

Radiation-induced processes and defects in purified CsI crystals

I.Garapyn, B.Pavlyk, B.Tsybulyak

Sensors Research Laboratory, I.Franko National Lviv University,
107 Tarnavsky St., 79017 Lviv, Ukraine

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Defect formation processes under γ-ray irradiation (up to doses of 10^4–$5\cdot10^6$ Gy) in purified CsI crystals have been studied using the electric conductivity measurements, optical absorption spectra and the thermostimulated depolarization currents. The processes of accumulation and destruction of defects have been found to run in different manners depending on the γ-irradiation dose. Starting from a dose of 10^5 Gy, the γ-irradiation affects appreciably the defect structure of the purified cesium iodide crystals.

Исследованы процессы дефектообразования под воздействием γ-облучения (дозами 10^4–$5\cdot10^6$ Гр) в очищенных кристаллах иодистого цезия с использованием методов электропроводности, оптической спектроскопии и токов термостимулированной деполяризации. Установлен различный характер процессов накопления и распада дефектов в зависимости от дозы облучения. γ-Облучение заметно влияет на дефектную структуру очищенных кристаллов иодистого цезия, начиная с дозы 10^5 Гр.

Color centers formation and radiation resistance of doped and undoped CsI scintillators depends to a great extent on the material purity and perfection [1, 2]. The presence of oxygen containing impurities affects significantly the main characteristics of the scintillators, storage coatings in memory devices, etc. [3, 4]. The method of cesium iodide single crystal growth with low content of oxygen-containing impurities has been proposed by us in [5]. The effect of raw material purification using different preparation methods has been studied in [6]. The conductivity, ionic thermocurrent and IR-spectra study allowed to conclude that the most effective purification is achieved for the cesium iodide crystal grown by the Stockbarger method when the melt is processed under vacuum in the presence of carbon sorbent.

The radiation resistance of CsI is known to be rather high [2–4, 7]. It is claimed [3] that CsI crystals undergo irradiation with doses up to 10^3 Gy without any noticeable damage. Hence, it is desirable to investigate the γ-ray damage in the purified CsI crystals under higher irradiation doses. This work is aimed at the study of defect formation and evolution in the purified CsI crystals. The electric conductivity and thermostimulated depolarization currents (TSDC) in γ-irradiated (up to doses $5\cdot10^6$ Gy) cesium iodide crystals with lowered oxygen-containing impurity content are considered.

The CsI single crystals were grown by the Stockbarger method from raw material purified by melt holding under vacuum in the presence of carbon sorbent [6]. The samples were γ-irradiated at room temperature using a ^{60}Co source at the dose rate 4000 R/s. The applied doses were 10^4 to $5\cdot10^6$ Gy. Temperature dependence of conductivity (σ) was measured in the range 300–700 K. In the crystals, TSDC and electrical conductivity measurements were performed in the same way as described elsewhere [6, 8]. For electric conductivity measurements, the samples of $4\times4\times8$ mm^3 size were used. For TSDC investigation, the samples were shaped as plates of 10×10×1 mm^3 size. Polarization was done at T_{pol} = 295 K and 373 K, polarization voltage (E_{pol} = 600 V) was applied for τ_{pol} = 20 min. The samples were heated from 100 to 450 K at a rate of 7 K/min. All measurements were carried out in vacuum about 10^{-2} Pa.

Free current carriers in irradiated crystals may include both ionic defects (vacancies, interstitial ions) and electron-hole pairs being accumulated during the excitation in traps of various origins. In the first case, the post-irradiation variation of conductivity can provide information concerning the formation and accumulation mechanisms of defects in the crystal ionic matrix. In the second case, we obtain information on the process of electron exchange (in terms of the band model of the crystal) between the bands and the local levels in the range of forbidden states. Studying the basic regularities of electron transport allows to reveal their connection with the processes of radiation-induced defect stabilization. Fig. 1 exhibits the results of thermally stimulated (TS) electric conductivity variations in CsI γ-irradiated to various doses. From this Figure, it is seen that the conductivity of γ-irradiated crystals at 300 K does not change with respect to that of unirradiated crystal. However, the heating of the irradiated samples stimulates ion-vacancy and electron-hole processes which define the conductivity. The TS conductivity increase of γ-irradiated crystals is observed in the temperature range 330–480 K, but the relative value of this increase is not proportional to dose value. The extent of the range where the TS conductivity increase of irradiated crystals takes place is different: 330–420 K for curve *2* (10^4 Gy), 300–430 K for curve 3 (10^5 Gy), 300–450 K for curve 4 (10^6 Gy). The effect of radiation-induced conductivity increase remains in the above mentioned temperature ranges, being defined in each particular case by dose value.

