Role of sodium in radiation defect formation in CsI crystals

L.N. Trefilova *, A.M. Kudin, L.V. Kovaleva, T.A. Charkina, A.I. Mitichkin,
L.E. Belenko

Scientific-Research Department of Alkali-Halide Crystals, STC, Institute for Single Crystals, National Academy of Sciences of Ukraine, Lenin Avenue 60, 61001 Kharkov, Ukraine

Abstract

Radiation defect formation processes in large dimension CsI crystal scintillators have been considered. It is shown that F-centers are efficiently formed in crystals doped with CO_3^{2-} and OH^- ions. Sodium ions harden CsI crystals against radio-chemical reactions of F-centers, and HCO_3^- ion formation. The use of sodium as a co-activator to increase the radiation stability of CsI(Tl) crystals has been considered. ⓒ 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Scintillation crystal; Color center; Radiation-induced defect; Absorption spectrum

1. Introduction

The radiation stability of CsI scintillators is determined by impurities within the crystal (Antoniv et al., 1975). Color centers are efficiently formed in crystals doped with CO_3^{2-} and OH^- ions. As was shown earlier (Grinyov et al., 1997), F-centers and HCO_3^- ions are formed in CsI crystals with these impurities after irradiation. It could be assumed that similar defects will be observed in irradiated CsI(Na) and CsI(Tl) scintillators, if there also contain noticeable amounts of CO_3^{2-} and OH^-. However, experiments show that CsI(Na) crystals with an optimal content of the activator Na are practically not colored under γ-irradiation, whereas color centers appear in CsI(Tl) crystals not only under the influence of ionizing irradiation, but also due to exposure to daylight. It turned out that additional doping of the crystals with sodium increases their radiation stability significantly. This article is devoted to examining the function of sodium ions in radiation defect formation processes in CsI scintillators.

* Corresponding author. Fax: +380-572-32-10-82.
E-mail address: shpil@isc.kharkov.com (L.N. Trefilova).

2. Experimental details

CsI, CsI(Na), CsI(Tl) crystals were studied. The concentration of activating cations and oxygen-containing anions were determined by chemical and optical methods. Absorption spectra in the UV-, IR- and visible regions were measured at room temperature using Hitachi-330 and UR-20 spectrophotometers. Radiation damage of CsI(Tl) crystals was judged by the changes in the optical density of $\varnothing 30$ mm $\times 60$ mm samples at a wavelength of 550 nm, measured using the appliance for SF-4 spectrophotometer according to the method described by Toporets (1961). Irradiation of the crystals was performed using a γ-source (^{60}Co) and daylight.

3. Radiation defect formation in CsI

It is known that non-activated CsI crystals are stable to ionizing irradiation. CsI crystals irradiated up to a dose of 10^5 Gy are not colored (Avakian and Smakula, 1960). F–H pairs formed during the irradiation process, recombine in approximately 1 μs (Yakovlev, 1984).

Fig. 1. Absorption spectra of γ-irradiated CsI crystals. Concentrations (mol%): CO_3^{2-}—5×10^{-4}, OH^-—2×10^{-2}; radiation dose: 2 (1), 10 (2), 100 (3), 5.5×10^3 Gy (4).
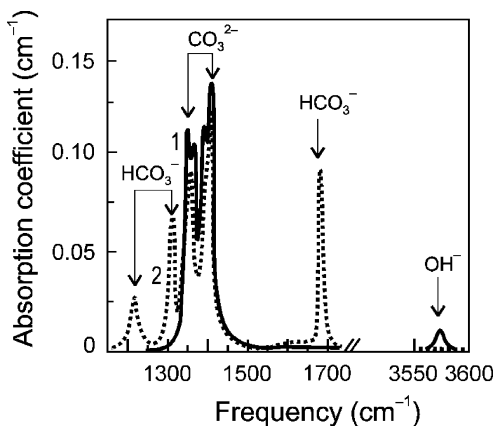

Fig. 2. IR-absorption spectra of CsI crystal before (1) and after (2) γ-irradiation with a dose of 100 Gy.

