



RADIOCHROMIC EFFECT IN THE POLYMER COMPOSITES BASED ON [NH₂(C₂H₅)₂]₂CuCl₄ MICROCRYSTALS

Yu. Chornii , A. Hrytsak, V. Kapustianyk 
*Faculty of Physics, Ivan Franko National University of Lviv,
50, Drahomanov St., Lviv, 79005, Ukraine,
e-mail: ychornii@gmail.com*

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The radiochromic effect was detected in the thermochromic [NH₂(C₂H₅)₂]₂CuCl₄ (DEA-CuCl₄) microcrystals incorporated into a polystyrene matrix. It has been found that this composite possesses thermochromic properties very similar to those of a bulk crystal, although its thermochromic phase transition was shifted toward higher temperatures due to tensions arising within the interface between the polystyrene matrix and the microcrystal. The similar doses of ionizing radiation cause much more pronounced changes in the thermochromic properties of the microcomposite in comparison with a bulk crystal. The main impact consists in the considerable shift of the phases transition temperature derived from the $D(T)$ hysteresis loops toward lower values. The observed changes should be considered a radiochromic effect, which is explained by breaking the chemical bonds between the polystyrene matrix and the microcrystals with a following relaxation of the surface strains. The transformation of the first order phase transition into the second order one under the influence of irradiation is also discussed.

Key words: microcomposites, ionizing radiation, phase transitions, absorption spectra, thermochromic effect.

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I. INTRODUCTION

The compounds of A₂MeCl₄ (Me = Cu, Co) family with a different type of the alkylammonium cations have been the subject of considerable attention due to the variety of phase transitions including those into the ferroelectric and magnetically ordered phase [1–8]. Besides, some of these compounds have noticeable thermochromic properties. Diethylammonium tetrachlorocuprate [NH₂(C₂H₅)₂]₂CuCl₄ (DEA-CuCl₄) crystals grown from a water solution undergo a clear discontinuous thermochromic phase transition (PT) at 311 K (at heating) accompanied with a sharp change of the sample color from green to pale yellow connected with the change in the copper ion coordination. Such a change manifests itself in the shift of the absorption bands corresponding to the internal transitions of Cu²⁺ ion by about 50 nm [4]. DEA-CuCl₄ crystals grown from alcohol were found to undergo the thermochromic phase transition at higher temperatures — 323 K (at heating) [1, 4]. It was suggested that the corresponding structural changes in the both modifications of DEA-CuCl₄ crystals are very similar [1, 2, 4].

The crystal structure of DEA-CuCl₄ consists of DEA⁺ cations and copper-halogen complexes (CHC) 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, 4, 7, 8].

The performed analysis shows that the key effect responsible for the thermochromic first order phase transition consists in the transformation of the square

planar CHC to the tetrahedral shape at heating [1, 2, 4]. Indeed, 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 distorted tetrahedral copper-halogen complexes [1, 4]. Due to their specific thermochromic properties, DEA-CuCl₄ crystals are considered prospective materials for a sensor technique, in particular, for thermography, as well as for the optical data storage. Unfortunately, their technical application is restrained because of hygroscopicity and instability of their spectral parameters after repeated thermal cycling near the PT [2, 4].

As was shown in our previous work [9], incorporation of the microcrystals (MCs) of the above mentioned substances into a polymer matrix could resolve these problems. Indeed, the material of such a type was found to possess a clear first order thermochromic phase transition similar to those in a single crystal. In this respect, these MCs differ advantageously from polymer nanocomposites with the sizes of nanocrystals limited by 10 nm. It was shown that the lateral tensions arising on the surface of NC suppress the square planar coordination characteristic of the low temperature phase of the bulk crystal. As a result, in DEA-CuCl₄ nanocrystals there was observed only a continuous thermochromic phase transition [10].

On the other hand, a significant effect of the polymer matrix on the phase transition temperature and nature was also detected in the microcomposites based on DEA-CuCl₄. Indeed, they were found to undergo a thermochromic phase transition at much higher temperatures in comparison with a bulk crystal [10],



which was explained by the lateral tension arising within the interface between the microcrystal and the polymer matrix. The shift of the phase transition temperature in this case should be considered as a piezochromic effect.

