

Radiation-induced defects formation in CsI crystals containing hydroxyl and carbonate ions

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HCO_3^- ions are formed in $\text{CsI}(\text{CO}_3)$ crystals along with color centers due to ionising irradiation. The increase of HCO_3^- ion concentration is accompanied by a drop of CO_3^{2-} one. This effect is of a volume character and results from hydroxyl ions presence in the crystal. A mechanism is proposed to explain HCO_3^- ions formation under irradiation and their decomposition in the course of crystal storage.

Под действием ионизирующего излучения в кристаллах $\text{CsI}(\text{CO}_3)$ наряду с центрами окраски образуются HCO_3^- ионы, рост количеств которых сопровождается уменьшением концентрации CO_3^{2-} ионов. Наблюдаемый эффект является объемным и обусловлен наличием в кристаллах ионов гидроксила. Предложен механизм образования HCO_3^- ионов при облучении и их разрушения в процессе хранения кристаллов.

Cesium iodide crystals are known to have the highest resistance against ionizing radiation among alkali halides crystals (AHC). The efficiency of radiation-induced defects accumulation in a crystal is defined to a significant extent by the material purity, and, according to [1], the radiation resistance of those crystals may attain 10 Mrad. The resistance of mass-produced crystals is substantially lower as a rule. Actual crystals contain usually extrinsic CO_3^{2-} -ions in amounts sufficient to be detected by IR spectrometry ($\geq 2 \cdot 10^{-5}$ mol. %) as well as OH^- ions, the content of the latter may attain $2 \cdot 10^{-2}$ mol. %, according to chemical analysis data. The presence of hydroxyl ions is known to favour the formation of stable color centers both in CsI [2] and in other AHC under irradiation [3]. Many researchers believe that the radiation instability of CsI based scintillators is associated with the presence of CO_3^{2-} impurity (see e.g. [4]). On the other hand, $\text{CsI}(\text{CO}_3)$ crystals are known to be

an effective scintillation material, i.e. the presence of CO_3^{2-} ions results in an enhanced emissive recombination of radiation-induced defects [5]. It remains still unclear what the impurity (carbonate or hydroxyl) stimulates the radiation-induced defect formation. The doubled dopation of crystals by above impurities may cause specific radiation-stimulated processes involving both of them. This work is aimed at the study of radiation-induced defects formation in CsI crystals containing extrinsic CO_3^{2-} and OH^- ions.

CsI crystals grown by Kiropoulos technique in a platinum crucible under inert gas (argon) atmosphere were used in this investigation. The initial special purity grade salt (total carbon content $8 \cdot 10^{-3}$ mol. %) was dehydrated previously in a vacuum drying chamber at 200°C and then in the growth furnace at 400°C . Crystals were not doped intentionally by any additives; nevertheless, the grown crystals contained mo-

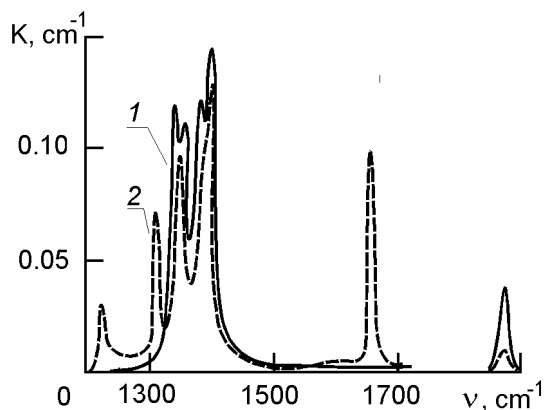


Fig. 1. IR absorption spectra of CsI(OH,CO₃) crystals before (1) and after (2) γ -irradiation.

lecular CO₃²⁻ and OH⁻ anions due to residual moisture present in the raw material and to some oxygen amount in the growth atmosphere as well as to the hydroxyl carbonization reaction occurring in the melt [8]. Samples of 30 mm in dia. and 60 mm in height cut out of grown crystals were irradiated by a ⁶⁰Co source of γ -radiation at the dose of 10 Krad. The presence of above-mentioned oxygen-containing impurities was controlled by IR spectroscopy (using characteristic vibrational spectra of molecular anions) as well as by chemical analysis. In what follows, the impurity content values are presented in molar per cent.