Fig. 1 shows the optical absorption spectra of CsI crystal doped with CO_3^{2-} and OH^- ions after γ-irradiation within the dose range 2–5.5×10^3 Gy. It is obvious that F-band absorption is revealed in the spectrum at 790 nm even after a low radiation dose, 2 Gy. With an increase in the radiation dose the intensity of the F-band becomes increases, therewith, absorption due to F-aggregate centers appears (X-band at 1150 nm). Absorption bands due to hole trapping centers are not observed. They are similar to absorption spectra of CsI crystals colored electrolytically by electrons or additively in vapors of alkali metal. It can be assumed that F-centers are specifically stabilized.

An intensive splited v_3-band of CO_3^{2-} ions in the region of 1350–1410 cm^{-1} and a weak band of OH^--ions in the region of 3576 cm^{-1} are seen in the IR-spectrum of the CsI crystal (Fig. 2). During irradiation the break-down of the OH^--band is accompanied by an intensity decrease of the
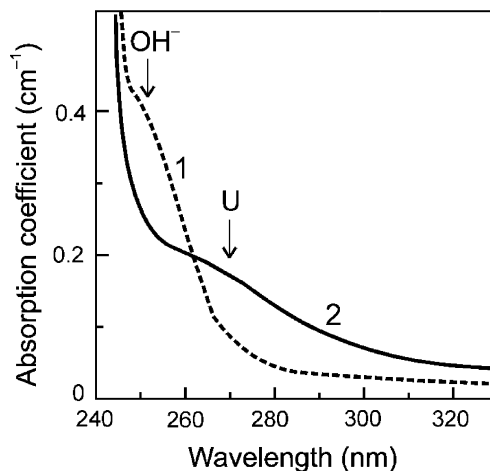

Fig. 3. UV absorption spectra of hydroxyl and carbonate-doped CsI crystals before irradiation (1) and after irradiation and discoloration (2).

CO_3^{2-} ion bands and the appearance of new bands at 1223, 1315, 1679 cm^{-1}. The position and the correlation of intensities of these bands allow us to ascribe them to absorption by HCO_3^- ions (Mitichkin et al., 1982). The effect of bicarbonate ions formation is volumetric and appears when the OH^--ion concentration is lower than the sensitivity of IR-spectroscopy method. A similar transformation "carbonate → bicarbonate" can be achieved by annealing the crystals in water and iodine hydrogen vapors without irradiation. In this case, the effect is only observed in the surface layer of the crystal.

The radiation-induced break-down of the carbonate and hydroxyl ions as well as the emergence of bicarbonate ions and F-centers can be explained by the decay of the excited ion (OH^-) with the formation of an oxygen ion in the anionic site (O_a^-) and a hydrogen ion in the interstitial site (H_i^0). The H_i^0 diffusion can lead to the interaction between H_i^0 and (CO_3^{2-}–V_a^+) dipole. As a result of it CO_3^{2-} ion will be transformed into HCO_3^-, and the anionic vacancy (V_a^+) into F-center:

$$(OH^-)^* \rightarrow O_a^- + H_i^0, \tag{1}$$

$$H_i^0 + CO_3^{2-} + V_a^+ \rightarrow HCO_3^- + F. \tag{2}$$
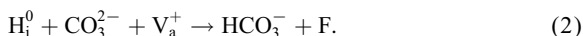
Reaction (1) is well-known. Reaction (2) is proposed to explain the observed effect and is probable due to the high diffusive ability of the hydrogen atom. This scheme explains the mechanism of stable electron color centers formation. The complementary to the F-center is the stable bicarbonate ion in the CsI lattice.