The above mentioned technological finding allows as to create a new thermochromic material for the sensor technique. The data reported in work [2] testify that the temperature of thermochromic phase transitions in DEA-CuCl₄ single crystal is considerably shifted under the influence of ionizing irradiation. Unfortunately, the shift in this parameter did not exceed 2 K even for a quite high dose of irradiation (20 R), which together with the already mentioned technological problems considerably limited practical application of single crystals in the sensors of radiation. A very similar situation was observed in the case of related single crystals of other compounds with an alkylammonium cation. Under such circumstances, the influence of ionizing radiation on the thermochromic properties of DEA-CuCl₄ microcrystals embedded into the polymer matrix demands a detailed study and looks very promising for practical application in the sensor technique.

II. EXPERIMENTAL

DEA-CuCl₄ single crystals are grown from an aqueous solution of CuCl₂×2H₂O and [(C₂H₅)₂NH₂]Cl salts, taken in a stoichiometric ratio, using the method of slow evaporation at room temperature [13]. When the sizes of the microcrystals precipitated from the supersaturated solution reached on average 200 μm, they were extracted from the solution. The preparation of the microcomposites consisted in the dispersion of DEA-CuCl₄ microcrystals in a liquid polymer. Afterwards, the liquid was thoroughly homogenized. Polystyrene (PS) was used as a polymer matrix. The use of such a matrix allows one to avoid the influence of significant mechanical stresses on MCs, which are commonly observed when using more “rigid” traditional polymers [11, 12].

The prepared composition was deposited on the BK7 glass substrate using a spin coating method. Afterwards, the samples were left at room temperature for 4 days to dry. As it follows from the optical microscopy data, the average sizes of the MCs were close to 200 μm. The samples produced in such a way were of a good quality and stability for the surrounding environment background. Contrary to the bulk crystals, the obtained microcomposites were not hygroscopic.

The nonpolarized absorption spectra of the microcomposites were investigated at different temperatures in the spectral region from 400 nm up to 950 nm using a computerized ZMR-3 monochromator with a spectral resolution of 1 nm and a computerized AvaSpec-2048L spectrometer with the CCD linear detector.

In order to compare the radiation effects in DEA-CuCl₄ single crystals [2, 5] and microcomposites, we used the similar source of ionizing radiation. The samples were irradiated by Co-60 (0.9 mR/h).

III. RESULTS AND DISCUSSION

The absorption spectra of DEA-CuCl₄ MCs incorporated into PS polymer were measured within the region of the transparency window in the low temperature “green” and high temperature “yellow” phase. They are shown in Fig. 1. In order to obtain the correct data in the region of quite high absorption within the spectral range of 700–950, we used thinner samples (thickness 1 mm), whereas thicker samples (thickness 3 mm) were investigated in the next experiments.

The transparency window in both phases is limited from the side of higher wavelengths by the edge of a broad complex absorption band. It has to be related to the internal transition of Cu²⁺ ion in the distorted CHC. The corresponding electron transitions were similar to those in the bulk crystals and were identified in [9, 10]. It has been confirmed that the tetrahedral metal-halogen complexes are observed in the high temperature phase, whereas the low temperature “green” phase is characterized by coexistence of the tetrahedral and square planar coordinations of copper ion. In the last case, the crystalline field is much stronger, which leads to the clear shift of the corresponding band. Due to this, the transparency window in the low temperature “green” phase manifests a considerable blue shift in comparison with those in the high temperature “yellow” phase. The sharp growth of absorption in the region of shorter wavelengths (below 500–550 nm) in the spectra of the MCs should be related to the edge of the ligand-metal type (Cl 3*p* → Cu 3*d*_{*x*²-*y*²}) charge transfer band [9, 10].

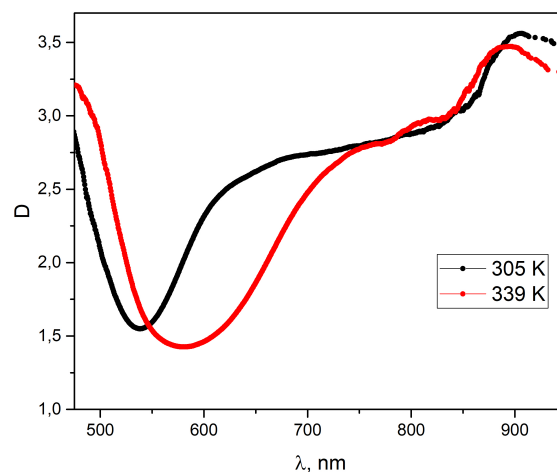


Fig. 1. The absorption spectra of DEA-CuCl₄+polystyrene microcomposite in the region of the transparency window corresponding to the “green” (305 K) and “yellow” (339 K) phases

