DYNAMICS OF RELAXATION PROCESSES IN γ-IRRADIATED CESIUM IODIDE CRYSTALS DOPED WITH CATION IMPURITIES

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Relaxation processes in γ-irradiated CsI—Cd and CsI—Ba crystals (up to doses of $1\times10^4-5\times10^6$ Gy) have been studied by measuring the electroconductivity (σ) and the ionic thermocurrent (ITC). The process of accumulation and destruction of defects was found to flow differently, depending on the γ-irradiation dose and the type of cation impurity. The creation of dipoles and the increase of σ have been revealed in CsI—Cd single crystals subjected to the irradiation with a dose of 10^5 Gy. At the same time, the irradiation of CsI—Ba crystals resulted in the decrease of σ and the drastic reduction of the concentration of dipoles. Possible mechanisms have been proposed to explain the revealed differences between the relaxation processes running in CsI—Cd and CsI—Ba crystals subjected to various doses of γ-radiation.

1. Introduction

Impurities in crystals substantially affect the electrical, optical, mechanical, and other structurally sensitive properties of materials which are important for their technical applications [1,2]. If the crystals are irradiated, their use is accompanied by the processes of generation of radiation-induced damages in them. These damages are closely connected with the structure and defectness of crystals before their irradiation treatment, because impurities strongly affect both the efficiency of defect generation and the following processes of defect stabilization.

The processes of radiation-induced defect formation in alkaline halide crystals (AHCs) doped with impurities have been described partially in the literature earlier. However, researches were mainly confined to face-centered crystals with the structure of the NaCl type [2—4]. In particular, the authors of work [2] pointed out that impurities of group IIB (Cd^{++}, Zn^{++}, Hg^{++}) behave as effective traps for electrons and reduce their own valent state due to irradiation. They also hinder the processes of formation of F-centers and colloids in the irradiated crystals [3]. The state of aggregation of radiation-induced color centers depends on the availability of impurities in crystals and on the dose of their irradiation.

The wide practical use of activated cesium iodide crystals in sensor and laser devices predetermines the necessity of their research in many directions. In particular, the issue "What type of current carriers is responsible for electrical transport processes in irradiated AHCs?" is a key for understanding the mechanisms of radiation-induced variation of their conductivity. Free current carriers in irradiated AHCs may include both ionic defects (vacancies, interstitial ions) and electron-hole pairs which are accumulated on the excitation in traps of various origins. In the first case, the post-radiation variation of the conductivity can serve as a source of information concerning the mechanisms of creation and accumulation of defects in the ionic matrix of the crystal, which is necessary for studying electron-lattice interactions. In the second case, we obtain information about the processes 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 one to reveal their connection with the processes of radiation-induced defect stabilization. These processes include the electron-hole stage (recharge) which promotes the stabilization of the mobile components of primary matrix defects — interstitial atoms or ions.

The processes of charge transfer and accumulation, and, consequently, all principal electrophysical phenomena in dielectric materials are governed by the parameters of electrically active defects which are present in the medium. Studying the parameters of electrically active defects and the mechanisms of charge relaxation is necessary for forecasting the electrophysical properties of materials and, accordingly, devices on their basis. However, the mechanisms of charge relaxation become essentially complicated if the relaxation of the bulk charge and the dipoles, stimulated by either the availability of impurities in the crystals or the absorbed dose of radiation, take place simultaneously in the insulator.

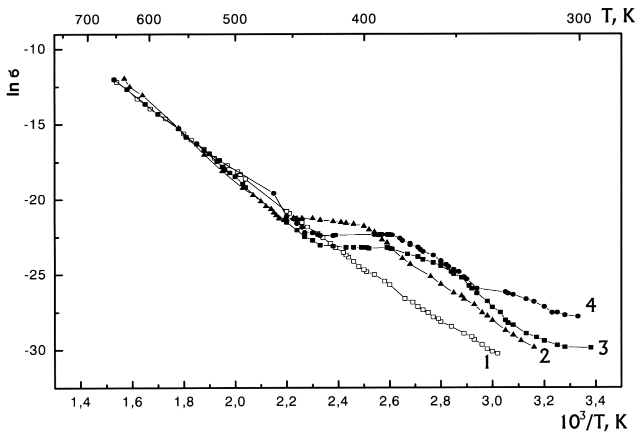

Fig. 1. Temperature dependences of the conductivity of CsI–Cd crystals γ-irradiated to various doses: non-irradiated specimen (*1*), 10^6 (*2*), 10^4 (*3*), and 10^5 Gy (*4*)

This work aimed at studying the dynamics of relaxation processes which run in CsI—Cd and CsI—Ba crystals subjected to various doses of γ-radiation (from 10^4 to 5×10^6 Gy).

