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Influence of iodine impurity on photochemical and emission processes in $CdBr_2$:Cu crystals

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Influence of iodine impurity on photochemical and emission processes in $CdBr_2$:Cu crystals have been studied under N_2 laser and X-ray excitation. After the materials irradiation by the integral emission of a deuterium lamp at 295 K, additional bands peaked near 395 and 625 nm were revealed that are due to Cu^{2+} and nCu^0 centers, respectively. The photochemical transformations in those systems have been shown to be related mainly to changes in the charge state of copper centers. UV irradiation of $CdBr_2$:Cu,I results in decreased X-ray luminescence intensity in the non-elementary 510 nm band, weakened 620 nm band and increased intensity of the photoluminescence band peaked at 490–500 nm at 85 K. After the colored samples were heated to about 300°C, no features due to the photochemical transformations have been observed in the spectral characteristics. The emission band peaked at 490 to 500 nm is related to the emissive annihilation of excitons localized at I^- ions. The photoluminescence in the 620 nm band is supposed to be due to complex centers containing anion vacancies and iodine ions.

Исследовано влияние примеси иода на фотохимические и излучательные процессы в кристаллах $CdBr_2$:Cu при возбуждении N_2-лазером и рентгеновским излучением. После облучения материалов при 295 К интегральным светом дейтериевой лампы в спектрах поглощения выявлены дополнительные полосы с максимумами около 395 и 625 нм, которые обусловлены Cu^{2+} и nCu^0-центрами, соответственно. Показано, что фотохимические преобразования в этих системах, в основном, связаны с изменением зарядового состояния медных центров. Действие УФ-света на $CdBr_2$:Cu,I приводит к уменьшению интенсивности рентгенолюминесценции в неэлементарной полосе 510 нм, ослаблению полосы 620 нм и увеличению интенсивности полосы с максимумом в области 490–500 нм фотолюминесценции при 85 К. После прогрева окрашенных образцов до температуры ~300°С особенности, вызванные фотохимическими преобразованиями, в спектральных характеристиках не проявляются. Полоса излучения с максимумом в области 490–500 нм связана с излучательной аннигиляцией экситонов, локализированных на ионах I^-. Фотолюминесценция в полосе 620 нм приписывается сложным центрам, в состав которых входят анионные вакансии и ионы иода.

The copper-activated cadmium bromide crystals are efficient photochromic materials [1–3]. The optical luminescent and photoelectrical properties of $CdBr_2$:CuCl and $CdBr_2$:CuBr were studied before in [1, 4, 5]. The photochemical transformations in those systems have been shown to be related mainly to changes in the charge state of activator centers. In this work, the effect of iodine impurity on photochemical and emission processes in $CdBr_2$:CuBr crystals has been studied.

As the investigation objects, the $CdBr_2$:CuBr (0.5 % by mass) and $CdBr_2$:CuBr (0.5 % by mass), CdI_2 (0.15 % by mass) crystals were used grown by the Stockbarger-Bridgeman technique in sealed quartz ampoules [6]. The examination procedures of the crystal luminescent characteristics have been described in [5, 7]. The

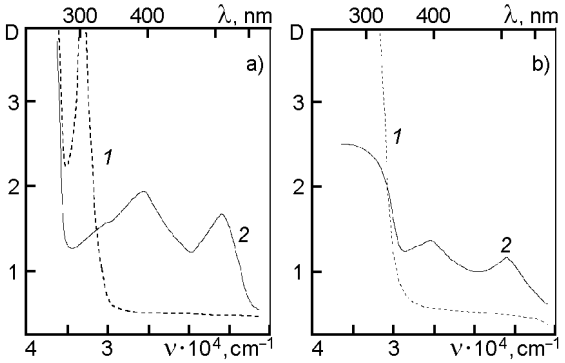

Fig. 1. (a) Absorption spectra of $CdBr_2$:Cu crystal at 295 K prior to (*1*) and after (*2*) coloration; (b) those of $CdBr_2$:Cu,I crystal at 295 K prior to (*1*) and after (*2*) coloration.

