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Formation of radiation-induced defects in CsI(Tl) crystals containing BO_2^- ions

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The presence of BO_2^- ions has been found to cause photochemical and radiation-chemical coloration of CsI(Tl) crystals, similarly to the case of CO_3^{2-} ions; the spectral composition of formed centers is the same in both cases. The formation mechanism of radiation-induced defects in CsI(Tl,BO_2) crystals due to BO_2^- ion destruction under F-center formation has been considered. A model of F-like color centers including thallium ions is discussed. Absorption bands at 430 and 520 nm are ascribed to transitions in Tl_2^+ center disturbed by an anionic vacancy while that at 830 nm, by transitions in F-center disturbed by a (Tl^+–Tl^+) one.

Установлено, что наличие BO_2^--ионов, как и CO_3^{2-}-ионов приводит к фото и радиационно-химическому окрашиванию кристаллов CsI(Tl), причем образующиеся центры окраски идентичны. Рассмотрен механизм образования радиационных дефектов в кристаллах CsI(Tl,BO_2), обусловленный разрушением BO_2^--ионов с образованием F-центров. Обсуждается модель F-подобных центров окраски, в состав которых входят ионы таллия. Полосы поглощения 430 и 520 нм связаны с переходами в центре Tl_2^+, возмущенном анионной вакансией, а полоса 830 нм – переходами в F-центре, возмущенном (Tl^+–Tl^+)-центром.

The photo- and radiation resistance of CsI(Tl) crystals is a vital problem due to their use as detecting systems in electromagnetic calorimeters. This fact is the base for the present work.

CsI(Tl) crystals are known to show a lower photo- and radiation resistance, in contrast to undoped CsI ones. Absorption spectra of crystals colored due to illumination and gamma irradiation are found to be identical to each other [1, 2]. Analysis of reasons for light and radiation damage of CsI(Tl) crystals has shown that, along with the known carbonate impurity [1–3], even trace amounts of borates ($5 \cdot 10^{-5}$ %) cause the crystal coloration, therewith, the crystal transparency gets worse to a greater extent in short-wavelength spectral region (Fig.1) while the absorption coefficient in the CsI(Tl) emission maximum (λ = 540 nm) increases from 0.01 to 0.035 cm^{-1} after a light exposure of the crystals. Even an insignificant deterioration of the transparency to intrinsic emission (ΔK = 0.01 cm^{-1}) is known to result in a considerable loss of scintillation light in the case of long-size scintillation modules [4].

To elucidate the role of borates in the deterioration of light and radiation resistance, we have grown CsI(Tl) crystals by Stockbarger technique in evacuated quartz ampoules of 50 mm diameter. The crystals contained thallium in a trace amount ($1.5 \cdot 10^{-4}$ % by mass) as well as in the

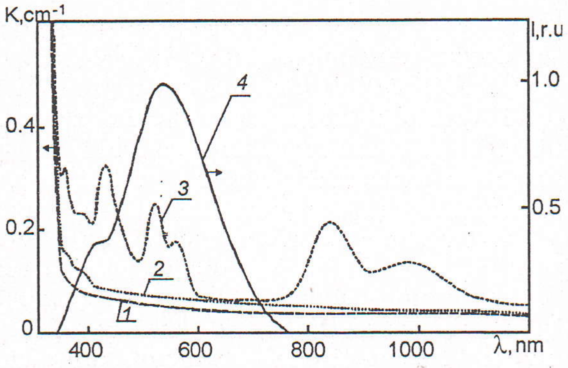

Fig.1. Absorption (1–3) and emission (4) spectra of CsI(Tl) and CsI(Tl,BO$_2$) crystals prior to (1) and after (2,3) irradiation by 10^4 Rad dose at different BO$_2^-$ ion concentrations. Absorption coefficient in the 1930 cm^{-1} band (K), cm^{-1}: $1 \cdot 10^{-3}$ (2) and $6 \cdot 10^{-3}$ (3).

concentration optimal for scintillators $(5–9) \cdot 10^{-2}$ % by mass and were doped intentionally by boric acid (0.005–0.01 % by mass of H$_3$BO$_3$ in the initial mixture). Both CsI raw material and boric acid were dried thoroughly by the heat treatment of ingredients at 100 °C and of the mixture at 250 °C under continuous evacuation using a forevacuum pump.

