

Transformations of molecular anions in irradiated cesium iodide crystals

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Photo- and radiation-induced chemical transformations in CsI and CsI(Tl) crystals containing molecular anions CO_3^{2-} , OH^- , BO_2^- have been studied. The ionizing radiation has been found to initiate the decomposition of hydroxyl ions under formation of H_i^0 . The diffusion of the latter in the solid solution results in a reaction causing formation of HCO_3^- ions and F and F-like centers in CsI and CsI(Tl) crystals, respectively. Radiation-chemical transformations of BO_2^- ions result in formation of BO_c^+ , O_a^- ions and F centers. The reactions of F-like color center formation occur in CsI(Tl) crystals containing the above-mentioned molecular anions also under action of photons having energy less than 3.8 eV.

Исследованы фото- и радиационно-химические превращения в кристаллах CsI и CsI(Tl), содержащих молекулярные анионы CO_3^{2-} , OH^- , BO_2^- . Установлено, что ионизирующее излучение в кристаллах CsI и CsI(Tl) инициирует разложение гидроксил-ионов с образованием H_i^0 , в результате диффузии которого в твердом растворе протекает реакция с образованием HCO_3^- -ионов и F- and F-подобных центров для CsI и CsI(Tl), соответственно. В результате радиационно-химических превращений BO_2^- -ионов образуются BO_c^+ , O_a^- ионы и F-центры. В кристаллах CsI(Tl) с рассмотренными молекулярными анионами указанные реакции с образованием F-подобных центров окраски протекают также и под действием фотонов с энергией меньше 3.8 эВ.

It has been established before [1–4] that molecular anions (MA) play an important part in radiation-induced defect formation in pure and doped cesium iodide crystals widely used as effective scintillation materials.

The single crystals grown from the melt often contain carbonate which is a very undesirable impurity in CsI(Na) [5] and especially in CsI [4] and CsI(Tl) [1]. Consideration of photo- and radiation-induced damage of CsI(Tl) crystals has shown that the crystal coloration is caused, along with the known carbonate impurity [1–3], by even trace amounts ($5 \cdot 10^{-5}$ % by mass) of borates. The present work is necessitated by contradictions in data on radiation-chemical transformations of carbonate ion [6–8] and

by the absence of similar information concerning borate ion.

The investigated crystals were grown using both Kiroopoulos technique in a platinum crucible under argon atmosphere and by Stockbarger one in evacuated quartz ampoules. The initial CsI (special purity grade) was dehydrated preliminarily at 200 and 400°C. TlI, Cs_2CO_3 , CsOH and H_3BO_3 , all special purity grade, were used as activating admixtures. In the last case, special measures were used for through dehydration of both cesium iodide and boric acid, taking into account the high hygroscopicity of the latter. Thallium concentration on grown crystals was from $1.5 \cdot 10^{-4}$ to $1 \cdot 10^{-1}$ % by mass.

The presence of oxygen-bearing impurities was controlled by IR spectroscopy (by

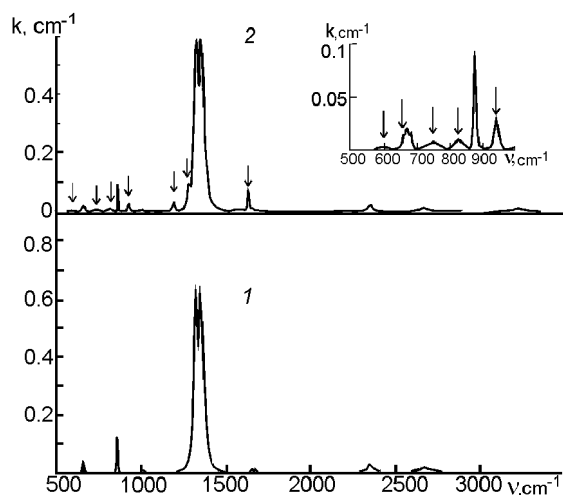


Fig.1. Absorption spectrum of $\text{Csl}(\text{CO}_3)$ crystal prior to gamma irradiation by ^{60}Co source (1) and after the irradiation dose 10^4 rad (2).

vibration spectra characteristic for molecular anions in $400\text{--}4000\text{ cm}^{-1}$ range) using an UR-20 spectrophotometer as well as by chemical analysis methods. The single-crystalline samples were irradiated by a gamma source (^{60}Co) at a dose of 10^4 rad, by non-filtered radiation of a mercury lamp and by daylight where the short-wavelength spectrum edge was limited by the glass transmission ($h\nu < 3.8\text{ eV}$).