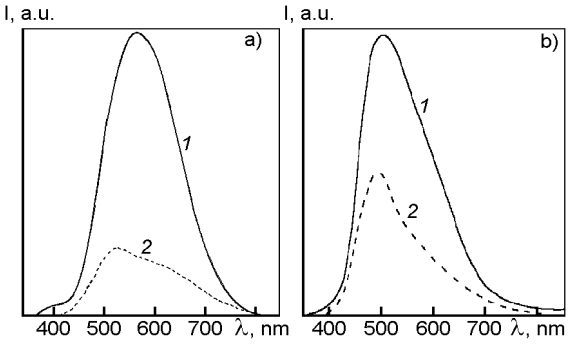

Fig. 2. (a) X-ray luminescence spectra of $CdBr_2$:Cu crystal at 85 K prior to (*1*) and after (*2*) coloration; (b) those of $CdBr_2$:Cu,I crystal at 85 K prior to (*1*) and after (*2*) coloration.

optical absorption spectra were recorded using a SPECORD M40 spectrophotometer. The samples were colored at room temperature by integral emission of a deuterium lamp for 5 min.

The absorption spectrum of $CdBr_2$ activated with CuBr admixture only taken at 295 K is characterized by the long-wavelength absorption edge at 270–280 nm and an intensive activator band peaked near 305 nm (Fig. 1a, curve 1). The crystal irradiation by a deuterium lamp results in a weakened 305 nm band and appearance of photo-induced bands at 395 and 625 nm (Fig. 1a, curve 2).

At room temperature, the $CdBr_2$:Cu,I is characterized by an additional intensive absorption in the near-edge region (270–290 nm). As a result, the band related to the copper admixture does not appear selectively against the absorption background due to centers assosiated with I^- ions [6], so only the long-wavelength tail of the activator absorption is recorded in the spectrum (cf. curves 1 in Figs. 1a and 1b). In the colored polyactivated crystal, a reduced activator absorption in the short-wavelength region and appearance of similar photo-induced absorption bands of lower intensity in the long-wavelength region is observed, too (Fig. 1b, curve 2).

The X-ray luminescence (XRL) spectra of uncolored $CdBr_2$:Cu are similar to those of $CdBr_2$ [8] and $CdBr_2$:Ag [9, 10]. At 85 K, those contain a broad intensive non-elementary band peaked near 560 nm and a weak band in the 350–400 nm region (Fig. 2a, curve 1). In colored $CdBr_2$:Cu, the luminescence intensity decreases and the spectral maximum shifts towards shorter wavelengths (Fig. 2a, curve 2). It follows from comparison of curves 1 and 2 in Fig. 2b that the coloration of $CdBr_2$:Cu,I crystal results also in a decreased intensity of the low-temperature luminescence and shift of its maximum from 510 to 500 nm.

The optical irradiation influences significantly the low-temperature (T = 85 K) photoluminescence (PL) of $CdBr_2$:Cu,I under N_2 laser (LGI-21, λ = 337.1 nm) excitation in the long-wavelength tail region of the activator absorption prior to coloration and in the absorption region of the photolysis products after the coloration. While in the first case, a band peaked near 620 nm and a shoulder in the 440 to 540 range are observed in the PL spectrum (Fig. 3, curve 1), it is just the emission peaked near 500 nm that predominates in the second case (Fig. 3, curve 2). The 620 nm emission is found to be more intense in $CdBr_2$:I and $CdBr_2$:Cu,I than in $CdBr_2$ and $CdBr_2$:Cu [4, 8]. The $CdBr_2$:Cu crystal coloration by UV irradiation results also in the intensity redistribution in the PL spectrum at 85 K in favor of the short-wavelength emission. Similar bands have been found in emission spectra of photochromic materials $CdBr_2$:Ag and $CdBr_2$:Ag,I under nitrogen laser excitation and after the coloration.

