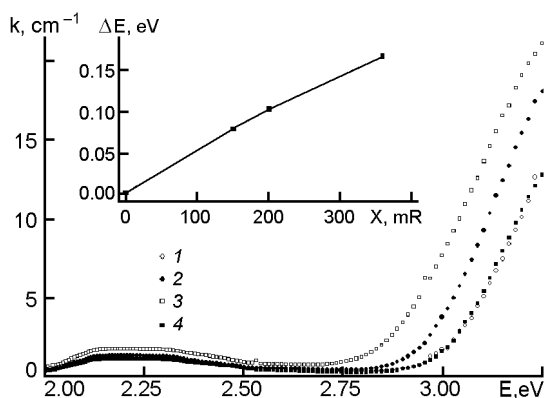


Fig. 3. Absorption spectra of DEAZC near the long-wave edge of the exciton band for samples irradiated with different ionizing irradiation doses. 1 – non-irrad, 2 – 151 mR, 3 – 360 mR, 4 – 140 h after irrad. The inset presents the dose dependence of the absorption edge shift measured for  $k = 10 \text{ cm}^{-1}$ .

dose dependence has been found to be much larger than for DEACC-II crystals [4], thus testifying to a higher sensitivity of the DEACC-I crystals to low ionizing radiation doses [13]. As it is clearly seen from the obtained absorption spectra, the DEAZC crystals (Fig. 3) are transparent essentially in the whole visible region. According to the classification proposed in [14], the optical absorption edge around 395 nm (3.14 eV) could be attributed to the exciton band, formed by the self-localized excitons. Under irradiation with different  $\gamma$ - and  $\beta$ -radiation doses of  $^{226}\text{Ra}$ , the low energy edge of this exciton band considerably shifts towards lower energies (Fig. 3). The mentioned edge shift shows almost linear dependence on the radiation exposure dose and reaches  $\Delta E = 0.16 \text{ eV}$  for the maximal dose of  $X = 360 \text{ mR}$  (inset in Fig. 3). It is interesting to note that after holding of the irradiated sample at room temperature (in our case, for 6 days) the crystal turns back to the initial state (see Fig. 4). The same effect could be achieved by annealing the sample at 350–370 K during several hours. Such a reversibility observed at least for the considered doses could find its practical application.

To clarify the nature of the mentioned exciton band, the absorption edge was studied in more detail. Taking into account its exponential dependence on energy (according to the empiric Urbach rule [11]), a traditional but somewhat modified method was used to approximate the absorption edge. The modification of the approximation function was due to the fact that the ab-

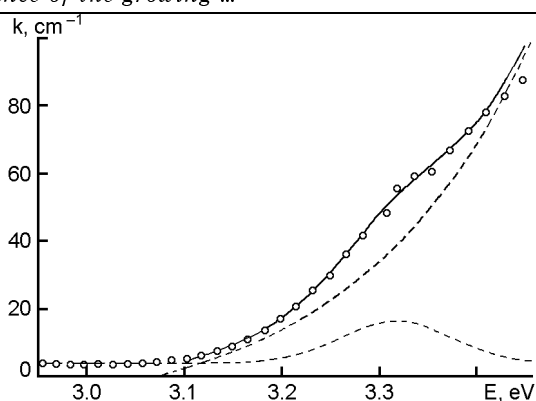


Fig. 4. Approximation of the adsorption edge of DEAZC crystal by Gaussian contour of the impurity absorption band and usual Urbach tail dependence (dotted line).

sorption edge was overlapped with the impurity absorption band. Under such circumstances, the edge was approximated using the complex function:

$$k = A + B \exp\left(-0.5 \left(\frac{E - E_c}{\omega}\right)^2\right) + k_0 \exp\left(\frac{\sigma}{k_B T} (E - E_0)\right), \quad (1)$$

where  $A, B$  are the constants;  $E$ , the photon energy (eV);  $E_c, \omega$ , the impurity band energy maximum and half-width, respectively;  $k_0, E_0, \sigma$ , the parameters of the Urbach's rule;  $k_B$ , the Boltzmann constant;  $T$ , temperature (K). The second term in this relation describes a Gaussian contour of the impurity absorption band and the last one is responsible for the usual exponential Urbach dependence. The performed approximation allowed to obtain the "pure" shape of long-wave absorption edge (Fig. 4). The analysis of obtained dependences revealed fulfillment of the Urbach rule (the family of  $\ln k(E)$  straight lines intersects in a single point for both phases) and allowed to determine its parameters for both phases. In particular, in the high-temperature phase ( $T > 308 \text{ K}$ ):  $E_0 = 3.79 \text{ eV}$ ,  $k_0 = 1035 \text{ cm}^{-1}$ ,  $\omega_0 = 660 \text{ cm}^{-1}$ ,  $\sigma_0 = 0.585$ , and in the low-temperature phase —  $E_0 = 3.92 \text{ eV}$ ,  $k_0 = 3740 \text{ cm}^{-1}$ ,  $\omega_0 = 710 \text{ cm}^{-1}$ ,  $\sigma_0 = 1.405$  (it is more convenient to present the effective energy of phonons  $\hbar\omega_0$  in  $\text{cm}^{-1}$  that enables comparing it with the vibration spectroscopy data). The obtained  $\sigma_0$  values testify to a weak exciton localization and, conse-

quently, moderate values of the exciton-phonon interaction (EPI) strength.