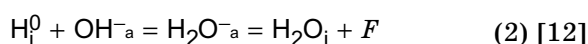
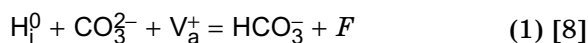
The vibration spectrum of a Csl crystal activated by Cs_2CO_3 is shown in Fig.1, curve 1. The concentration of CO_3^{2-} ion was rather high ($3 \cdot 10^{-4}\%$ by mass) allowing to observe all characteristic bands in the spectrum. At CO_3^{2-} ion concentrations less than $5 \cdot 10^{-5}\%$, only the most intense ν_2 and ν_3 bands are observable.

The local symmetry of CO_3^{2-} ion is lowered in the Csl lattice down to C_{2v} due to effect of the anion vacancy compensating the excess charge and positioned in the anionic site nearest to the CO_3^{2-} ion. In this case, degenerate ν_3 and ν_4 vibrations are splitted while the totally symmetric ν_1 one becomes active in the IR spectral range [9, 10]. Thus, the observed IR spectral bands can be attributed to following basic and complex frequencies (in cm^{-1}) of CO_3^{2-} ion: 667.5 (ν_4), 678.5 (ν_4), 878 (ν_2), 1033 (ν_1), 1362 (ν_3), 1385 (ν_3), 1693 ($\nu_1 + \nu_4$), 1705 ($\nu_1 + \nu_4$), 2390 ($\nu_1 + \nu_3$), 2410 ($\nu_1 + \nu_3$), 2690 ($2\nu_3$), 2770 ($2\nu_3$).

IR absorption spectrum of a $\text{Csl}(\text{CO}_3)$ crystal gamma-irradiated by 10^4 rad dose is presented also in Fig.1 (curve 2). No manifestations of the OH^- ion presence were observed in vibration and electron spectra of the crystal. According to chemical analysis data, the OH^- concentration was $4 \cdot 10^{-4}\%$. As a result of the irradiation, intensities of bands characteristic for CO_3^{2-} ion decrease, but new bands appear with maxima at 593, 663, 745, 830, 947, 1223, 1315, 1679, 3318 cm^{-1} . Those are to be attributed to HCO_3^- ions [8] that is in agreement with interpretation of [11]. Besides, several new bands are observed in the range of 1595–1640 cm^{-1} which may be connected with bending ν_2 vibrations in H_2O molecule [9]. No other bands were revealed in the vibration spectrum of the irradiated $\text{Csl}(\text{CO}_3)$ crystal.

According to [6], in $\text{Csl}(\text{CO}_3)$ crystals subjected to ionizing irradiation, CO_3^{2-} ions are transformed partly into single-charged CO_3^- ones due to hole capture as well as are decomposed into CO molecules and CO_2^- ions, this is why these impurities are observed sometimes in unirradiated crystals. In our opinion, it is just HCO_3^- ions and H_2O molecules that are formed in irradiated $\text{Csl}(\text{CO}_3)$ crystals.

We have found before [8] that both CO_3^{2-} and OH^- ions are revealed in Csl crystals, no matter what either carbonate or hydroxyl ion is used as the dopant; only relative amounts of revealed ions are varied. According to [12], OH^- ions dissociate under formation H_1^0 and O_a^- ions when being subjected to the ionizing irradiation. The following radiation-chemical reactions occur as a result of H_1^0 atoms diffusion in the crystal lattice:



It is to note that the reaction (1) is reversible with respect to CO_3^{2-} ions builded into the lattice in the form of impurity-vacancy dipoles. If CO_3^{2-} ions are dissociated off from the anion vacancy, then products of reaction (1) are very stable. In this case, the reversibility of the reaction under consid-