When the $CdBr_2$:Cu,I crystal is heated from 85 up to 295 K, the 620 nm PL intensity decreases significantly and it is not observed essentially at temperatures above 250 K. The crystal emission peaked at 490 to 500 nm also is characterized by a strong temperature quenching. The temperature dependence of PL for $CdBr_2$:Cu,I in that band is similar to that of $CdBr_2$ and $CdBr_2$:Cd peaked at 490 nm caused by the incontrolled iodine impurity [8, 11].

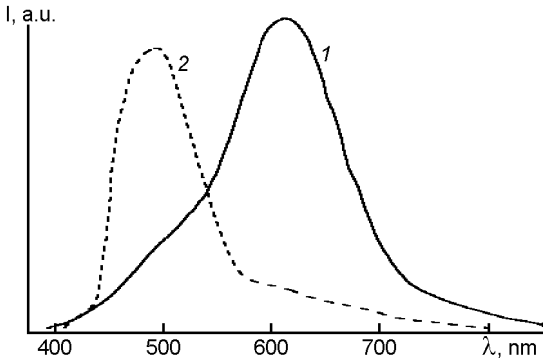

Fig. 3. Photoluminescence spectra of $CdBr_2$:Cu,I crystal at 85 K prior to (*1*) and after (*2*) coloration.

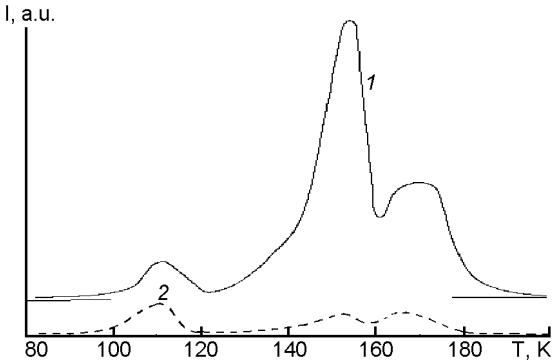

Fig. 4. Thermostimulated luminescence curves of $CdBr_2$:Cu,I crystal X-ray excited at 85 K prior to (*1*) and after (*2*) coloration.

The additional activation by CdI_2 does not influence essentially the thermostimulated luminescence (TSL) of photochromic $CdBr_2$:Cu. Under X-ray excitation at 85 K, $CdBr_2$:Cu,I stores a relatively small light sum. At the TSL curve, thermal peaks are observed at 112, 152, and 168 K as well as a shoulder in the 130 to 135 K range (Fig. 4, curve 1). The crystal coloration results in a considerably weakened TSL, no new peaks being observed in the TSL curve (Fig. 4, curve 2). Using the Urbach method, the depths of capture levels responsible for the TSL of $CdBr_2$:Cu,I have been estimated. For the 112, 152, and 168 K peaks, the thermal activation energy values $E_T \approx 0.20$; 0.29, and 0.33 eV, respectively, have been obtained.

The initial spectral characteristics of photochromic crystals on the basis of cadmium bromide are restored after the sample decoloration attained by heating in a sealed quartz ampoule in air up to about 300°C. No optical decoloration was observed for those samples.

Thus, the $CdBr_2$:Cu,I crystals are also photochromic ones. The photochemical transformations in this material run somewhat less intensively than in $CdBr_2$:Cu. The studied results of the UV irradiation effect on the absorption spectra show, that the photochemical transformations in the copper-activated cadmium bromide crystals are similar to those in $CdBr_2$:Ag [12] and $CdBr_2$:Cu [13, 14]. In the optical absorption spectrum of $CdCl_2$ crystals activated by small amount of AgCl, the activator band has been revealed at 227 nm, the intensity increases in parallel with the impurity concentration [12]. The $CdCl_2$:Ag irradiation by γ rays or neutrons results in weakening of the 227 nm band near the absorption edge and appearing bands near 397 nm and 515 nm. Those bands become weakened under optical decoloration (350 nm) while the 227 nm one is intensified. By EPR, a paramagnetic center has been found in the irradiated $CdCl_2$:Ag, that is ascribed to the substituting Ag^{2+} ion. Studying the isothermal tail of the EPR signal and of the optical absorption bands, it has been established that the absorption at 397 nm correspond to that paramagnetic center. Consideration of the EPR signal shows that the wave function of non-coupled holes extends not only on the central Ag^{2+} ion but also on the Cl^- ligand ions. Such a formation is considered to be a cluster consisting of one Ag^{2+} ion and six Cl^- ones.