It is interesting to note that the frequency  $\omega_0$  of effective phonon involved in EPI in the high-temperature phase correlates fairly well with the vibration frequency of the organic cation (the scissor vibration  $\nu_r(\text{NH}_2)$  of the amide group [15] or the symmetric stretching mode  $\nu(\text{C}-\text{N})$  [16]). Meanwhile, in the low temperature phase, the effective phonon frequency lies in the region of crystal water libration vibrations  $\rho(\text{H}_2\text{O})$  [17]. Thus, taking into account presence of the two hydrogen bond types, namely,  $\text{N}-\text{H}\cdots\text{Cl}$  and  $\text{O}-\text{H}\cdots\text{Cl}$ , in the crystal structure, we can assume that the exciton is localized at the organic group in the first case and at the crystal water molecules in the second case. This assumption correlates fairly well with the data [8] concerning the partial dehydration of the DEAZC crystals at the PT (under heating). The ionizing irradiation causes most likely breaking of the  $\text{O}-\text{H}\cdots\text{Cl}$  hydrogen bonds followed by rebuilding of their network. This causes a smearing of the exciton levels in the field of newly formed structural defects resulting in lowering of the exciton band edge energy.

Fig. 5 presents the absorption spectra of  $[\text{NH}_2(\text{C}_2\text{H}_5)_2]_2\text{Cu}_{0.25}\text{Zn}_{0.75}\text{Cl}_4$  ( $\text{DEAC}_{0.25}\text{Z}_{0.75}\text{C}$ ) solid solution taken at 294 K (Fig. 5a) and 321 K (Fig. 5b). In the 1.5–2.2 eV range, each spectrum can be resolved into the three Gaussian contours A, C and D denoted for distinctness similarly to the bands observed for DEACC-I and DEACC-II crystals. Contrary to the DEACC, the A and B bands in the  $\text{DEAC}_{0.25}\text{Z}_{0.75}\text{C}$  crystals are fused together due to very close positions of the  $d_{yz,xz}$  and  $d_{x^2-y^2}$  terms in the energy diagram of the tetrahedrally coordinated copper ion [18]. The peak energies of A and B bands in both phases (1.570 and 1.905 eV at 294 K; 1.568 and 1.89 eV at 321 K, respectively) were found to be in the region of electron transitions of the flattened tetrahedrally coordinated copper ion. The D contour (1.944 eV at 294 K; 1.941 eV at 321 K) could be attributed to the absorption band of copper ion in the planar square coordination. Thus, the square and tetrahedral anions coexist in both phases of  $\text{DEAC}_{0.25}\text{Z}_{0.75}\text{C}$  solid solution. This fact correlates well with the absence of the discontinuous thermochromic effect in the considered compounds. Nevertheless, at the transition into the high temperature phase, the area under the A contour (which is propor-

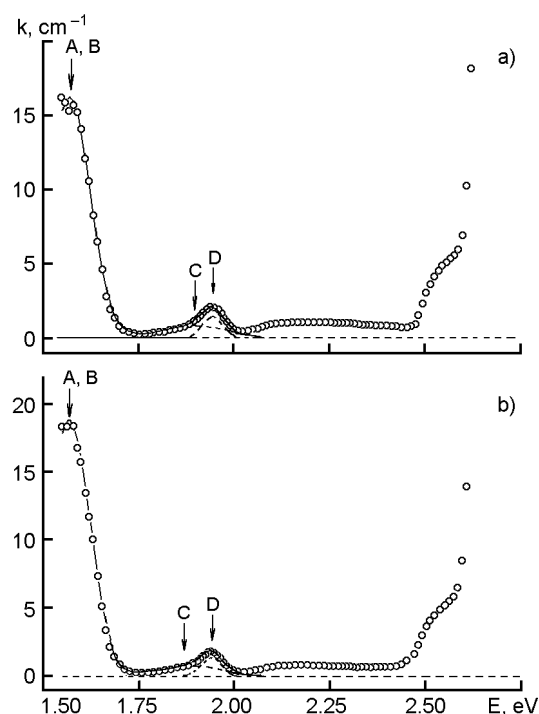


Fig. 5. Absorption spectra of DEACZC taken at  $T = 294$  K (a); and  $T = 321$  K (b). The solid lines show the fitting curves resulting from the Gaussian contours shown by dotted lines.