At 330 K, the conductivity of a sample γ-irradiated with a dose 10^4 Gy (Fig. 1, curve *2*) is one order higher as compared to the unirradiated and remains unchanged up to 420 K. Above this temperature, the curves lnσ ($10^3/T$, K^{-1}) for the irradiated and unirradiated crystals practically coincide, evidencing the annealing of radiation-induced defects. Considering the curves *3*, *4*

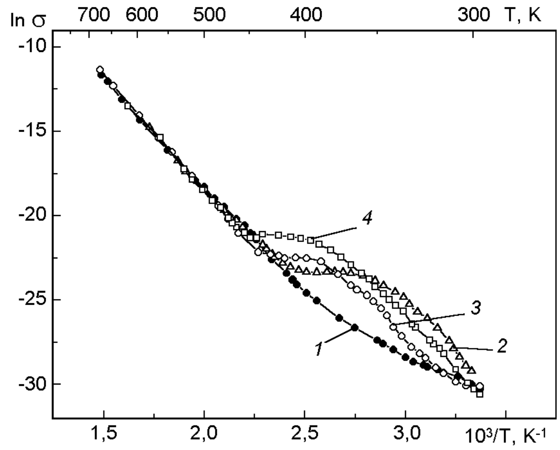

Fig. 1. Conductivity of γ-irradiated cesium iodide vs reciprocal absolute temperature: Initial (*1*), $1\cdot10^4$ Gy (*2*), $1\cdot10^5$ Gy (*3*), $1\cdot10^6$ Gy (*4*).

in Fig. 1, we can conclude that for samples irradiated to doses 10^5, 10^6 Gy, this process (annealing) is finished at 430 and 450 K, respectively. It is to note the plateaus within temperature intervals of 360–420 K (curve *2*), 390–430 K (curve *3*), and 400–450 K (curve *4*) in the conductivity curves of irradiated crystals. Within these temperature intervals, the value of conductivity and, hence, the number of majority current carriers remains constant.

The thermostimulated variation of conductivity in γ-irradiated crystals can be explained as follows. The heating of irradiated specimens stimulates the migration of radiation-induced defects and results in their annealing accompanied by recombination processes. Moreover, the thermally induced decay of various type color centers and their annealing is accompanied by a variety of electron-hole, excitonic, and ionic processes. Thus, the character of the temperature dependence of conductivity is defined by releasing of vacancies when electron and hole centers become thermally decayed, i.e. by the intensity of recombination processes.

The color center formation is evidenced by the optical absorption spectra of the irradiated crystals. The typical bands are found to appear in only at a dose of $5\cdot10^5$ Gy (Fig. 2, curve *1*). This is, in particular, a band in the range of 300–480 nm, which corresponds to the optical transition of I_3^--centers. The latter are unstable [9], are excited under irradiation and may dissociate intensively into H-, V_K-, V_F-centers. As the irradiation dose increases to 10^6 Gy and above, the optical spectroscopy data (Fig. 2,

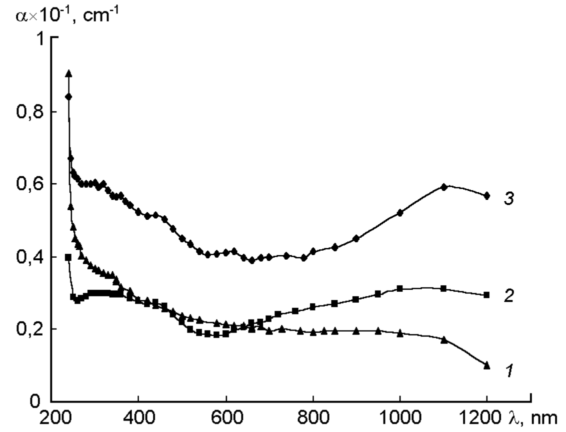

Fig. 2. Optical absorption spectra of cesium iodide γ-irradiated with doses: $5\cdot10^5$ Gy (*1*), $1\cdot10^6$ Gy (*2*), $5\cdot10^6$ Gy (*3*).

curves *2*, *3*) show that F-centers (~780 nm) and their aggregates (~1100 nm) are formed, thus resulting in a reduced concentration of free anion vacancies and, correspondingly, in a decreased radiation-induced σ in the range 300–450 K (Fig. 1, curve *4*). At a dose of $5\cdot10^6$ Gy, the efficiency of defect formation increases, which is evidenced by an increased intensity of the absorption bands (Fig. 2, curve *3*). A significant formation of both hole I_3^--centers and electron *F*-centers has been detected. The aggregation of the latter causes the appearance of an intense band in IR spectral region (Fig. 2, curve *3*).