The temperature dependences of the optical density of the microcomposites with a polystyrene matrix obtained at the constant wavelength are compared with those for the samples irradiated with different doses of radiation using Co-60 isotope (Fig.2, λ = 633 nm). The pristine sample is characterized by the hysteresis loop of a nearly

rectangular shape similar to those observed in a bulk crystal [9]. The sharp jumps of the absorption coefficient reveal the temperatures of the thermochromic PT at cooling ($T_t = 312$ K) and heating ($T_t = 327.6$ K) reflecting its first order.

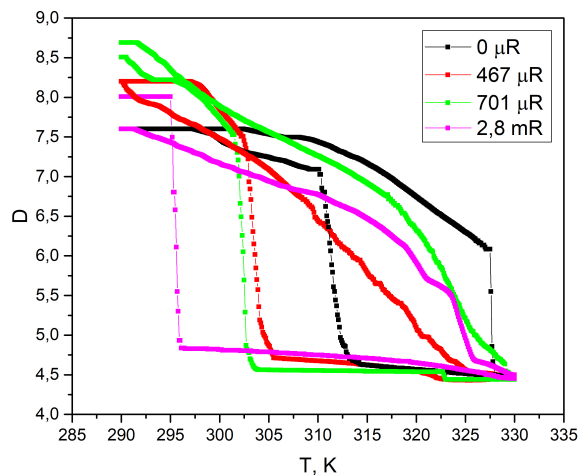


Fig. 2. The temperature dependences of the optical density of DEA- CuCl_4 MCs at $\lambda = 633$ nm

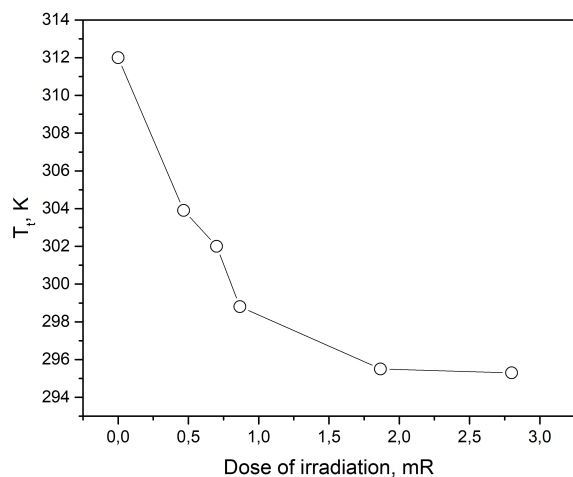


Fig. 3. Dependence of the phase transition temperature on the exposure dose of radiation

On the other hand, the microcomposites are characterized by a broader and more diffused hysteresis loops, than in the case of a bulk crystal. Nevertheless, one can conclude that the composites based on DEA- CuCl_4 MCs undergo a clear first order PT accompanied with a considerable change of the sample colour from light green to pale yellow (Fig. 1). The observed considerable shift of the PT temperature in the MCs compared to the case of a bulk crystal as well as a little distorted shape of the hysteresis loop should be explained by the influence of the polymer matrix and surface phenomena that still are important in the microcomposite [10].

It is also necessary to note a significant effect of a polymer matrix type on the physical and chemical properties of the thermochromic MCs. Comparison with the data presented in [10] shows that the shift of the phase transition temperature is much more pronounced in the composite based on polystyrene than in the latex-based microcomposites. Because polystyrene is a more “rigid” polymer, it significantly affects the anion geometry of the crystals due to the piezochromic effect, thereby shifting the phase transition temperature to higher values. Latex belongs to more flexible polymers, therefore, its influence on anion complexes is less pronounced. The conclusion concerning the polymer matrices’ stiffness was based on the comparison of their Young’s modulus [13, 14].

On the other hand, a clear hysteresis loop observed in this case looks the most attractive for the practical application of the obtained microcomposite. As is clear from Fig. 3, the thermochromic properties of the MCs based on DEA- CuCl_4 were found to be very sensitive to ionizing irradiation. Its impact consists in the considerable shift of the phase transition temperature derived from the $D(T)$ hysteresis loops toward lower values. Moreover, comparatively low doses of irradiation cause the distortion of the loops, reflecting a diffuse nature of the phase transition at heating. In spite of this, as it is clearly seen from the shape of the loops, at cooling the phase transition keeps a clear discontinuous nature.