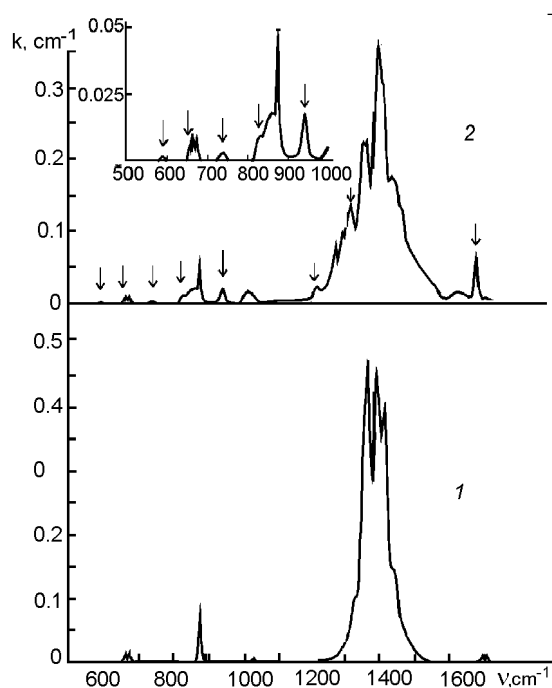


Fig.2. Absorption spectrum of $\text{CsI}(\text{Tl}, \text{CO}_3)$ crystal prior to (1) and after the irradiation (2). Characteristic bands of HCO_3^- ion are pointed by arrows.

eration is defined not by electronic processes but by ionic ones (diffusion of F centers).

To separate contributions of surface and volume to the radiation-stimulated process of bicarbonate ion formation, the measurements were made using samples of different thicknesses (5 and 60 mm) as well as those where the surface layer was taken off by the additional post-irradiation polishing. In all cases, the absorption coefficient measured in the most intense absorption band of HCO_3^- ions (1679 cm^{-1}) has the same value. The coincidence of measurement results allows to state that the effect of bicarbonate ion formation has the volume character. The radiation-induced absorption band in the range $1595\text{--}1640 \text{ cm}^{-1}$ due to H_2O molecules does not manifest itself when the surface layer is removed. This evidences that the irradiation-initiated formation of molecular water takes place within the surface layer while the reaction (2) in the crystal volume is of a low efficiency and cannot be confirmed using absorption methods, unlike (1).

Chemical reactions involving carbonate and hydroxyl ions and color center formation take place in $\text{CsI}(\text{CO}_3)$ crystals under gamma and UV irradiation. In thallium-

doped $\text{CsI}(\text{CO}_3)$, radiation defects in the form of color centers, H_2O molecules and HCO_3^- ions arise not only due to ionizing radiation but also under daylight action ($h\nu < 3.8 \text{ eV}$).

In IR absorption spectra of $\text{CsI}(\text{Tl}, \text{CO}_3)$ crystals, ν_1 , ν_2 and ν_4 bands of CO_3^{2-} ion remain unchanged while the ν_3 one becomes broadened and additional bands appear in 1330 and 1440 cm^{-1} regions (Fig.2, curve 1). Their intensity increases in parallel with the content of thallium as well as with that of carbonate. The appearance of additional bands seems to be in connection with the disturbing effect of the neighbouring Tl^+ ion. The vibration spectrum of $\text{CsI}(\text{Tl}, \text{CO}_3)$ crystals irradiated by ionizing light as well as by daylight is more complex as compared to that of irradiated $\text{CsI}(\text{CO}_3)$ ones. Fig.2 (curve 2) presents a typical vibration spectrum of $\text{CsI}(\text{Tl}, \text{CO}_3)$ crystal exposed to daylight. Along with the appearance of bands characteristic for HCO_3^- ions and water molecules, the structure of ν_1 , ν_2 bands becomes more complicated, additional maxima at 1270 , 1290 , 1305 cm^{-1} arise in the ν_3 band region as well as the absorption in 1440 and 1500 cm^{-1} regions increases. It is noteworthy that the process of radiation-induced defect formation resulting in changes of $\text{CsI}(\text{Tl}, \text{CO}_3)$ vibration spectra depends on the source power and irradiation dose. This is due to diffusion processes occurring in the crystal both during irradiation and when it is over.

Unlike carbonate ion having no absorption bands in the region of the fundamental absorption edge of CsI crystal and in the visible spectral region, there is a band in 253 nm region corresponding to the electron absorption of hydroxyl ion [12]. Irradiation of crystals containing the above impurities by light from the fundamental absorption drop region or in the OH^- band results in formation of the same radiation-induced defects as under the ionizing irradiation due to OH^- ions dissociation causing H_i^0 and O_a^- ions formation.