According to published data, the main vibrations of CO₃²⁻ ions in the CsI crystal matrix are positioned in 880 (ν_2), 1350–1440 (ν_3) and 665–675 cm⁻¹ (ν_4) [5], the characteristic vibration frequency for OH⁻ ion is 3576 cm⁻¹ [3].

Analysis of IR spectra has shown that CO₃²⁻ ion absorption bands are typical for practically all crystals grown; moreover, OH⁻ ion absorption is revealed in some cases. In Fig. 1, the IR spectrum of a crystal containing 2·10⁻³ % of CO₃ and 2·10⁻² of OH is shown.

As is seen from Fig. 1, intensity of band corresponding to the most intense (ν_3) vibration of carbonate ion exceeds significantly that of hydroxyl ion thus evidencing a low oscillator strength of the latter [3]. Perhaps this is just the reason explaining the fact that OH⁻ ions do not revealed as a rule by IR spectroscopy while they are determined reliably by chemical methods.

In electron absorption spectra of CsI crystals containing hydroxyl ions, a characteristic band of OH⁻ ion is present near to 252 nm [3] (see Fig. 2, curve 1).

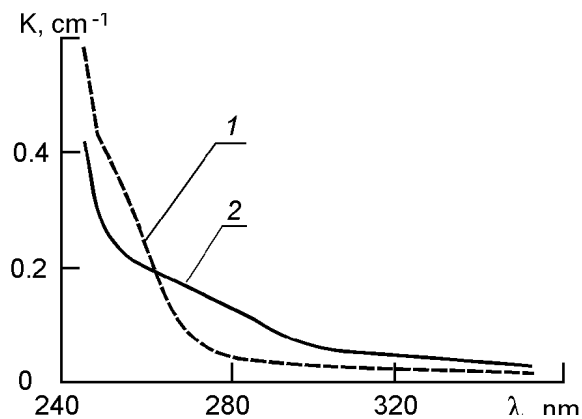


Fig. 2. UV absorption spectra of hydroxyl-doped CsI crystals before irradiation (1) and after irradiation and discoloration in the course of reduction (2).

Irradiation of crystals causes the occurrence of an intense absorption in the region of F and F-aggregate color centers and a hole band near to 460 nm, that is in agreement with [2]. The absorption spectrum of the irradiated crystal is time-variant: F-type center bands and the hole one (460 nm) disappear completely, while an increase of absorption in the 270 nm typical for U centers family absorption is observed at the expense of absorption drop in the OH⁻ band region (Fig. 2, curve 2).

A deterioration of the OH⁻ band is also observed in IR spectra of colored crystals CsI(OH,CO₃), the band deterioration is accompanied by an intensity decrease of bands characteristic for CO₃²⁻ ions (Fig. 1, curve 2). Therewith, a series of new bands is appeared: 593, 663, 745, 830, 947, 1223, 1315, 1679, 3318 cm⁻¹. Positions and intensities ratios of those bands allow to ascribe them to the bicarbonate ion absorption [6]. Similar radiation-chemical transformations occur also in irradiated CsI(CO₃) crystals. Despite of the fact that OH⁻ ion absorption does not manifest itself in IR spectra of those crystals, the formation of bicarbonate ion at the expense of carbonate one is observed in all cases.