Carbonate ions are the discharge for interstitial hydrogen atoms migrating in crystal. After the formation of F-centers stabilized with bicarbonate ions (reaction 2) some of the hydrogen atoms can also interact with them creating H_a^- ions

(U-centers). These are revealed in the absorption spectrum of irradiated CsI crystal (Fig. 3). The obtained results differ from that published in the literature (Morato and Luty, 1980). According to these results U-bands are not observed in the absorption spectra of alkali halide crystals containing only OH^- ions irradiated at room temperature. This difference is connected with the presence of CO_3^{2-} ions in CsI lattice, which significantly influences the transformation of radiation defects in crystals containing hydroxyl ions.

4. Role of Na activator in radiation-chemical coloration of CsI(Na) crystals

According to Panova et al. (1989) the irradiation of CsI(Na) crystals with a dose from 0.1–10 Gy does not lead to stable F-centers or sodium colloid formation if the activator content is lower than the limit dissolubility of NaI in CsI (9×10^{-3}%). Crystals with concentrations of oxygen-containing impurities lower than the sensitivity of the IR-spectroscopy method ($CO_3^{2-} < 10^{-5}$%, $OH^- < 1 \times 10^{-3}$%) were studied by Panova et al. (1989). It was expected that the increase of mentioned impurities content in CsI(Na) will lead to a significant decrease in the radiation stability of the material according to the mechanism stated above. However, experiments did not confirm this expectation.

Fig. 4 shows the absorption spectra of irradiated CsI(Na) and CsI crystals doped with carbonate and hydroxyl ions. OH^- and CO_3^{2-} ions content in both crystals is equal. The F-band in the absorption spectrum of CsI(Na) crystal does not appear after irradiation with the same dose, while it is seen in the absorption spectrum of the CsI crystal. From this it is concluded that sodium ions increase the radiation hardness of CsI crystals containing carbonate and hydroxyl ions.
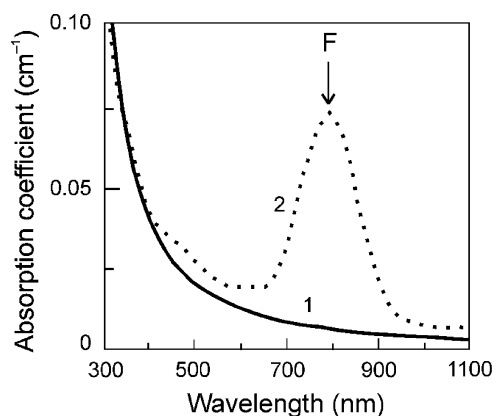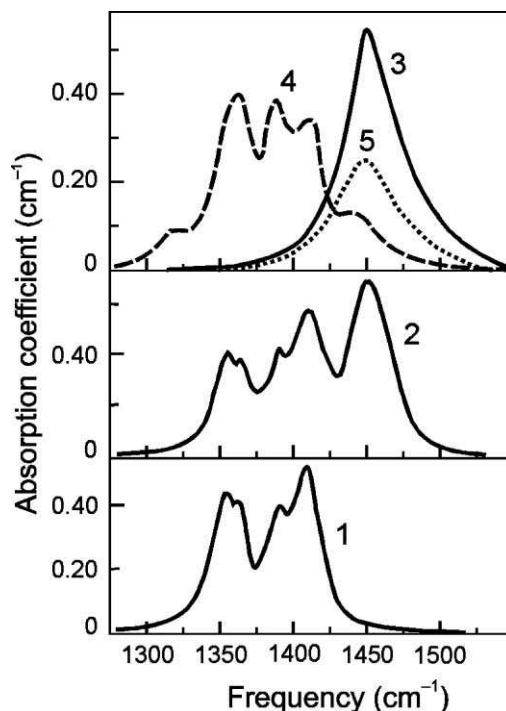

Fig. 5. IR absorption of CO_3^{2-} ions in CsI (1), CsI(Na) (2,3), CsI(Tl) (4) and CsI(Na,Tl) (5) crystals. Concentrations (mol%): CO_3^{2-}—1×10^{-3} (1), 2×10^{-3} (2), 4×10^{-3} (3), 7×10^{-4} (4), 2×10^{-3} (5), Na—1.7×10^{-3} (2), 1×10^{-2} (3), 1×10^{-2} (5), Tl—1×10^{-1} (4,5).