No radiation-induced defects are formed in $\text{CsI}(\text{OH}, \text{CO}_3)$ crystals under irradiation by light quanta of less than 3.8 eV energy. In the case of $\text{CsI}(\text{Tl})$ crystals bearing carbonate and hydroxyl ions, the photochemical transformations considered above take place under the action of photons of less than 3.8 eV energy, and moreover at a

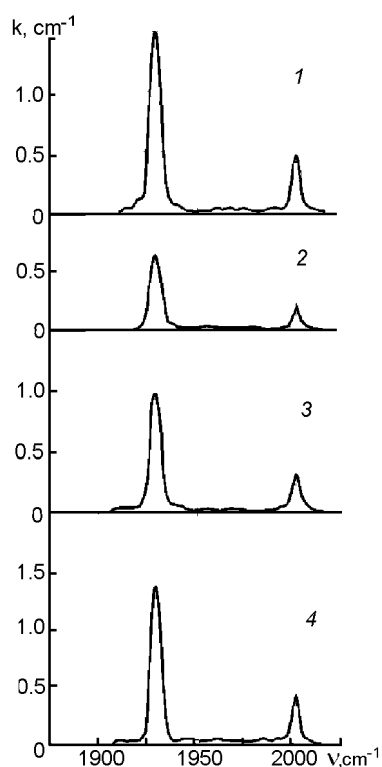


Fig.3. Absorption bands of BO_2^- ion ν_3 vibration in $\text{CsI}(\text{Tl}, \text{BO}_2)$ crystal prior to daylight irradiation (1), after the irradiation (2), after a subsequent dark storage at 300 K for three days (3) and 17 days (4).

higher efficiency than under ionizing irradiation. Therewith, along with the color center formation, considerable changes in the vibration spectra of colored crystals are observed.

We have revealed no photochemical transformations induced by photons of < 3.8 eV in CsI crystals bearing carbonate and hydroxyl ions but containing no thallium. Therefore, we suppose that the charge carrier delocalization is possible due to thallium presence. In fact, $\text{CsI}(\text{Tl})$ crystals grown under conditions eliminating the melt interaction with air components though are not colored due to daylight irradiation [13] but show an appreciable phosphorescence as compared to undoped ones. This points to the decisive role of thallium in the charge carrier delocalization processes. The daylight irradiation of $\text{CsI}(\text{Tl})$ crystals can be supposed to stimulate the formation of Tl^0 centers and hole ones having different thermal stabilities. The decomposition of those centers may be accompanied either by phosphorescence or by an emissionless annihilations that initiated, e.g., hydroxyl ion decomposition. This is in

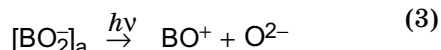
agreement with the mechanism of electron excitation delocalization in $\text{KCl}(\text{Tl})$ crystals proposed in [14].

The study of IR absorption spectra of CsI crystals doped intentionally by boric acid has shown that borates enter these crystals usually as molecular anion of metaboric acid, BO_2^- , even if orthoboric acid H_3BO_3 is introduced. This is due to thermal decomposition of the latter at rather low temperatures.

Fig.3 shows the absorption spectrum typical for incompletely symmetric stretching ν_3 vibration of BO_2^- anion consisting of two narrow lines 1930 and 2000 cm^{-1} attributed to the natural ratio of ^{11}B and ^{10}B , respectively [15, 16]. Photochemical transformations of BO_2^- ion are considered taking as an example variations in ν_3 vibration band due to daylight illumination of a $\text{CsI}(\text{Tl}, \text{BO}_2)$ crystal followed by an exposure in darkness. It follows from the presented IR spectra that the majority of BO_2^- ions undergoes photochemical decomposition (Fig.3, curve 2) with subsequent partial recovery during the post-irradiation dark storage (curves 3 and 4). The photochemical decomposition of BO_2^- ion is accompanied also by an intensity redistribution of color center absorption bands in UV, visible and near IR spectral ranges. As in the case of $\text{CsI}(\text{Tl})$ bearing CO_3^{2-} and OH^- ions, color centers forming due to photo- and gamma-irradiation are identical.