To discriminate contributions of surface and volume processes to the radiation-stimulated bicarbonate ion formation, measurements were performed both on samples of different thicknesses (5 and 60 mm) and on those with the surface layer eliminated by post-irradiation polishing. In all cases, the absorption coefficient measured for the most intense band of HCO₃⁻ ions (1679 cm⁻¹) was the same. The coincidence of results obtained

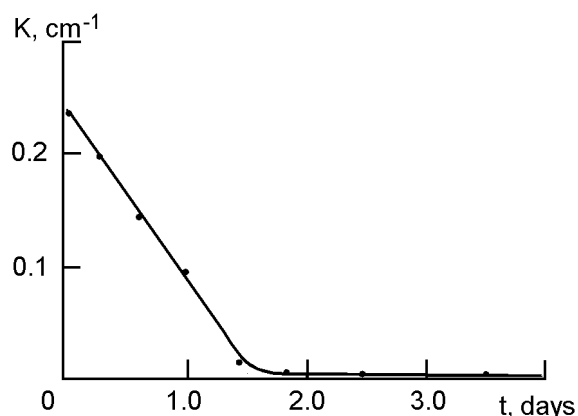
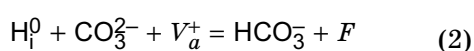
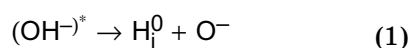


Fig. 3. Absorption coefficient of HCO_3^- ion local vibration 1679 cm^{-1} as a function of the time from the irradiation completion.

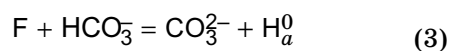
allows to consider the observed effect as that related to the crystal volume.

In contrast to the case of crystals containing bicarbonate *ab initio* [6], HCO_3^- ions arisen due to irradiation are unstable. Their decay and recovery of initial carbonate ion concentration is observed in crystals when stored in the dark. Fig. 3 presents the time dependence of the HCO_3^- absorption decrease, starting from the irradiation completion moment.

Let the possible mechanism of bicarbonate formation be considered. Under irradiation of AHC containing hydroxyl ions, the latter undergo the dissociation. In this case, the following radiation-stimulated reaction become possible:



The reaction (1) is well-known for AHC [3]. The (2) one proposed to explain the observed effect is of a good probability due to a high diffusivity of hydrogen atoms. Similar H_i^0 reactions with CN^- and HS^- in AHC were described in [3]. A specific feature of the reaction (2) is that products formed are separated spatially, since, in Csl at room temperature, the compensation of the excess CO_3^{2-} ion charge by anionic vacancy occurs as a rule in locally [7]. Diffusion of F centers in the course of crystal storage results in bicarbonate ion decay:



resulting in the formation of carbonate ion and hydrogen atom in the anionic vacancy (U_3 center).

According to the mechanism proposed, the HCO_3^- ion decay in irradiated crystals is limited not by electron processes but by ionic ones (diffusion of F centers). It is just the effective transformation of F centers into F-aggregate ones [9] that evidences a rather fast diffusion of F centers in Csl at room temperature.

The scheme proposed explains the mechanism of stable radiation-induced defects formation: since HCO_3^- ion is decayed when affected by F center, it can be considered as an analogue of hole center. The reasonability of that analogy can be checked studying the additive coloration of the crystal. Special experiments have confirmed that the HCO_3^- formation takes place only under Csl coloration in halogene vapor only but not in that of the metal.

The fact that all irradiated $\text{Csl}(\text{CO}_3)$ crystals exhibited HCO_3^- formation at the expense of CO_3^{2-} ion concentration allows to propose the use of the effect revealed as a test for the presence of OH^- ions in the matrix and for a rough estimation of their amount. At the same irradiation dose, intensity of bicarbonate ion absorption for crystals grown in platinum crucibles is higher than for those obtained in quartz ampoules. This can be explained by that quartz favours a substantial decrease of the hydroxyl ion concentration in the crystal due to formation of silicates insoluble in the Csl melt; this process involves oxygen-containing impurities [8].

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Утворення радіаційних дефектів у кристалах CsI, що містять іони гідроксилу і карбонату

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Під впливом іонізуючого випромінювання в кристалах CsI(CO₃), окрім центрів забарвлення, утворюються HCO₃⁻ іони; збільшення їх кількості супроводжується зменшенням концентрації іонів CO₃²⁻. Цей ефект має об'ємний характер і обумовлений присутністю гідроксильних іонів у кристалах. Запропоновано механізм утворення HCO₃⁻ іонів при опроміненні та їх руйнування в процесі зберігання кристалів.