Basing on the obtained results, authors [12] have concluded that the 227 nm absorption band may be due to intracenter transitions in Ag^+ ions. The band peaked near 515 nm has been observed before [10] in the absorption spectra of colored photochromic $CdBr_2$:Ag. The nature of this band is associated with the colloidal silver centers. Similar features are observed in the absorption spectra of $CdCl_2$ crystals activated with CuCl and $CuCl_2$ [1, 2]. Prior to UV irradiation, these materials show a band peaked at 280 nm that is ascribed to Cu^+. After the irradiation, this band intensity decreases and two new bands at 390 and 590 nm appear. The nature of the 390 nm band is associated with Cu^{2+} while that of the 590 nm one, with Cu^0 colloids. Spectral characteristics of thin film $CdCl_2$:CuCl photochromic materials are interpreted in a similar fashion [13-15].

The lattice of $CdBr_2$:Cu photochromic material contains also two positions of copper impurity ions [1, 2, 5]. The single-charged copper ions are situated in regular

sites in the Cd^{2+} position form acceptor centers $(Cu^{+}_{Cd})^{-}$ while those in the interstitial octahedral voids, the donor centers Cu^{+}_{i}. These centers form light-sensitive neutral complexes (associated donor-acceptor pairs) $\{(Cu^{+}_{Cd})^{-}-Cu^{+}_{i}\}$. Such formations are dipole centers and the 280 K peak in the thermostimulated depolarization of the electret state in non-colored $CdBr_2:Cu^{+}$ samples are ascribed thereto [5].

The activator band at 302–305 nm observed in the absorption spectra of non-colored cadmium bromide crystal with copper impurity can be ascribed to the parity-forbidden intraionic $3d^{10} \rightarrow 3d^{9}4s$ transition, the exclusion being raised in part due to Cu^{+} ion displacement with respect to the center of the ligand consisting of Br^{-}, I^{-} ions [15]. Or, as in the $CdCl_2$:Ag system [12], this band is related to the permitted $3d^{10} \rightarrow 3d^{9}4p$ transitions in the activator centers. The considerable intensity increase of that band as the impurity concentration in the photochromic material increases and its insignificant decrease in the absorption spectrum of $CdBr_2$:CuBr (0.05 % mol.) as the temperature is elevated from 77 to 280 K [2] testifies in favor of the second hypothesis.

The material coloration under illumination is associated as a rule with photoionization of intrinsic or extrinsic centers. During the photochemical reactions running under irradiation of $CdBr_2$:Cu with light absorbable efficiently in the near-edge region by Cu^{+} centers, the photoinduced decomposition of the light-sensitive copper complexes is observed [1, 2, 5]. In this case, the concentration of the centers associated with single-charged copper ions decreases due to photothermal ionization of Cu^{+}_{Cd} and electron delocalization from these centers to Cu^{+}_{i}. Cluster centers $(Cu^{2+}X^{-}_{6})^{4-}$ where X are halide ions appear as well as nCu^{0} type colloids that are responsible for the photoinduced absorption bands peaked near 395 and 625 nm, respectively. The coloration (darkening) of cadmium bromide photochromic materials with a high concentration of copper impurity occurs in thin subsurface layers as a result of strong absorption of the photoactive radiation. The obtained data point to the colloidal coloration mechanism. The reverse decoloration process runs through oxidation of Cu^{0} centers by Cu^{2+} ions [14]. Since the same photoinduced changes are observed in the absorption spectra of the studied single- and polyactivated photochromic cadmium bromide crystals, the photostimulated changes of the spectral characteristics are due mainly to the copper center recharging [5] and, to a lesser extent, to photolysis of the crystal matrix [8].