It is also necessary to note that the observed radiation effects are partially reversible. Indeed, the phase transition temperature (measured at cooling) starts to increase when the sample is kept at room temperature during a comparatively long time (Fig. 4, 5). Moreover, it is interesting to note a partial restoring of the discontinuous nature of the thermochromic phase transition when the sample was kept at least 350 hours after irradiation. Nevertheless, both these effects reach saturation near 700 hours. Afterwards, the shape of the hysteresis loop as well as the temperature of the phase transition at cooling do not reveal any changes. It has been also found that annealing of a sample in the high temperature phase at 340 K practically could not affect this remnant effect of irradiation.

The observed strong dependence of the phase transition order and temperature on the dose of irradiation demands a more detailed consideration. The parameters and shape of the observed hysteresis loops would supply important information about the corresponding transformation of the MCs structure. First of all, it is necessary to explain the strong impact of a polymer matrix on its thermochromic properties. According to the data presented in Ref. [9], polymer microcomposites are characterized by a much higher temperature of the phase transition than a single crystal. It has been shown that a more “rigid” polystyrene matrix more significantly affects the geometry of the anionic $[\text{CuCl}_4]^{2-}$ complex than a “softer” latex matrix [9] and, as a result, the shift of the transition temperature in the first case was found to be much more pronounced. For the pristine samples investigated in this work, this temperature

measured at heating (Fig. 2) was found to be higher by 17 K than in the single crystal grown from the aqueous solution ($T_t = 311$ K). It is clear that the observed effect is connected, first of all, with the tensions arising within the interface between the matrix and the microcrystal. One can conclude that polystyrene chains during the process of polymerization create chemical bonds, mostly with structural groups of diethylammonium cation — methyl, methylene groups and ammonium heads. These bonds cause a considerable lateral tension within the surface layers of the microcrystal [9, 10].

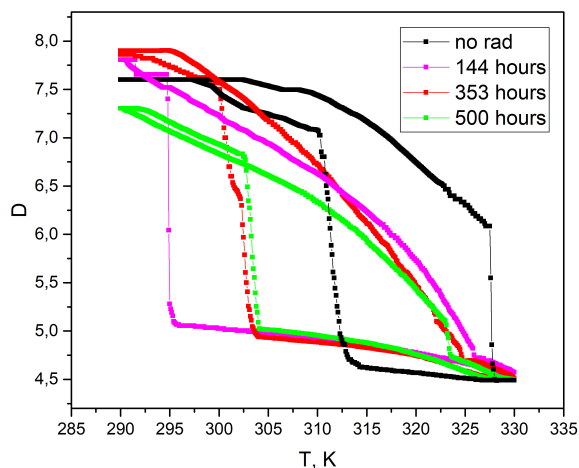


Fig. 4. The temperature dependence of the optical density of DEA-CuCl₄ MCs at $\lambda = 633$ nm for different values of the time elapsed since irradiation

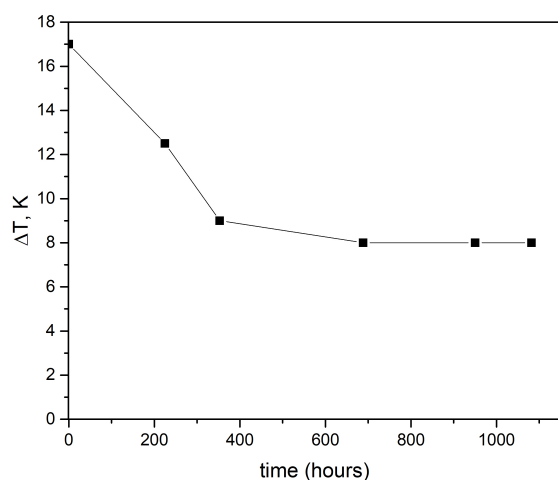


Fig. 5. The dependence of the phase transition temperature shifts on the values of the time elapsed since irradiation

The nature of the phase transition in the mechanically free MC should be very similar to that in a bulk crystal. According to the structural data [1], the driving force for the phase transition is thus entropic in nature with the increasing thermal motion of the DEA cations at heating

leading to a weakening of the hydrogen bonding, which allows the eventual transformation to a more disordered high-temperature phase. In the low-temperature phase, the strong H-bonds cause distortion of the electron cloud of chlorine ions, and this allows a part of the $[\text{CuCl}_4]^{2-}$ anions to acquire the distorted planar form. In the high-temperature phase with weak H-bonds, the copper ion is in the tetrahedral environment. These discontinuous changes in the geometry of the $[\text{CuCl}_4]^{2-}$ chromophore cause the thermochromic nature of the phase transition [1].