Let us consider the IR-absorption of non-irradiated CsI(Na) crystals shown in Fig. 5 (curve 2, 3) to explain the observed effect. Sodium exerts the greatest influence on the position of the carbonate absorption bands in CsI lattice in the range of the partially symmetrical ν_3-oscillation (curve 1). An additional band with the maximum of 1450 cm^{-1} appears with the increase of sodium content. This band coincides with the ν_3-oscillation of CO_3^{2-} in Na$_2$CO$_3$ monoclinic lattice (Buijs and Schutte, 1961; Zemann, 1957), where four sodium ions are present in the nearest surroundings of carbonate as well as in the face-centered cubic lattice (it includes six nearest-neighbor cations), but the surroundings are distorted by the presence of the anionic vacancy. As it was determined experimentally, if the sodium content is 4–6 times higher than the carbonate content, only one band at 1450 cm^{-1} will remain in the range of ν_3-oscillation (curve 3) this denotes the formation of nNa$^+$–CO_3^{2-} complexes, where n—the number of Na ions in the nearest surroundings of the carbonate ion. We could say that $1 \leqslant n \leqslant 6$. We need to carry out additional investigations to determine the value of n. In the case Na$^+$–CO_3^{2-}–Na$^+$ quasi-molecule being situated on cationic and anionic sites without compensating vacancy is formed, then $n = 2$.

It should be pointed out that the intensity of the carbonate bands in CsI(Na) crystals after irradiation does not

Fig. 4. Absorption spectra of γ-irradiated CsI(Na) (1) and CsI (2) crystals. Concentrations (mol%): CO_3^{2-}—1×10^{-3} (1,2), OH^-—9×10^{-3} (1,2), Na$^+$—9×10^{-3} (1).

change and no bands appear which conform to bicarbonate absorption. Sodium ions suppress the course of the radiation-chemical reaction (2). A similar effect is observed in NaI crystals containing OH^- and CO_3^{2-}. The F-band does not appear in the absorption spectra after irradiation as well as the bicarbonate ions bands in the oscillation spectra. Thus, an efficient channel of stable F-centers formation in CsI(Na) is not realized.

5. Photo- and radio-chemical coloration of CsI(Tl) crystal

The radiation damage of CsI(Tl) crystals in comparison with CsI crystals essentially depends on the dopant. The presence of carbonate and hydroxyl ions in CsI(Tl) leads to the efficient formation of color centers not only under the influence of ionizing irradiation, but also due to the daylight.

Let us consider absorption peculiarities of CO_3^{2-} ions in CsI(Tl) crystals. Fig. 5 (curve 4) and Fig. 6 (curve 1) show absorption spectrum of carbonate ions in the v_3-oscillation region. It is obvious, that additional bands with maxima at 1320 and 1440 cm^{-1} are revealed along with bands at 1350 and 1410 cm^{-1} typical of CO_3^{2-} ions in CsI crystals. The appearance of these bands is probably conditioned by the disturbing influence of Tl^+ ions. With an increase in thallium content the intensity of additional bands becomes higher. If thallium content is an order of magnitude greater than that of carbonate, the bands in the range of 1350–1410 cm^{-1} always appear, unlike CsI(Na) crystals. It should be supposed, that a considerable fraction of the CO_3^{2-} ions does not form complexes with the activator.