Anionic vacancies compensating the excess charge in the case when bivalent anions are present were suggested to play an important part in the formation and aggregation processes of color centers in $\text{CsI}(\text{Tl})$ crystals [1–3]. Moreover, according to [3], bivalent oxygen-bearing impurities favour also formation of stable hole-type color centers. Therefore, the role of the isovalent BO_2^- anion in the photo- and radiation resistance of $\text{CsI}(\text{Tl})$ crystals is of a particular interest. According to [15], the BO_2^- ion is a 5.3 Å long linear group which is positioned within the CsI lattice in an anionic site along the (100) direction without the compensating vacancy.

Studies of photochemical transformations in $\text{CsI}(\text{Tl}, \text{BO}_2)$ crystals evidence the dissociation of BO_2^- ions in light (Fig.3, curve 2). This results obviously in the formation of BO^+ radical typical for boron and of O^{2-} ion:



If the reaction equation (3) is valid, then an anionic vacancy (V_a^+) should be positioned in the nearest anionic site to neutralize the bivalent oxygen. Otherwise, O^{2-} ion loses one electron and so is transformed into O^- one, since the existence of isolated O^{2-} ions in alkali halide crystals at room temperature is unlikely [12]. Thus, free electrons may arise in the course of BO_2^- ion photodissociation which are captured effectively by extrinsic and structure defects (V_a^+). At temperatures close to room one, it is just bivacancies that are the most stable defects because of the high mobility of single vacancies; these bivacancies may be of the predominant importance in the color center formation and evolution processes. The role of bivacancies is of a particular significance in photo- and radiation-induced chemical transformations taking place in quenched and strained crystals where the bivacancy concentration may be 5–7 decimal orders higher as compared to the equilibrium one [17]. When the crystal is stored in dark, the bivacancies present in a concentration exceeding the equilibrium one are transformed into clusters, while under action of light or ionizing radiation, the involving of bivacancies into radiation-chemical processes resulting in the color center formation is more likely. It can be supposed that in $\text{CsI}(\text{Tl}, \text{BO}_2)$ crystals the negative O^{2-} ion remains in the anionic site after the photo-stimulated decomposition of BO_2^- , while the positive BO^+ ion is displaced first into the interstitial position and then into the cationic site. Then the reaction (3) involving a bivacancy can be presented as



Thus, the photochemical decomposition of BO_2^- ion which is evidenced by IR spectra may result in formation of BO^+ radical in the cationic site, oxygen ion in the anionic one and a F center. The fact of reaction (5) is confirmed, at least for the case of $\text{CsI}(\text{Tl}, \text{BO}_2)$ crystals, by the formation of F-like color centers in the course of photo- and radiation-induced chemical transformations. As to $\text{CsI}(\text{BO}_2)$ crystals without thal-

lium dopant, any dissociation of borate ion was not observed under daylight or gamma irradiation at BO_2^- concentrations less than $5 \cdot 10^{-4}$ % by mass. It follows from this fact that reactions (4) and (5) are reversible for $\text{CsI}(\text{BO}_2)$ and the reaction products are not separated in space, unlike the case of $\text{CsI}(\text{CO}_3)$ crystals.

The formation of F centers resulting from photo- and radiation-stimulated chemical transformations and playing a decisive part in the rise of stable color centers is a typical peculiarity of molecular anions CO_3^{2-} , OH^- studied before in [1] as well as BO_2^- [13].

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Перетворення молекулярних аніонів в опромінених кристалах йодиду цезію

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Досліджено фото- і радіаційно-хімічні перетворення в кристалах CsI і CsI(Tl), що містять молекулярні аніони CO_3^{2-} , OH^- , VO_2^- . Встановлено, що йонізуюче проміння ініціює в кристалах CsI і CsI(Tl) розклад гідроксил-йонів з утворенням H_1^0 , внаслідок дифузії якого у твердому розчині протікає реакція з утворенням HCO_3^- йонів та F- і F-подібних центрів відповідно для CsI і CsI(Tl). Внаслідок радіаційно-хімічних перетворень VO_2^- йонів утворюються VO_c^+ , O_a^- та F-центри. У кристалах CsI(Tl) з розглянутими молекулярними аніонами згадані реакції з утворенням F-подібних центрів забарвлення проходять також під впливом фотонів з енергією менше 3.8 еВ.