The presence of oxygen-containing impurities was checked by absorption bands of molecular anions in the IR spectral region using an UR-20 spectrophotomrter. Electron absorption spectra were measured in the 300–1200 nm range on a SF-26 spectrophotometer. The content of molecular anions SO$_4^{2-}$, CO$_3^{2-}$, NO$_3^-$, NO$_2^-$ and IO$_3^-$ in the studied crystals was under the sensitivity limit of the optical determination method ($<2 \cdot 10^{-5}$ % by mass) and that of OH$^-$ impurity lower than the determination threshold of optical and chemical methods ($<1 \cdot 10^{-4}$ % by mass).

It was found from IR absorption spectra that borates are included in CsI crystals in the form of metaboric acid molecular anion BO$_2^-$ even when orthoboric acid H$_3$BO$_3$ was introduced intentionally: this is due to thermal decomposition of the latter at relatively low temperatures.

Fig.2 presents the absorption spectrum typical for the incompletely symmetric ν_3-vibration of BO$_2^-$ anion consisting of two narrow bands 1930 and 2000 cm^{-1} ascribed to the natural ratio of ^{11}B and ^{10}B isotopes, respectively [5, 6]. Photochemical transformations of BO$_2^-$ ion are considered using evolution of the ν_3-vibration band after the CsI(Tl,BO$_2$) crystal illumination by daylight with $\lambda > 320$ nm succeeded by a dark exposure as an example. It follows from presented IR spectra that most of BO$_2^-$ ions are subjected to photochemical decomposition (Fig.2, curve 2) with a partial recovery in the course of dark storage after the illumination is over (curves 3 and 4). Absorption coefficient values in the 1930 cm^{-1} band are $K_1 = 0.148$, $K_2 = 0.061$, $K_3 = 0.096$ and $K_4 = 0.137$ cm^{-1}, respectively.

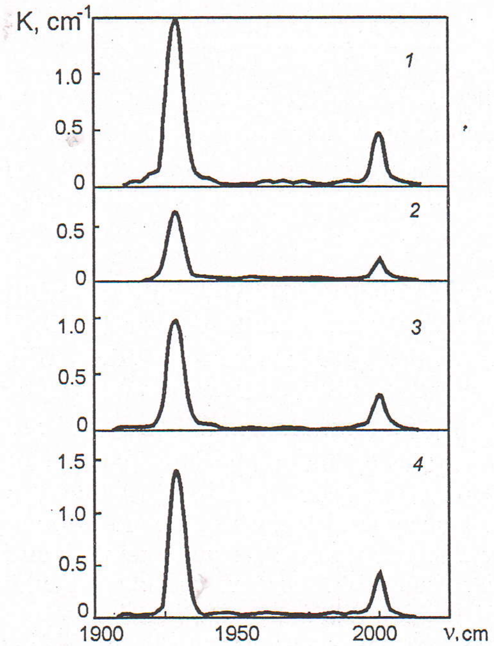

Fig.2. Absorption band of ν_3-vibration for BO$_2^-$ ions in CsI(Tl,BO$_2$) crystal prior to (1) and after (2) daylight illumination with subsequent dark exposure for three (3) and 17 days (4) at 300 K.

The process of BO$_2^-$ ion photochemical decomposition is accompaniel also by an intensity redistribution of color center absorption bands in UV, visible and near IR spectral ranges (Fig.3). When a CsI(Tl,BO$_2$) crystal is illuminated by light with $\lambda > 320$ nm, color centers are accumulated in the short-wavelength spectral region, in particular, those absorbing in 395 and 465 nm bands ascribed to Tl$_2^+$ centers [1–3] (Fig.3, curve 2). Under subsequent crystal storage in the dark, these centers are decomposed while an intensification of long-wavelength absorption bands occurs in 700–1100 nm range typical for F-like centers (F, F$_i$,F$_A$, M) and colloids [3, 7, 8] absorption in CsI crystals. The same is true for 430 and