It has been shown [16] that the copper impurity in KCl•KI:Cu forms complex centers of $(Cu^{+}I^{-})$ type with iodine ions. The association of impurity ions at the isovalent substitution may be due to their ability to form a more strong chemical binding with one another than with halide ions of the crystal luminophor matrix. That is why in alkali chlorides with bromide and iodide impurities, ions of activators such as Tl^{+}, Ag^{+} and Cu^{+} try to allocation for Br^{-} and I^{-} ions that exhibit a stronger polarizability than Cl^{-} [17, 18]. Such an interaction of Sn^{2+} and I^{-} activator centers was revealed before [19] by TSL method in cadmium bromide crystals with tin and iodine impurities. Taking into account those results, the clarification in the short-wavelength (region where the impurities absorb) at the $CdBr_2$:Cu,I coloration can be supposed to be caused by lowering concentration of Cu^{+} centers associated with I^{-} ions.

The decreased sensitivity of $CdBr_2$:Cu to UV radiation when being activated with iodine impurity can be explained by that the I^{-} ions in $CdBr_2$ are the hole trapping centers, since those are characterized by a lower electronegativity as compared to Br^{-} ones [17, 20]. As a result, the hole trapping probability of the $(Cu^{+}_{Cd})^{-}$ is decreased and the light-sensitive complex $\{(Cu^{+}_{Cd})^{-}-Cu^{+}_{i}\}$ centers in $CdBr_2$:Cu,I are somewhat more resistant against UV than in $CdBr_2$:Cu. When $CdBr_2$:Cu is doped with chlorine impurity having a higher electronegativity than Br^{-} ions, the hole trapping probability of the $(Cu^{+}_{Cd})^{-}$ is increased. That is why the photostimulated decomposition processes of light-sensitive copper complexes, the formation of Cu^{2+}_{Cd} substitution centers and associations of copper atoms in that material are relatively higher efficient [4].

In XRL and PL spectra of $CdBr_2$:Cu and $CdBr_2$:Cu,I crystals low-doped with copper, no bands associated with Cu^{+} and Cu^{2+} centers have been observed. It has been confirmed [8, 11, 18] that the broad 560 nm XRL band of unactivated $CdBr_2$ at 85 K consists of elementary bands peaked near 490, 545, and 645 nm. The emission at 545 nm excited intensively by X quanta at low temperatures in unactivated [8] as well as in some activated [9, 11, 18] cadmium bromide crystals is interpreted as the intrinsic emission, being due to emissive re-

combination of triplet exciton states of (V_k + e^-) type [8].

It has been noticed above that the emission of $CdBr_2$ and $CdBr_2$:Cd crystals peaked near 490 to 500 nm is associated with the uncontrolled iodine impurity. It follows also from the obtained results that the XRL maximum shift from 560 to 490–500 nm at the additional doping of $CdBr_2$:Cu with CdI_2 is due to the emission intensity redistribution in favor of centers associated with I^- ions. The luminescence peaked near 490 nm observed in intentionally undoped and iodine-doped cadmium bromide crystals is associated with triplet excitons localized at I^- [9, 18].

In [21–23], it has been shown that the emission of alkali halide crystals (AHC) in the α band is due to tunneling transitions in the $F...V_k(BrI^-)$ and $F...V_k(I_2^-)$ pairs. The radiation-induced silver atoms Ag^0 formed in AHC interact efficiently with anion vacancies V_a^+ [24]. It has been reported [25] that the $Cu^0V_a^+$ type centers are formed photothermally in KCl:CuCl crystal due to migration of a V_a^+ vacancy associated with a Cu^0 atom (but not a free vacancy) towards that atom. Taking into account the results of those studies as well as those of [8, 9, 11], the PL of $CdBr_2$ based crystals peaked near 620 nm can be supposed to be due to complex centers (associates) containing anionic vacancies and iodine impurity. This conclusion is testified by the fact that the 620 nm band emission is intensive in $CdBr_2$:I and $CdBr_2$:Cu,I crystals. The luminescence in this region may be related to emissive transitions in anion excitons localized near anion vacancies (α luminescence) [8, 21–23].