The defect structure re-building in CsI crystals exposed to various doses of γ-irradiaton was also studied by TSDC method. This method makes it possible to study the defects causing changes in the conductivity of crystals under investigation. The TSDC spectra of radiation-exposed CsI (Fig. 3, curve *1b*) revealed a broad maximum at 310 K. The intensity of TSDC maximum of the sample γ-irradiated at a dose of $5\cdot10^5$ Gy is raised by more than two orders with respect to the similar maximum for the unirradiated crystal (Fig. 3, curve *1a*) and indicates a sharp increase of defect concentration. The intensity of above-mentioned maximum decreases twice for 10^6 Gy dose. Since this maximum is caused by migration processes of free vacancies in CsI [10], this fact testifies for re-building of the defect structure under irradiation. The analysis of TSDC spectra and the data obtained at varying polarization conditions (E_{pol}, τ_{pol}, T_{pol}) allowed to conclude that the

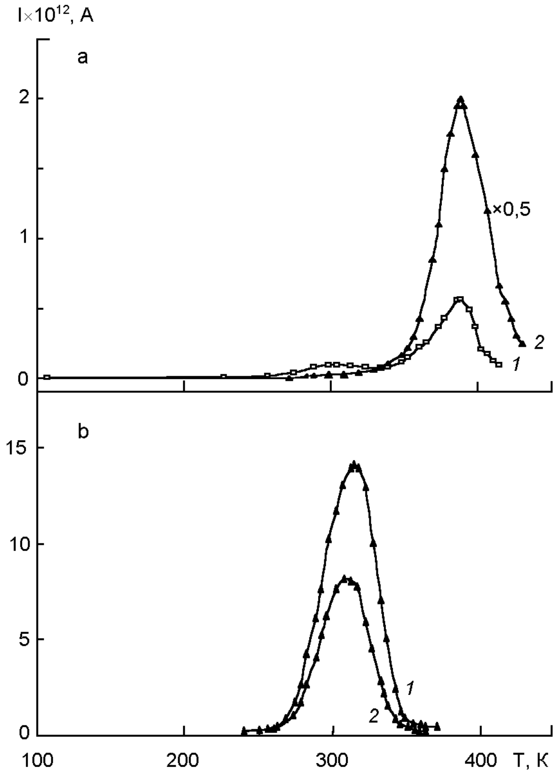

Fig. 3. TSDC spectra of CsI: unirradiated (a): T_{pol} = 295 K (*1*), T_{pol} = 375 K (*2*); γ-irradiated to various doses (b) $-5\cdot10^5$ Gy (*1*), $1\cdot10^6$ Gy (*2*); T_{pol} = 295 K.

revealed relaxation processes in γ-irradiated CsI crystals are caused by migration and redistribution of volume charge. The shape of curves and calculated activation energy values evidence the contribution from both cationic and anionic vacancies into these processes. The activation energy value (E_a = 0.74 eV) for CsI irradiated by $5\cdot10^5$ Gy (Fig. 3, curve *1b*) is sufficient for migration of both anionic (0.32 eV), and cationic (0.56 eV) vacancies. Perhaps the sharp increase of cationic vacancy concentration is caused by thermal decay of I_3^--centers which is accompanied by release of v_c-, because I_3^--centers are unstable in the temperature range 320–340 K [9]. The intense ITC maxima become apparent exactly at this temperature.

The sharp intensity decrease of TSDC maxima is observed for cesium iodide γ-irradiated at a dose of 10^6 Gy (Fig. 3, curve *2b*) and can be explained both by recombination processes and aggregation of *F*-centers. The calculated activation energy of corresponding relaxation processes is 0.59 eV. As the deterioration of radiation resistance is defined by the formation of color centers and their aggregates, we believe that γ-irradiation affects appreciably the defect structure of the purified cesium iodide crystals starting from a dose of 10^5 Gy.

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References

1. I.Garapyn, I.Hud, B.Pavlyk, *Ukr.Fiz.Zh.*, **51**, 587 (2006).
2. M.Nikl, *Phys.Stat.Sol.(a)*, **178**, 595 (2000).
3. M.Globus, B.Grinyov, Inorganic Scintillators, Acta, Kharkov (2000) [in Russian].
4. L.N.Trefilova, A.M.Kudin, L.V.Kovaleva et al., *Radiat.Meas.*, **33**, 687 (2001).
5. I.P.Antoniv, I.V.Garapyn, R.I.Didyk, *Rad. Eff. and Def. in Sol.*, **133–134**, 57 (1995).
6. I.Garapyn, I.Hud, B.Pavlyk, *Radiat.Meas.*, **38**, 475 (2004).
7. P.Avakian, A.Smakula, *Phys.Rev.*, **131**, 2007 (1960).
8. Ya.Struk, *Fizich.Elektron.*, **36**, 42 (1989).
9. V.Kolotilin, V.Shtan'ko, *Fiz.Tverd.Tela*, **26**, 236 (1984).
10. I.Hud, B.Pavlyk, Ya.Struk, *Ukr.Fiz.Zh.*, **35**, 362 (1990).

Радіаційно-індуковані процеси та дефекти в очищених кристалах CsI

І.В.Гарапин, Б.В.Павлик, Б.З.Цибуляк

Досліджено процеси дефектоутворення під впливом γ-опромінення (дозами 10^4–$5\cdot10^6$ Гр) в очищених кристалах CsI з використанням вимірювань електропровідності, оптичної спектроскопії та струмів термостимульованої деполяризації. Встановлено, що процеси накопичення та розпаду дефектів протікають по-різному, залежно від дози опромінення. γ-Опромінення помітно впливає на дефектну структуру очищених кристалів йодистого цезію, починаючи з дози 10^5 Гр.