2. Experimental Part

2.1. Preparation of specimens

The cadmium- and barium-doped cesium iodide single crystals intended for studying were grown from the melt in air, following the Kiropoulos method (KM), and in evacuated quartz ampoules, following the Stockbarger method (SM). While growing crystals in air, the impurities (Cd^{2+}, Ba^{2+}) were introduced in the form of iodides into the melt during the growth process [5]. On the growing of single crystals in vacuum by the Stockbarger method, the raw material was cleared making use of a coal sorbent and applying the technique developed at our laboratory [5,6]. In this case, impurities were added into the blend. The concentrations of the impurities introduced did not exceed the threshold of their solubility in CsI single crystals [6] and amounted to 0.2 mol.% for cadmium and 0.03 mol.% for barium.

The specimens' dimensions were $4 \times 4 \times 8$ mm^3 for measuring the electroconductivity and $1 \times 10 \times 10$ mm^3 for measuring ITCs.

The specimens were γ-irradiated in preliminary evacuated ampoules (the residual pressure $p = 1.3 \times 10^{-4}$ Pa) by applying a Co^{60} source of radiation (the energy of quanta $E_{h\nu} = 1.25$ MeV) with a power of 4500 R/s.

2.2. Measuring procedures

In order to study the dynamics of relaxation processes in γ-irradiated CsI—Ba and CsI—Cd crystals, we used the methods of measuring the electroconductivity and the ITCs, as well as optical spectroscopy. The ITCs were measured on facilities described in detail in work [7]. The temperature dependence of the radiation-induced electroconductivity of single crystals was studied following the method described in work [8]. Together with the spectra of optical absorption, these methods made it possible to obtain the correlated results of researches of the influence of various doses of γ-radiation on changes in the defect structure of crystals under investigation. The calculations of the activation energy of relaxation processes were carried out following the Garlick—Gibson method (the initial rise method) [9].

3. Results and Discussions

3.1. Electroconductivity researches of CsI—Cd and CsI—Ba single crystals

While studying the features of the defect formation mechanism in single crystals with cation dopants, an important difference between the behaviors of Cd^{2+} and Ba^{2+} impurities in the cesium iodide matrix lattice and, as a consequence, substantial differences in the defect formations and the relaxation processes in CsI—Cd and CsI—Ba crystals have been revealed [10]. The observable differences between the electrophysical properties of these crystals were explained by the availability of impurities taking into account the dimensional and charging effects. The defect formation mechanism is defined by the type of a solid solution, which emerges owing to the introduction of bivalent metals into the cesium iodide lattice.

Differences in the courses of the defect accumulation and destruction were also observed in the irradiated crystals with different cation dopants.

Fig. 1 exhibits the results of researches of thermally stimulated variations of the electroconductivity in CsI—Cd specimens γ-irradiated to various doses. From this figure, one can see that γ-irradiation leads to the enhancement of the conductivity of these crystals. For example, the values of σ for irradiated (curves *2–4*) and non-irradiated (curve *1*) crystals differ by up to two orders of magnitude. The largest growth of σ was observed on irradiating the specimen with a dose of 10^5 Gy (curve *4*).

At higher temperatures (430–460 K), the effect of radiation-induced enhancement of the conductivity disappears, so that the curves $\ln\sigma$ versus $10^3/T$ for the irradiated and non-irradiated crystals practically coincide, which evidences for the annealing of radiation-induced defects. Heating the irradiated specimens stimulates the migration of radiation-induced defects and leads to their annealing accompanied by recombination processes. Moreover, the thermally induced destruction of color centers of various types and their annealing are accompanied by a variety of electron-hole, excitonic, and ionic processes. The character of the temperature dependence of the conductivity is defined by the releasing of vacancies when electron and hole centers become thermally destructed, i.e. by the intensity of recombination processes.