The intensity decrease of the CO_3^{2-} bands and the appearance of bands due to HCO_3^- ions are observed in the IR-absorption spectra of carbonate under the influence of
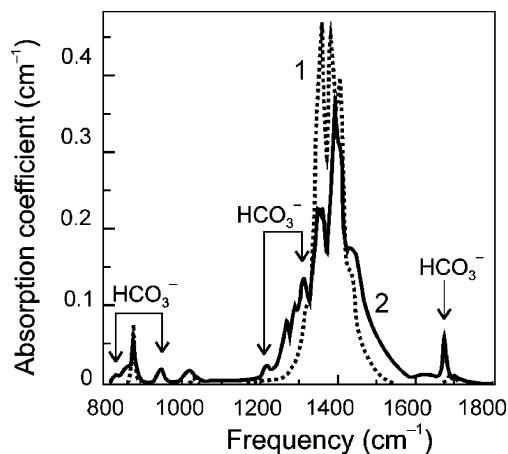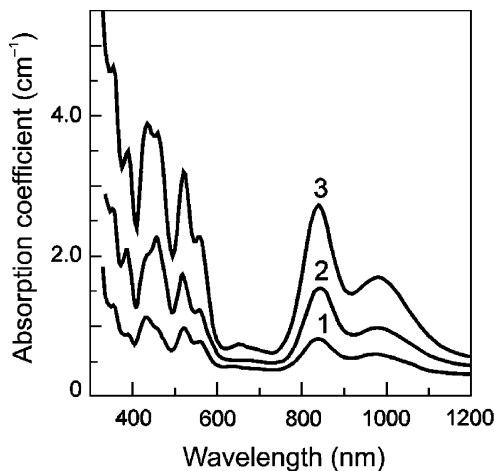

Fig. 7. Absorption spectra of CsI(Tl) crystals colored under irradiation (^{60}Co, 10^3 Gy) (1,3) and due to the daylight (2). Concentration (mol%): Tl—9×10^{-2}, CO_3^{2-}—7×10^{-4}, OH^-—6×10^{-3}.

ionizing irradiation or due to exposure to daylight (Fig. 6, curve 2). HCO_3^- ions formation shows that reaction (2) runs under irradiation in CsI(Tl) as well as in non-activated CsI crystals. F-centers are formed as a result of this reaction. However, no band at 790 nm appears in the absorption spectrum. Bands with maxima at 355, 390, 430, 470, 520, 560, 840 and 975 nm are observed instead of absorption bands due to F- and F-aggregate centers (Fig. 7). F-centers in CsI are rather mobile, therefore the absence of the band at 790 nm can be explained by their transformations into F_A-centers via diffusion processes. However, according to published data (Mednikov and Shtan'ko, 1978) the bands stated above are connected with the absorption of trapped-electron centers due to thallium dimers—Tl_2^+ and Tl_2^0. The argument for such a conclusion is the C_4 symmetry of these centers. Tl_2^+ and Tl_2^0 trapped-electron centers answers the requirements since its position is along the cation–cation direction.

The results mentioned in the article can be explained by the following. Stable (at room temperature) trapped-electron color centers (at 430, 520, 560, 840 and 975 nm) have F_{AA} structure of (Tl^+–Tl^+–F)-type. The properties of such color centers conform to published data and the results of our work, namely: (i) the nature of color center is activating (due to thallium dimers); (ii) the color center is due to trapped electrons (of F-type) and will be formed in CsI(Tl) crystals doped with CO_3^{2-} and OH^- by exposure to daylight; (iii) the color center is optically active and optical ionization of the color center is possible in the band at 430 nm and in the short-wave region of the spectrum with the next electron capture by free dimers with Tl_2^+ center formation (at 390, 470 nm); (iv) the thallium dimer has an axis of C_4 symmetry—an F-center close by a dimer can take four equivalent positions, i.e. the absorption and the
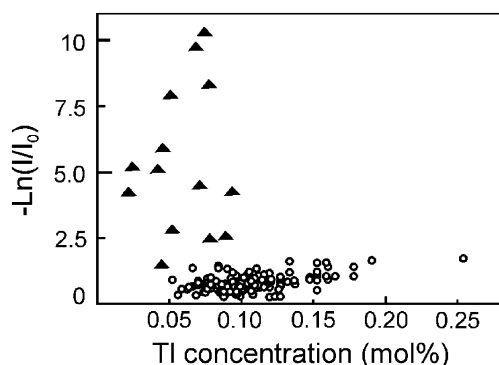

Fig. 6. IR-absorption spectra of CsI(Tl) crystal before (1) and after daylight irradiation (2). Concentration (mol%): Tl—9×10^{-2}, CO_3^{2-}—7×10^{-4}, OH^-—6×10^{-3}.