tional to the oscillator strength) increases (from 2.188 to 2.565 a.u.) and correspondingly decreases for D contour (from 0.099 to 0.084 a.u.). Such a behavior correlates well with the trend to increasing ratio of tetrahedral to square anions number at transition into the high-temperature phase. That trend is general for DEACC compounds. As it was expected, in  $\text{DEAC}_{0.25}\text{Z}_{0.75}\text{C}$  solid solution, the spectral transparency window broadens from 0.2 to 0.4 eV in comparison to DEACC-II crystals. An absorption band appears in  $\text{DEAC}_{0.25}\text{Z}_{0.75}\text{C}$  crystal near 2.5–2.6 eV due to the charge transfer connected with the electron transition from the Cl  $3\pi$ -orbitals on the  $\text{Cu}^{2+}$   $3d$ -orbitals. The almost vertical low-energy edge of the mentioned charge transfer band does not manifest any significant tailing that testifies to the considerable lowering of the EPI strength in comparison with the case of the both DEACC modifications.

Thus, the investigations have shown that both modifications of DEACC crystals contain the anions of similar symmetry in both phases. However, in the low-temperature phase, the ratio of the octahedrally coordinated (square) complexes to the tetrahedrally coordinated ones is higher for the DEACC-II crystals. This fact could be explained by temperature-dependent labile nature of

$\text{CuCl}_4(\text{H}_2\text{O})_2$  complexes that could be formed due to water absorption from the aqueous solution during growing. Both phases of  $\text{DEAC}_{0.25}\text{Zn}_{0.75}\text{C}$  solid solution contain anions of both above-mentioned configurations, however, the ratio of the octahedrally coordinated complexes to tetrahedrally coordinated ones increases with temperature elevation. As a result, no discontinuous thermochromic effect is observed in the considered compounds corresponding to 25 % substitution of zinc by copper. This fact correlates well with the data of spectral investigation of  $[\text{NH}_2(\text{C}_2\text{H}_5)_2]_2\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Cl}_4$  ( $\text{DEAC}_{0.5}\text{Zn}_{0.5}\text{C}$ ) solid solutions [13] that also does not manifest a discontinuous thermochromic effect. The spectral transparency window in the  $\text{DEAC}_{0.25}\text{Zn}_{0.75}\text{C}$  crystals (0.4 eV) acquires the intermediate value between that for  $\text{DEACC-II}$  (0.2 eV) and  $\text{DEAC}_{0.5}\text{Zn}_{0.5}\text{C}$  (0.5 eV) [13]. It is of interest that the dependence of the long-wave edge position of the exciton band on the ionizing radiation dose is linear at least up to 360 mR. Taking into account the reversibility of this effect in the mentioned dose range, one could suggest the perspectives of its application in sensor technique.

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## Вплив умов вирощування на термохромні властивості кристалів $[\text{NH}_2(\text{C}_2\text{H}_5)_2]_2\text{Cu}_x\text{Zn}_{1-x}\text{Cl}_4$

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Досліджено спектри поглинання кристалів  $[\text{NH}_2(\text{C}_2\text{H}_5)_2]_2\text{CuCl}_4$ , вирощених зі спиртового розчину, і  $[\text{NH}_2(\text{C}_2\text{H}_5)_2]_2\text{ZnCl}_4 \cdot n\text{H}_2\text{O}$ ,  $[\text{NH}_2(\text{C}_2\text{H}_5)_2]_2\text{Cu}_{0.25}\text{Zn}_{0.75}\text{Cl}_4$ , вирощених із водних розчинів, у видимій області спектра та вплив на них іонізуючого опромінення. Показано, що кристал  $[\text{NH}_2(\text{C}_2\text{H}_5)_2]_2\text{CuCl}_4$ , вирощений зі спиртового розчину, зазнає термохромний фазовий перехід при вищій температурі ( $T_T^h = 324.5 \text{ K}$ ) у порівнянні з аналогічним кристалом, вирощеним з водного розчину, а також має вищу чутливість до дії іонізуючого опромінення. 75 %-не заміщення іонів міді іонами цинку при переході до твердого розчину  $[\text{NH}_2(\text{C}_2\text{H}_5)_2]_2\text{Cu}_{0.25}\text{Zn}_{0.75}\text{Cl}_4$  супроводжується зміною характеру термохромного фазового переходу зі стрибкоподібного на неперервний. Виявлено високу чутливість положення довгохвильового краю екситонної смуги поглинання у кристалогідраті  $[\text{NH}_2(\text{C}_2\text{H}_5)_2]_2\text{ZnCl}_4 \cdot n\text{H}_2\text{O}$  до малих доз іонізуючого випромінювання.