Several peculiar points — additional maxima and points of inflection – can be discerned in the curve of the temperature dependence of $\ln\sigma$. The availability of such points is determined by the sensitivity of the crystal to the irradiation dose. The complicated character of the dependence $\ln\sigma = f(10^3/T)$ suggests that each peak corresponds to a certain elementary thermally activated process, which is characterized by a specific value of the activation energy and a specific temperature of the maximum T_m.

We point out the availability of plateaus within the temperature intervals of 380–430 (curve *3*), 380–440 (curve *4*), and 420–460 K (curve *2*) in the conductivity curves of irradiated crystals. Within these temperature intervals, the value of conductivity and, hence, the number of majority current carriers remain constant.

The apparent behavior of the temperature dependence of σ of the crystals is explained by the running of the following processes. The electroconductivity of CsI—Cd crystals that were irradiated at 293 K depends on the irradiation dose and is governed by the availability of electron (F, M, and X) and hole (H, V_2, and V_3) centers which are revealed by optical absorption spectra (Fig. 2). For example, upon irradiating the specimen up to a dose of 5×10^5 Gy (curve *1*), there appear insignificant bands in the range of 260–400 nm, which are stimulated by the formation of the family of hole (V_2 and V_3) color centers (CCs). The radiation-induced formation of these centers is connected, first of all, with the increase of the concentration of cation vacancies V_c^- in CsI single crystals doped with cation impurities. As the irradiation dose increases up to 10^6 Gy, the intensities of these bands grow (curve *2*). At a dose of 5×10^6 Gy (curve *3*), a band caused by the H-centers [11] appears in the range of 420–440 nm, and bands with low intensities are observed in the range of 760–840 nm (F-centers) and

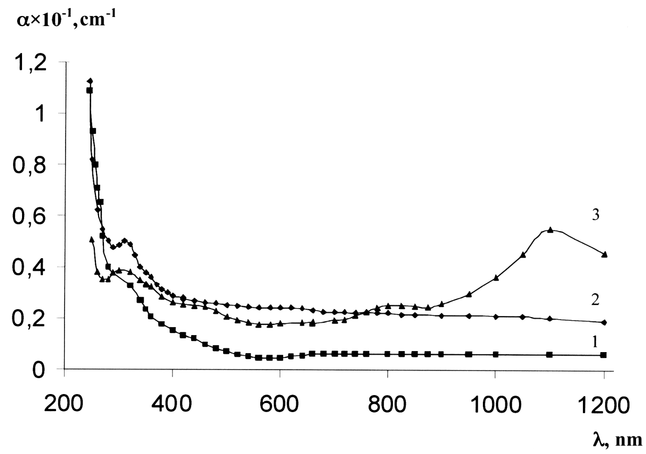

Fig. 2. Optical absorption spectra of CsI–Cd crystals γ-irradiated to various doses: 5×10^5 (*1*), 10^6 (*2*), and 5×10^6 Gy (*3*)

1000–1200 nm (M-centers). The intensities of the latter were lower as compared with those in undoped crystals. Therefore, the availability of cation dopants restrains the process of accumulation of F-centers and their aggregates. Such an influence of bivalent impurities is related to two factors: first, to a reduction of the number of free anion vacancies V_a^+ which are necessary for the electron F-CCs to be created; and, secondly, to the property of Cd^{2+} cations to capture radiation-excited electrons, forming the activator electron CCs Cd^+ and Cd^0. These processes affect the intensity of the formation of self-trapped excitons and the realization of the exciton mechanism of defect formation.

The peculiarities of the thermally stimulated change of the electroconductivity of γ-irradiated CsI—Cd crystals which were described above are caused by the following processes. On irradiating the specimens to $10^5 - 10^6$-Gy doses, the emergence of the family of hole I_3^- color centers was established. In the course of heating, the thermally induced destruction of these centers occurs at temperatures 320—340 K [12] and is accompanied by the releasing of V_c^- vacancies, which stimulates the observed increase of electroconductivity (Fig. 1, curves *3* and *4*). As the irradiation dose increases to 10^6 Gy and further, the optical spectroscopy data (Fig. 2, curves *3* and *4*) testify that F-centers and their aggregates are formed, which leads to a reduction of the concentration of free anion vacancies and, correspondingly, to a reduction of radiation-induced σ in the range 300–380 K (Fig. 1, curve *2*). The activation energy for radiation-induced conductivity in γ-irradiated CsI–Cd crystals is $E_a = 0.88$ eV in the interval 333—385 K.