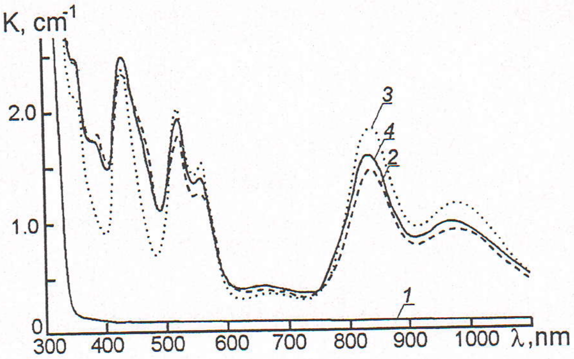

Fig.3. Absorption spectra of CsI(Tl,BO$_2$) crystal prior to (1) and after (2) daylight illumination with subsequent dark exposure for 17 days at 300 K (3) and 273 K (4).

520 nm absorption bands (Fig.3, curve 3) which are ascribed molecular activator centers Tl_2^0 [1−3].

A supposition was voiced [1−3] that anionic vacancies compensating the excess charge in the case of bivalent anion impurities play a substantial part in the formation and aggregation processes of complex activator color centers in CsI(Tl) crystals. Moreover, according to [3], bivalent oxygen-containing impurities favor also formation of stable hole color centers with absorption ands at 250, 300−310 and and 400−405 nm. Therefore, the photo- and radiation resistance of CsI(Tl) crystals with an isovalent BO_2^- anion impurity is untrivial. According to [5], BO_2^- ion is a 5.3 Å long linear molecule situated within CsI lattice in anionic site along (100) direction without the compensating vacancy under some lattice deformation (I^- ion is of 4.4 ÅA in diameter).

Formation of color centers at CsI(Tl) crystals irradiation by quanta having an energy exceeding the forbidden gap width (E_g = 6.3 eV) or by gamma quanta is associated both with the elemental charge carriers capturing by traps resulting from prior-to-irradiation effects and with the Frenkel defects generation. The spectral composition of color centers formed in CsI(Tl) crystal is the same in both cases. Of particular interest is the CsI(Tl,BO$_2$) photochemical coloration mechanism under action of light quanta with an energy considerably less than the gap width ($h\nu < 3.9$ eV). Since we have not found radiation induced defects, including color centers, in CsI(BO$_2$) crystals irradiated by daylight, we believe that the charge carrier delocalization in CsI(Tl,BO$_2$) crystals is possible due to thallium presence. In fact, CsI(Tl) crystals grown in vacuum show an appreciable phosphorescence though are not colored by daylight, while the afterglow is essentially absent in CsI(BO$_2$). Fig.4 presents time dependence of the afterglow in CsI(Tl) and CsI(BO$_2$) crystals illuminated by daylight for 3 h. The illuminated CsI(Tl) crystal shows a considerable afterglow with the spectral composition coincident with that of scintillations. A similar effect was observed also for KCl crystals activated by Tl or Ag at illumination by light quanta from the C band region having energy less than the gap width. Therewith, the same color centers as at X-ray irradiation are formed [9].

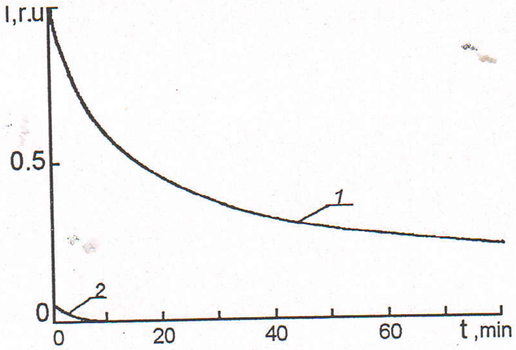

Fig.4. Time dependence of afterglow for CsI(Tl) (1) and CsI(BO$_2$) (2) crystals after daylight illumination.