The influence of the tension arising on the microcrystal surface on the organic groups ordering would be hardly considered in detail because of the complexity of the investigated composite system. Nevertheless, one can conclude that this process leads to a considerable asymmetry of the corresponding double well potential for DEA cations [15]. By analogy with a model proposed for other crystals undergoing an order-disorder phase transition [16], one can suggest that in this case the potential barriers between the “deep” and the “shallow” wells preventing disorder of the above mentioned group become higher. As a result, the phase transition temperature increases. Taking into account some random character of the chemical bonds created by the polymer matrix with the microcrystals, the clearly discontinuous phase transition becomes more diffused in the microcomposite in comparison with that in a bulk crystal [9]. This is reflected in a more diffused shape of the hysteresis loop corresponding to a pristine sample compared to that in DEA-CuCl₄ single crystal.

The radiation effects in the MCs and bulk crystals look considerably different. The influence of the small doses of radiation on a single crystal was related to the breaking and following rearrangements of the hydrogen bonds [2, 5]. Nevertheless, the corresponding changes in the phase transition temperature were found to be very small. The commensurate doses of ionizing radiation cause much more pronounced changes in the thermochromic properties of the MCs. One concludes, that the key moment consists in the effects within the interface between a matrix and a microcrystal. The indirectly ionizing high energy gamma-quanta from Co-60 cause a series of processes in the condensed matter: photoeffect, the Compton effect, the birth of electron-positron pairs. The arising charged particles together with beta-particles from the isotope waste their energy on the processes of ionization and radiation. In the final stage of these processes, due to the dissipated energy of the particles, one can observe the breaking of the chemical bonds. In a bulk crystal, due to further rearrangements and relaxation of these bonds, one can observe comparatively small structural changes and shifts of the phase transition temperature and the corresponding effects are mostly reversible.

A much more pronounced shift of the phase transition temperature under the commensurate doses of irradiation would be explained, first of all, by the breaking of the chemical bonds between the polymer matrix and the microcrystals. These bonds are hardly restored

even during a long time after irradiation. Their breaking leads to diminishing the strains and the temperature of phase transition shifts toward lower values, closer to those characteristic of a bulk crystal. It is necessary to note that the influence of ionizing irradiation possesses a random character with respect to different microcrystals of the composite. Due to this, the thermodynamic conditions of the phase transition into a high temperature phase may deviate between different microcrystals. Therefore, individual microcrystals should undergo the phase transition at different temperatures, since the corresponding potential barrier within the asymmetric double well potential preventing the disordering of the organic groups will be different. Such a model explains why the thermochromic phase transition in MCs acquires on average, a continuous nature at heating run. A partial return to the discontinuous nature of the phase transition after keeping the sample for a long time after irradiation reflects a partial restoration of the chemical bonds between the matrix and DEA-CuCl₄ microcrystals, which, however, cannot be considered a full return to their original state before irradiation. It is also worth noting that in the high temperature disordered phase the above mentioned double well potential is expected to be symmetric. Due to this, the phase transition tested at cooling manifests a clear first order both for the pristine and irradiated samples (Fig. 2 and Fig. 4).

IV. CONCLUSIONS

On the basis of the performed investigations it has been shown that DEA-CuCl₄ microcrystals embedded into a polystyrene matrix are characterized by extremely large sensitivity to a quite low dose of ionizing radiation. Just prepared microcomposites reveal a discontinuous thermochromic phase transition at the temperature much higher than that in a bulk crystal. This shift is explained by tensions arising within the interface between the polystyrene matrix and the microcrystal.