Fig. 8. The dependence of optical density increase of irradiated CsI(Tl) (▲) and CsI(Tl,Na) (◯) crystals on the wavelength 550 nm (5.5×10^3 Gy) on thallium concentration. The content of CO_3^{2-} ions is (10^{-5}–1×10^{-3}) mol%.

luminescence of the F_{AA} center are characterized by a high degree of polarization; and (v) C_4 symmetry can be observed for F_{AA} depending on the experimental circumstances.

Thus, it is assumed that the nature of coloration in CsI(Tl) crystal is similar to that in CsI crystals. F_{AA} centers are responsible for absorption spectra at 430, 520, 560, 840 and 975 nm. The F-like nature of the band at 840 nm as well as the F-band is verified by its shift to the short-wave region with decreasing temperature. Although the arguments for this model are not direct proofs, there are no known experimental results which contradict this point of view.

6. Use of sodium as co-activator in CsI(Tl) crystal

If CsI(Tl) crystals are additionally doped with sodium ions, the bands typical for ($n\mathrm{Na}^+$–CO_3^{2-}–V_a) complexes in CsI(Na) are observed in the IR-spectra (Fig. 5, curve 5). CsI(Tl,Na) crystals containing OH^- and CO_3^{2-} are photostable. They are colored to a lesser extent under γ-irradiation in comparison with similary doped CsI(Tl) crystals. As is seen in Fig. 8, the increase of the optical density of irradiated CsI(Tl,Na) crystals is proportional to the Tl-content and does not depend on the CO_3^{2-}-content.

Thus, Na^+ ions lead to radiation hardening of CsI crystals by suppressing the radiation-induced formation of F-centers and bicarbonate ions.

It can be supposed that the scintillation properties of double doped CsI(Tl,Na) crystals will differ from standard CsI(Tl) characteristics (Schotanus et al., 1990). The luminescence spectrum of CsI(Tl) consists of two activator luminescence bands at 405 and 550 nm with the ratio of intensities $1:5$. Na ions are also the centers of the luminescence with the maximum at 420 nm. By reason of this the intensity of the luminescence in CsI(Tl,Na) in the range of 420 nm will exceed the same one at 550 nm, if the thallium content is not high ($< 10^{-2}$%). The higher is

the thallium content, the less is the importance of the band at 420 nm for total spectrum. As a result of the present experiments it was determined that the spectral composition of the luminescence, light yield, decay time of double doped CsI(Tl,Na) crystals correspond to those characteristics of CsI(Tl) crystal by the thallium concentration not lower than 9×10^{-2} mol%.

7. Conclusions

1. Stable F-center formation in CsI and CsI(Tl) crystals is connected with radiation–chemical transformations of CO_3^{2-} and OH^- ions into the HCO_3^- ion.

2. Sodium suppresses the formation of HCO_3^- ions and F-centers in CsI(Na) crystals and forms ($n\mathrm{Na}^+$–CO_3^{2-}–V_a^+) complexes.

3. A model and a mechanism of activator color centers responsible for absorption bands at 430, 520, 560, 840, 975 nm have been proposed. According to these F-center diffusion to thallium dimers leads to color center formation of the F_{AA} type.

4. ($n\mathrm{Na}^+$–CO_3^{2-}–V_a^+) complexes in CsI(Tl,Na) as well as in CsI(Na) suppress F-center formation, and thus the radiation stability of CsI(Tl,Na) crystals increases.

5. The presence of Na^+ as a co-activator in CsI(Tl) crystal does not lead to changes in the main characteristics of the scintillator, if the activator content is higher than 9×10^{-2} mol%Tl.

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