According to the proposed mechanism of electron excitations delocalization due to the activator ion ionization, an electron entering the conductance band is captured by the neighboring activator ion under formation of a Tl^0 or Ag^0 center, while the hole may be delocalized from Tl^{2+} or Ag^{2+} center forming a V_k center prior to the ionized ion passes into relaxed state. As to CsI(Tl) crystals, the daylight illumination can be supposed to stimulate also the formation of Tl^0 centers and hole ones of different thermal stability; their decomposition may be accompanied by phosphorescence. The fact that the BO_2^- ion dissociation in light plays an important part in photochemical transformations occurring in CsI(Tl) crystals containing borate impurity is confirmed by IR spectra (Fig.2, curve 2). Perhaps BO^+ radical typical for boron and O^{2-} ion are formed in this process:

$$[BO_2^-]_a \xrightarrow{h\nu} BO^+ + O^{2-}. \qquad (1)$$

The existence of isolated O^{2-} ions in alkali halide crystals at room temperature is known to be unlikely due to negative electron affinity of $\mathrm{O^-}$ ion [10]. Therefore, the stabilization of bivalent oxygen requires the presence of an anion vacancy ($\mathrm{V_a{}^+}$) in the nearest anionic site, otherwise $\mathrm{O^{2-}}$ ion loses an electron and is transformed into $\mathrm{O^-}$ one. Thus, free electrons may arise in the course of $\mathrm{BO_2^-}$ ion photodissociation: those are trapped effectively by extrinsic and structure defects ($\mathrm{V_a{}^+}$). At temperatures near the room one, it it just bivacancies that are the most stable ones due to a high mobility of single vacancies. These bivacancies play a predominant role in color center formation and evolution. That role is of particular importance in photochamical and radiation-chemical transformations occurring in quenched crystals where the bivacancy concentration may exceed the equilibrium one by 5–7 decimal orders [11]. While the excess bivacancies transform into clusters when crystals are stored in dark, the process of bivacancies participation in radiation-chemical transformations resulting in color center formation is more probable to run under light or ionizing radiation action. In $\mathrm{CsI(Tl,BO_2)}$ crystals, a negative ion $\mathrm{O^{2-}}$ can be supposed to remain in anionic site after the photostimulated decay of $\mathrm{BO_2^-}$ ion while the positive $\mathrm{BO^+}$ one is displaced into interstitial position and then into cationic site. Then, the reaction (1) including a bivacancy can be presented by the following scheme:

$$[\mathrm{BO_2^-}]_\mathrm{a} + [\mathrm{V_c^-V_a^+}] \rightarrow [\mathrm{BO_i^+} + \mathrm{V_c^-}] + \mathrm{O_a^{2-}} + \mathrm{V_a^+} \rightarrow$$
$$\rightarrow [\mathrm{BO^+}]_\mathrm{c} + \mathrm{O_a^-} + e + \mathrm{V_a^+} \rightarrow [\mathrm{BO^+}]_\mathrm{c} + \mathrm{O_a^-} + \mathrm{F} \quad (2)$$

According to reaction (2), in the course of $\mathrm{BO_2^-}$ ion photochemical decay observed by means of IR spectra (Fig.2), a $\mathrm{BO^+}$ radical in cationic site, an oxygen ion in anionic one and an F center are possible to be formed. Thus, $\mathrm{BO_2^-}$ ions stimulate the F centers formation similarly to $\mathrm{CCO_3^{2-}}$ and $\mathrm{OH^-}$ ones considered before [12].