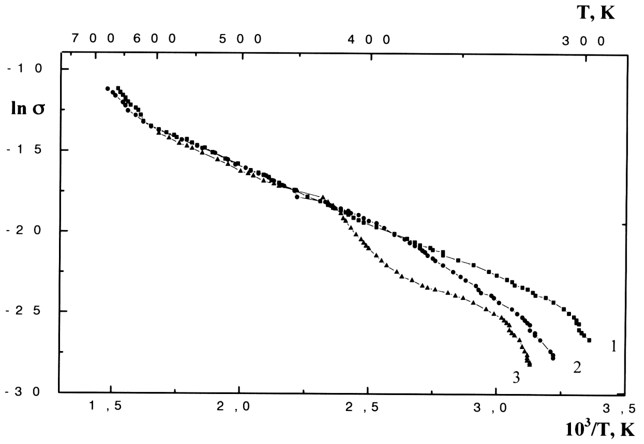

Fig. 3. Temperature dependences of the conductivity of CsI–Ba crystals γ-irradiated to various doses: non-irradiated specimen (*1*), 10^6 (*2*), and 5×10^6 Gy (*3*)

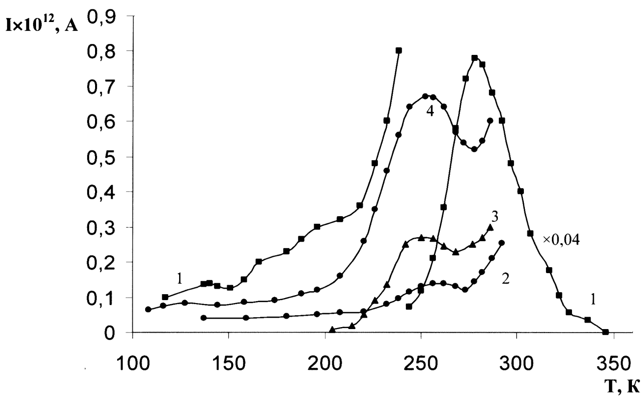

Fig. 4. ITC spectra of CsI–Cd crystals γ-irradiated to various doses: 10^5 (*1*, $T_{\rm pol} = 295$ K), 5×10^5 (*2*), 10^6 (*3*), and 5×10^6 Gy (*4*, $T_{\rm pol} = 203$ K)

In the case of γ-irradiated CsI—Ba crystals (Fig. 3), a different behaviors of the curves of the dependence $\ln \sigma = f(10^3/T)$ were observed. Irradiating the barium-doped crystals brought about a reduction of their conductivity (curves *2* and *3*), and the reduction was more substantial for the higher irradiation dose. The plateaus, which were observed in the conductivity curves of irradiated CsI—Cd crystals (Fig. 1), were absent in this case. The results of our previous researches, quoted in work [13], showed that it is at γ-radiation doses of 10^6 Gy and higher that intensive bands in the range of 260–440 nm (V_2-, V_3-, and H-CCs), 760–840 nm (F-CCs), and 1000–1200 nm (M- and X-CCs) appear in the optical spectra of CsI—Ba crystals. The efficiency of the formation of electron color centers and their aggregates in CsI–Ba crystals is considerably lower in comparison with that in pure cesium iodide crystals; nevertheless, it was higher than that in CsI—Cd crystals. Thus, a reduction of the conductivity of CsI—Ba crystals under high-dose γ-irradiation is caused by a decreasing of the number of anion vacancies owing to the formation of F-CCs and their aggregates.

3.2. ITC studies in CsI—Cd and CsI—Ba single crystals

The transport processes and the reconstruction of a defect structure in CsI—Cd and CsI—Ba crystals subjected to various doses of γ radiation were also studied by the ITC method. This method enabled the defects, which had caused changes in the electroconductivity of crystals under investigation, to be identified.

The effect of the generation of dipoles in CsI—Cd single crystals γ-irradiated to a dose of 10^5 Gy was discovered. The ITC spectra revealed three low-temperature maxima at 140, 170, and 200 K we connect with dipole relaxation and a high-temperature maximum at 290 K (Fig. 4, curve *1*). No low-temperature maxima connected with dipole relaxation were observed in the spectra of non-irradiated CsI—Cd crystals [10]. This means that, under the action of 10^5-Gy irradiation, the formation of Cd^{++}–V_c^- (at 140 K) and Cd^+–V_c^- (at 170 K) dipoles and dipolones of the type V_a^+–V_c^- (at 200 K) may occur at the initial stages.