Ionizing radiation causes much more pronounced changes in the thermochromic properties of the MCs in

comparison with a bulk crystal under the influence of similar doses of irradiation. The impact consists in the considerable shift of the phase transition temperature derived from the $D(T)$ hysteresis loops toward lower values. Moreover, comparatively low doses of irradiation cause also a diffused nature of the phase transition at heating. One can conclude that the key moment in the radiation effects is connected with the changes within the interface between a matrix and a microcrystal. A pronounced shift of the phase transition temperature under the comparatively low doses of irradiation is explained by the breaking of the chemical bonds between the polymer matrix and the microcrystals. These bonds are hardly restored even during a long time after irradiation. Their breaking leads to the diminishing of the strains, and the temperature of phase transition decreases toward the values closer to those for a bulk crystal. On the other hand, influence of ionizing irradiation possesses a random character with respect to different microcrystals of the composite. Due to this, the conditions of the phase transition into the high temperature phase may vary between the different microcrystals, and the transition temperature would be different. As a result, the phase transition at heating for an anentire composite was found to be continuous as it is clearly seen in $D(T)$ hysteresis loop.

The discovered extremely high sensitivity of the thermochromic microcomposites based on DEA-CuCl₄ to the comparatively low doses of ionizing radiation, which should be classified as a radiochromic effect, looks very attractive for practical application. This material appeared to be not hygroscopic, it is mechanically stable and very technological. Although the observed radiation effects are only partially reversible, the very simple technology of the preparation of the composites indicates their possible application for the creation of cheap individual radiation dose sensors.

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РАДІОХРОМНИЙ ЕФЕКТ У ПОЛІМЕРНИХ КОМПЗИТАХ НА ОСНОВІ МІКРОКРИСТАЛІВ $[\text{NH}_2(\text{C}_2\text{H}_5)_2]_2\text{CuCl}_4$

Ю. Чорній, А. Грицак, В. Капустяник

Фізичний факультет, Львівський національний університет імені Івана Франка, вул. Драгоманова, 50, 79005, Львів, Україна

Радіохромний ефект виявлено в полімерних композитах на основі мікрокристалів $[\text{NH}_2(\text{C}_2\text{H}_5)_2]_2\text{CuCl}_4$ (DEA-CuCl₄). Досліджено спектри поглинання мікрокристалів DEA-CuCl₄, упродовжених у полістирольну матрицю. Вивчено вплив йонізаційного випромінювання на термохромні властивості цього мікрокомпозита. Показано, що мікрокристали DEA-CuCl₄, упродовжені в полістирольну матрицю, характеризуються надзвичайно високою чутливістю до порівняно низьких доз йонізаційного випромінювання. Установлено, що цей композит із середнім розміром мікрокристалів 200 мкм має термохромні властивості, подібні до властивостей об'ємного монокристала, хоча притаманний йому стрибкоподібний термохромний фазовий перехід зміщений до вищих температур порівняно з об'ємним кристалом. Це зміщення пояснюємо напруженнями, які виникають на межі між полістирольною матрицею та мікрокристалом. Йонізаційне випромінювання викликає набагато істотніші зміни термохромних властивостей МК порівняно з об'ємним кристалом під впливом аналогічних доз опромінення. Основний вплив полягає в значному зниженні температури фазового переходу, отриманої з петель гістерезису $D(T)$. Помітне зміщення температури термохромного фазового переходу за відносно низьких доз опромінення, яке можна розглядати як радіохромний ефект, пояснюємо розривом хімічних зв'язків між полімерною матрицею та мікрокристалами. Це приводить до зменшення поверхневих деформацій і зміщення температури фазового переходу в бік нижчих значень. З іншого боку, вплив йонізаційного опромінення має випадковий характер щодо різних мікрокристалів у структурі композита. Через це умови фазового переходу у високотемпературну фазу для різних мікрокристалів відрізняються і температура переходу набуває різних значень для різних мікрокристалів. Унаслідок цього фазовий перехід для композита загалом, визначений під час нагрівання, має неперервний характер, як це чітко видно з петлі гістерезису $D(T)$. Отриманий матеріал негігроскопічний, механічно стійкий і технологічний. Незважаючи на те, що виявлені радіаційні ефекти є лише частково оборотними, дуже проста технологія приготування композитів передбачає їхнє застосування для створення дешевих індивідуальних датчиків дози йонізаційного опромінення.

Ключові слова: мікрокомпозити, йонізаційне випромінювання, фазові переходи, спектри поглинання, термохромний ефект.