It follows from the above that the photochemical decomposition of $\mathrm{BO_2^-}$ ions in $\mathrm{CsI(Tl,BO_2)}$ crystals results in formation of F centers and hole ones in UV spectral region; those are transformed into more complex centers of $\mathrm{V_2 ... V}_n$ type, possibly stabilized by the activator, in the course of migration and evolution. Moreover, as is seen in Fig.3, absorption bands ascribed to activator centers $\mathrm{Tl_2^+}$ and $\mathrm{Tl_2^0}$ are observed in the visible spectral range as well as longer-wavelength bands in the near IR region ascribed to complex coagulums [3, 13]. Photo- and gamma-irradiated $\mathrm{CsI(Tl,BO_2)}$ crystals with low activator content ($1.5 \cdot 10^{1964}$ % of Tl) do not exhibit those bands in absorption spectra, in contrast to crystals containing $(5–9) \cdot 10^{-2}$ % of Tl. This fact evidences a significant importance of pair activator centers for the formation of color centers stable at room temperature, similarly to all crystals with CsCl structure activated by mercury-like ions [13, 14]. According to the latter works, the formation of ($\mathrm{Tl^+–Tl^+}$) type centers is characterized by a threshold value of activating ion concentration. The model of $\mathrm{A_2^+}$ and $\mathrm{A_2^0}$ centers is based also on a superlinear concentration dependence of absorption and emission bands related to these centers and anisotropy of their optical properties. No photochemical decomposition of $\mathrm{BO_2^-}$ ions was revealed in $\mathrm{CsI(BO_2)}$ and $\mathrm{CsI(Tl,BO_2)}$ crystals with low $\mathrm{Tl^+}$ ion content ($1.5 \cdot 10^{-4}$ %), perhaps due to the reversibility of reaction (2) in the absence of ($\mathrm{Tl^+–Tl^+}$) centers. While in KCl(Tl) crystals the formation of activator electron color centers is due to ionization of $\mathrm{Tl^+}$ ions, in the case of $\mathrm{CsI(Tl,BO_2)}$ it is just $\mathrm{O^{2-}}$ ions forming at decomposition of $\mathrm{BO_2^-}$ ones that may serve as electron source. In this case, delocalized electrons may be trapped both by anionic vacancies under F centers formation and by ($\mathrm{Tl^+–Tl^+}$) centers under $\mathrm{Tl_2^+}$ color center generation. However, in CsI(Tl) crystals doped additionally both by $\mathrm{CO_3^{2-}}$ or $\mathrm{OH^-}$ ions anf by $\mathrm{BO_2^-}$ ones, two overlapping bands at 840 and 990 nm are observed in the IR spectral region instead of the F-one with maximum at 790 nm.

The F-center disturbation by homologic and bivalent cations is cnown to result in a long-wavelength shift and splitting of the F band [7, 8]. There is no literature data on disturbance of F-centers by mercury-like ions. A high mobility of F-centers in CsI crystals at room temperature stimulates the colloid formation in $\mathrm{CsI(CO_3)}$, CsI(OH) at relatively low irradiation doses; that may cause the generation of stable F-like centers near thallium ions in CsI(Tl). The 840 nm band observed in $\mathrm{CsI(Tl,BO_2)}$ crystals and ascribed to activator coagulums seems to be due to transitions in F-center disturbed by activator ions, since the appearance of that

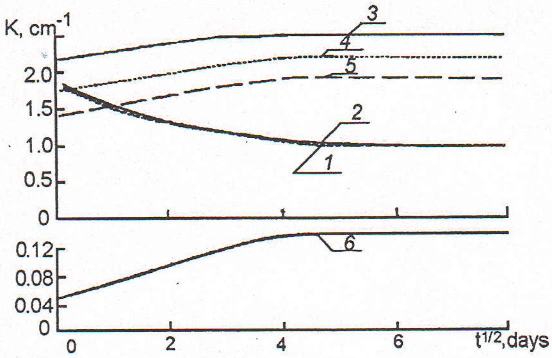

Fig.5. Dependence of color center absorption bands for a CsI(Tl,BO_2) crystal illuminated by daylight on the dark exposure duration at 300 K. Wavelengths, nm: 390 (1), 465 (2), 430 (3), 520 (4), 840 (5), 1930 cm^{-1} absorption band of BO_2^- ion (6).

band is defined by the presence of a threshold thallium concentration. It is to note that the intensity ratio of 840, 430 and 520 nm bands remains constant for different activator concentrations and irradiation doses in CsI(Tl,BO_2) and CsI(Tl,CO_3) crystals. This can be an evidence that electron transitions causing the above bands occur in a common center including an F-center along with activator ions.

A typical feature of CsI(Tl) crystals with a borate admixture consists in a pronounced intensity redistribution between color center absorption bands occurring during a prolonged time period after the irradiation is over. The time dependence of absorption band intensity $K = f(\sqrt{t})$ for activator color centers taken during the dark storage of photochemically colored CsI(Tl,BO_2) crystals at 300 K (Fig.5) exhibits a linear section. This evidences the presence of a diffusion-controlled slow component in the color center transformation kinetics. The equal slopes of $K = f(\sqrt{t})$ dependences for 430, 520 and 840 nm bands confirms their belonging to a common center. Moreover, as could be expected, the decay kinetics of 390 and 465 nm bands belonging to Tl_2^+ center turns out to be the same. The observed intensity increase of 430, 520 and 840 nm absorption bands seems to be due to to thermal ionization of Tl_2^+ centers. Therewith, delocalized electrons may be captured repeatedly by anionic vacancies under formation of F-centers which, due to diffusion, are involved both in the formation of electron color centers $(Tl^+-Tl^+-V_a)+e$ and in the BO_2^- ion reduction reaction (2).