In order to study dipole relaxation, a specimen has to be polarized at a temperature, at which these dipoles are mobile [14]. Therefore, we carried out researches of γ-irradiated CsI—Cd crystals at the temperature of polarization of 203 K. The increase of the irradiation dose up to $5\times10^5 - 5\times10^6$ Gy (Fig. 4, curves *2*–*4*) caused the destruction of dipoles (the low-temperature maxima are absent from the ITC spectra) and the gradual growth of the high-temperature maximum which became shifted down to 250 K. The detailed analysis of the ITC and optical absorption spectra showed that the physical nature of the high-temperature maximum is connected to the relaxation of the charge in the bulk, namely, to the migration processes of free cation and anion vacancies ($E_a = 0.61$ eV); as it does in the case of non-irradiated crystals. However, the intensity of this maximum after the specimen having been irradiated to a dose of 10^5 Gy was an order of magnitude higher than that in the case of non-irradiated crystals, which evidences for the increase of the free vacancy concentration.

The results obtained obviously correlate well with those of the researches of the electroconductivity of the same crystals. Provided the indicated dose of irradiation, the conductivity increased by two orders of magnitude in the temperature interval from 300 to 380 K. As was pointed out above, this temperature is enough for the thermally stimulated destruction of the family of radiation-induced I_3^--centers and the release of V_c^-. These centers possess low optical stability in AHCs. Being excited, the I_3^--centers may intensively decay following the scheme

$$I_3^-(V_c^- e^+ i_a^0) \longrightarrow \begin{array}{l} H(i_a^0) + V_F(V_c^- e^+), \\ H(i_a^0) + V_K(e^+) + V_c^-, \\ H(i_a^0) + V_c^- V_a^+, \end{array}$$

where H, V_F, and V_K are color centers.

Hence, the growth of the concentration of free cation vacancies V_c^-, due to their release in the course of the destruction of I_3^--centers, brings about the growth of the ITC maximum amplitude at 300 K. The same vacancies contribute to the electroconductivity σ.

We have not observed the aggregation of I_3^--centers, which was observed earlier in face-centered crystals. The authors of work [15] have demonstrated the formation of I_3^--centers in crystals of the KI type. Owing to the high mobility of iodine in the lattice, these centers aggregate readily, forming iodine clusters. Nevertheless, the mobility of iodine obviously decreases in crystals with big cations (Rb, Cs), and the aggregation processes do not occur there, which was confirmed by our researches. Moreover, in doped crystals, I_3^--centers become stabilized, because the impurities act as traps for interstitial iodine atoms and hamper the aggregation process.

No maxima connected to the dipole relaxation within the temperature interval of 100–200 K were revealed in the ITC spectra of γ-irradiated CsI—Ba crystals (Fig. 5). The influence of γ-radiation on these single crystals manifested itself through a drastic reduction of the concentration of dipoles, which had been revealed earlier by analyzing the ITC spectra of non-irradiated crystals [13]; such a reduction may be a result of the dipole destruction or aggregation in the course of irradiation. These results correlate well with the data of works [4,16], where similar results were observed for other AHCs, namely, KBr—M^{2+}, KCl—M^{2+}, and NaCl—M^{2+}. We are inclined to believe that the aggregation of dipoles dominates over their destruction in CsI—Ba crystals under irradiation, because the observed reduction of the conductivity evidences for the lowering of the free vacancy concentration.

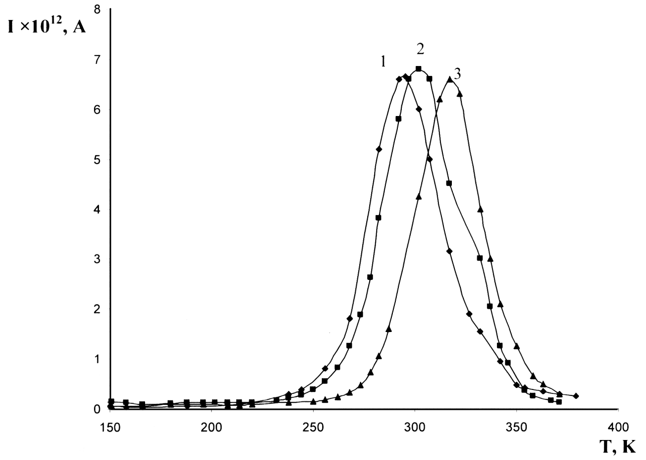

Fig. 5. ITC spectra of CsI–Ba crystals γ-irradiated to various doses: 5×10^5 (*1*), 10^6 (*2*), and 5×10^6 Gy (*3*). $T_{\rm pol} = 295$ K