It follows from consideration of the obtained obtained and literature data that the increasing of intensity of the 490 nm luminescence and the decreased one in longer-wavelength bands at 85 K after UV irradiation at 295 K of $CdBr_2$:Cu,I samples, that were heat-treated previously, are caused by a change of the copper impurity change charge state [5] as well as by the crystal matrix photolysis [8]. The weakening of the 620 nm luminescence band after coloration of $CdBr_2$:Cu based photochromic materials can be explained by formation of Cd_i^0 and $Cu^0V_a^+$ centers. The emission peaked at 490 nm in colored cadmium bromide crystals with copper impurity must be due to excitation of heteronuclear excitons (BrI) both under light absorption by I^- ions and under recombination of charge carriers (delocalized from photothermally formed Cd_i^0 centers) on iodine ions [8,11]. A heat treatment of the irradiated crystals results in annealing of the photolysis products. In this case, the concentration of α centers (responsible for the long-wavelength emission) increases.

The additional activation of $CdBr_2$:Cu with iodine impurity does not result in new peaks at the TSL curve. The 108–112 and 170 K peaks are revealed also in TSL curves of $CdBr_2$:CdI_2. The TSL curves of cadmium bromide with Ag+ impurity contain peaks at 112, 132, 150, and 170 K [10]. After X-ray excitation, the TSL curve of unactivated crystal is represented by the main non-elementary peak at 173 K and weak ones at 108–112 and 132 K. The nature of TSL peaks was discussed in [8, 11]. It follows from the results of the photochromic materials results TSL that the copper impurity does not form activator centers in $CdBr_2$ but influences mainly the relative charge carrier population in levels of different depths typical of the crystal matrix. The relative weak TSL peak at 169–173 K due to delocalization of heteronuclear V_k centers (BrI^-) [8] testifies in favor of the hypothesis at the interaction of cation and anion centers in $CdBr_2$:Cu,I.

The considerable quenching of the recombination luminescence under X-ray excitation in subsurface layers of optically colored copper-doped cadmium bromide is caused by non-radiative recombination of excitation-generated charge carriers on the photochemical reaction products [4, 5, 26] as well as by the light scattering on atomic copper cogulators (nCu^0) localized at linear defects of the crystal structure [5]. The yield and spectral composition of PL, XRL, and TSL in colored $CdBr_2$:Cu and $CdBr_2$:Cu,I are influenced partly by reabsorption due to the additional absorption of the photolysis products in the spectral region where the emission bands are observed of centers typical for the material matrix as well as of those associated with the anion impurity.

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Вплив домішки йоду на фотохімічні та випромінювальні процеси в кристалах $CdBr_2$:Cu

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Вивчено вплив домішки йоду на фотохімічні та випромінювальні процеси в кристалах $CdBr_2$:Cu при збудженні N_2-лазером та рентгенівським випромінюванням. Після опромінення матеріалів при 295 К інтегральним світлом дейтерієвої лампи у спектрах поглинання виявлено додаткові смуги з максимумами близько 395 і 625 нм, які зумовлені Cu^{2+} і nCu^0-центрами, відповідно. Показано, що фотохімічні перетворення у цих системах, в основному, пов'язані зі зміною зарядового стану мідних центрів. Дія УФ-світла на $CdBr_2$:Cu,I приводить до зменшення інтенсивності рентгенолюмінесценції у неелементарній смузі 510 нм, послаблення смуги фотолюмінесценції 620 нм та підсилення інтенсивності смуги фотолюмінесценції з максимумом в області 490–500 нм при 85 К. Після прогріву забарвлених зразків до температури ~300°С особливості, викликані фотохімічними перетвореннями, в спектральних характеристиках не проявляються. Смуга випромінювання з максимумом в області 490–500 нм пов'язується з випромінювальною анігіляцією екситонів, локалізованих на іонах I^-. Фотолюмінесценція в смузі 620 нм приписується складним центрам, в склад яких входять аніонні вакансії та іони йоду.