An illumination of CsI(Tl,BO_2) crystals by light with $h\nu < 3.9$ eV and the subsequent dark exposure at 273 K has shown that the color center generation processes become hindered as the temperature decreases (Fig.3, curve 4) that may be caused, on the one hand, by thermal stability of electron color center responsive for 390 and 465 nm absorption band (their decomposition temperature is 343 K) and, on the other hand, by retardation of diffusion processes. It is just transitions in the $(Tl^+-Tl^+)+e$ center disturbed by anionic vacancy that are probably responsible for visible range bands 430 and 520 nm while the non-elementary long-wavelength band (840 nm) is ralated to transitions in a F-center disturbed by (Tl^+-Tl^+) one. Using the common notations, the above centers can be presented as $Tl_2^+-V_a^+$ for short-wavelength bands and $F-(Tl^+-Tl^+)-$ for 840 nm one.

It is to note that, in contrast to other oxygen-containing impurities (e.g. CO_3^{2-}, NO_3^-, NO_2^-, IO_3^-) which are decomposed at relatively low temperatures and thus can be eliminated by high-temperature treatment of raw material and/or melt (except for SO_4^{2-} having the decomposition temperature exceeding 1000 °C), decomposed borates remain in the melt and thus in the crystal as BO_2^- ions. The formation of BO_2^- from BO^+ in dark is possible also at the expense of hydroxyls and oxygen ions. The process of BO_2^- recovery is of diffusion character evidenced by a linear section of $K = f(\sqrt{t})$ dependence for 1930 cm^{-1} band of ν_3 vibration (Fig.5, curve 6).

Thus, a specific feature of studied photochemical and radiation-stimulated transformation in CsI(Tl,BO_2) crystals consists in the capturing of delocalized charge carriers resulting in the generation of color centers in the short-wavelength spectral region, including Tl_2^+ centers, with their subsequent evolution into more stable centers of $(Tl^+-Tl^+-V_a)+e$ type decomposing at 420–440 K. The Tl_2^+ centers are responsible for 390 and 465 nm absorption bands; this is in agreement with interpretation of other authors [1–3, 13, 14]. As to absorption bands in visible and near IR ranges, we have proposed the model of $(Tl^+-Tl^+-V_a)+e$ center in contrast to the Tl_2^0 one. Therewith, it is just transitions in the $(Tl^+{-}Tl^+{-}V_a)+e$ center disturbed by anionic vacancy that are responsible for visible-range bands 430 and 520 nm while the long-wavelength 840 nm band is related to transisitons in F center disturbed by $(Tl^+{-}Tl^+)$ one.

Literature data on concentration dependences and polarized luminescence [14] defining the A_2^- and A_2^0 center model in CsCl type crystals activated by mercury-like ions are not in contradiction with the center model proposed by us. Structures and specific features of activator color centers in $CsI(Tl,CO_3)$, CsI(Tl,OH) and $CsI(Tl,BO_2)$ will be considered in detail elsewhere.

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Утворення радіаційних дефектів у кристалах CsI(Tl) з домішкою іонів BO_2^-

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Встановлено, що присутність BO_2^- іонів, CO_3^{2-} -іонів, призводить до фото- і радіаційно-хімічного забарвлення кристалів CsI(Tl), при цьому утворені центри забарвлення ідентичні. Розглянуто механізм утворення радіаційних дефектів у кристалах $CsI(Tl,BO_2)$, обумовлений розпадом BO_2^- іонів з виникненням F-центрів. Обговорюється модель F-подібних центрів забарвлення, до складу яких входять іони таллію. Смуги поглинання 430 і 520 нм пов'язані з переходами в центрі Tl_2^+, збуреному аніонною вакансією, а смуга 830 нм – переходами в F-центрі, збуреному $(Tl^+{-}Tl^+)$ центром.