The intensity of the second maximum, which was revealed near 300 K and is connected with the charge polarization in the bulk, did not vary as the irradiation dose increased (Fig. 5), which also testifies that the changes of the current carrier concentration were minor. Basing on the analysis of the ITC spectra of irradiated CsI—Ba crystals that were obtained under different conditions of the specimen polarization, we may assert that this maximum is generated by the complicated migration processes of anion V_a^+ and cation V_c^- vacancies. The calculated activation energy for the relaxation process concerned amounts to $E_a = 0.46$ eV. Provided that the irradiation doses are not lower than 10^6 Gy, the processes of aggregation of both dipoles and electron color centers prevail in the crystals. The character of changes of the depolarization processes and the electroconductivity in γ-irradiated CsI–Ba crystals is governed by the intensity of the running of two competing processes: generation of color centers and their simultaneous recombination.

4. Conclusions

The researches carried out allowed us to reveal and explain the differences in the course of the relaxation processes in CsI—Cd and CsI—Ba crystals subjected to various doses of γ-radiation within the interval from 10^4 to 5×10^6 Gy.

The observed distinctions of the electrophysical properties of CsI crystals doped with cation impurities, which were revealed and explained by us in the case of non-irradiated crystals, have manifested themselves after the crystal irradiation as well. The emergence of the family of hole I_3^- color centers at γ-irradiation of CsI–Cd crystals to doses higher than 10^4 Gy has been discovered. The thermally induced destruction of these centers is accompanied by the releasing of V_c^- vacancies, which stimulates the increase of both the ITCs and the electroconductivity σ. The generation of dipoles of the types Cd^{++}–V_c^- and Cd^+–V_c^- at the irradiation dose of 10^5 Gy can be explained by the probable occurrence of a Cd^{++} impurity in the matrix lattice at the initial stages of γ-irradiation.

The influence of γ-radiation on CsI—Ba single crystals consisted in a drastic reduction of the dipole concentration as a result of dipole aggregation, and a lowering of the crystal conductivity owing to the decrease of the number of free anion and cation vacancies. Two competing processes — the generation of color centers and their simultaneous recombination — define the character of variations of the depolarization processes and the electroconductivity σ in γ-irradiated CsI—Ba crystals.

Distinctions between the relaxation processes running in CsI—Cd and CsI—Ba crystals subjected to various doses of γ-radiation have been revealed. These distinctions are connected with the peculiarities of the impurity entering into the crystalline matrix lattice and, as a consequence, with different runnings of the processes of defect accumulation and destruction under irradiation. The radiation resistance of the investigated CsI—Ba crystals was higher in comparison with that of CsI–Cd ones.

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ДИНАМІКА РЕЛАКСАЦІЙНИХ ПРОЦЕСІВ В γ-ОПРОМІНЕНИХ КРИСТАЛАХ ЙОДИСТОГО ЦЕЗІЮ, ЛЕГОВАНИХ КАТІОННИМИ ДОМІШКАМИ

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Р е з ю м е

Релаксаційні процеси в γ-опромінених (10^4—$5 \cdot 10^6$ Гр) кристалах CsI—Cd та CsI—Ba досліджено методом електропровідності та струмів термостимульованої деполяризації. Встановлено відмінності у перебігу процесів накопичення та руйнування дефектів у досліджуваних кристалах залежно від дози γ-опромінення та типу катіонної домішки. Виявлено ефект генерації диполів та зростання електропровідності в монокристалах CsI—Cd під дією γ-опромінення дозою 10^5 Гр. Опромінення кристалів CsI—Ba призвело до пониження їхньої електропровідності та різкого зменшення концентрації диполів. Запропоновано механізми, які пояснюють відмінності протікання релаксаційних процесів у кристалах CsI—Cd та CsI—Ba під дією різних доз γ-опромінення.