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Radiation damage of CsI:Eu crystals

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The problems of radiation damage and afterglow nature for CsI:Eu crystal are discussed. It was determined that the luminescence parameters depend on the X-ray irradiation conditions. Irradiation leads to emission suppression at doses less than 100 Gy when the induced absorption was not observed yet. Hole (V_F^- and I_3^-) and activator' color centers formation lead to partial decrease of the intrinsic UV and the activator luminescence, but it is not the dominating process of the radiation-induced phenomenon. The reverse dependences of afterglow and Eu^{2+} luminescence on irradiation dose were detected. Radiation induced luminescence quenching is determined by a modification of the activator centers structure.

В работе обсуждаются проблемы радиационной стойкости и природы послесвечения кристаллов CsI:Eu. Установлено, что параметры свечения зависят от условий рентгеновского воздействия. Облучение приводит к подавлению свечения при дозах менее 100 Gy, когда наведенное поглощение еще не наблюдается. Образование дырочных (V_F^- и I_3^-) и активаторных центров окраски может привести к частичному снижению собственной УФ и активаторной люминесценции, но не является доминирующим процессом радиационно-наведенных явлений. Обнаружена обратная зависимость послесвечения и люминесценции Eu^{2+} ионов от дозы облучения. Радиационно-наведенное тушение люминесценции обусловлено изменением структуры активатор центров.

1. Introduction

Crystals based on cesium iodide (CsI, CsI:Tl, CsI:Na) are widely used in scintillation technique [1]. Application of such scintillators in high energy physics (projects BELLE, BaBar, PiBeta etc.) brings additional requirements to the radiation damage level [1–4]. As a rule, degradation of scintillation properties in such crystals is connected with the appearance of color centers that lower transparency at the emission wavelength. More detailed investigations [5] show that besides the transparency loss there could also occur a deterioration of the luminescence mechanism itself.

Over the last years, it was shown that in some Eu-containing iodides (CaI_2, SrI_2, $CsBa_2I_5$, $CsBa_2Br_5$ etc.) scintillation output attains record high values [2]. As a matter of course there also appeared reports about the studies of CsI:Eu scintillators [6–8].

In CsI:Eu crystals the divalent ion acts as an activator. This kind of doping requires compensation of the excess charge. The structure of the centers in CsI:Eu hasn't been studied well enough yet. In the first place, it was taken to be (Eu^{2+} — v_c^-) [9]. However, recent thorough investigations using EPR, MCDA, ENDOR methods [10] demonstrated a more complex structure of europium ion centers in CsCl lattice. Owing to the complex activator centers structure we can assume that charge carriers capture will lead to changes in the center structure and, as a result, the luminescence will change under the influence of irradiation in this type of crystals. That is why, the aim of the present work is the luminescence study of irradiated CsI:Eu crystals.

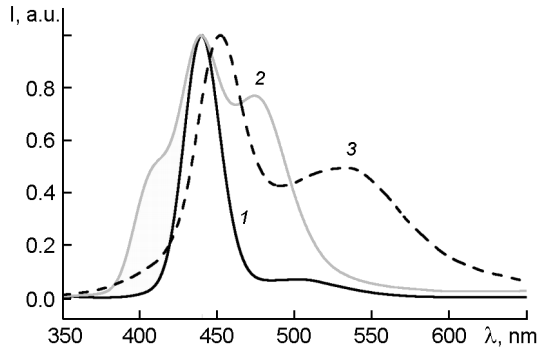

Fig. 1. Photoluminescence of CsI:Eu (10^{-3}%) crystal excited by 340 (*1*), 240 (*2*), 230 nm (*3*).

2. Experimental

Europium activated (CsI:Eu) crystals were grown by Czochralski method in dry Ar atmosphere from dehydrated CsI and EuI_2 raw materials. Typical dimension of crystals was 30 mm in diameter and 70 mm in length. Content of Eu^{2+} ions was varied from 10^{-5} to $5 \cdot 10^{-1}$ mass. % in the crystals. Absorption spectra were registered using spectrometer SPECORD 40. For determination of luminescence FLS'920 spectrofluorimeter was used. Xenon lamp Xe900, 450V was used as a source of UV excitation. Irradiation of the samples was realized by X-ray tubes (Cu, 30 mA, 40 kV, 1 Gy/min and W, 10 mA, 150 kV, 10 Gy/min). Thermostimulated luminescence (TSL) curves were carried out with a heating rate of 0.2 degree per second in 300–580 K range.

3. Results

Absorption spectrum of the crystal of CsI:Eu consists of two wide bands within the range of 250–310 and 330–430 nm corresponding to $^8S(4f^7) \rightarrow 4f^6\ 5d$ transitions in Eu^{2+} ions [9]. Considering high radiation stability of pure CsI crystals, the revealing of color centers by absorption methods can only be possible at extremely high irradiation doses [11–15]. Absorption bands, related to V-type centers, are in the range of 290–460 nm. This implies that radiation-induced bands are overlapped with the activator absorption of CsI:Eu, which complicates their identification. No changes in the absorption spectrum were detected up to the dose of 500 Gy. This is the reason we used more sensitive luminescent method to investigate of radiation influence in CsI:Eu crystals.

Photo-luminescence spectrum of CsI:Eu crystal, containing 10^{-3} % Eu^{2+}, is shown in Fig. 1. The main narrow fluorescence peak at 441 nm ($H_{1/2} = 0.15$ eV) is excited in the area of Eu^{2+} absorption (250–380 nm), and the additional bands of 410, 450, 478, 525, 580 nm are excited within the range of 220–240 nm at the tail of the fundamental absorption. Complicated structure of emission testifies presence of several luminescent centers.

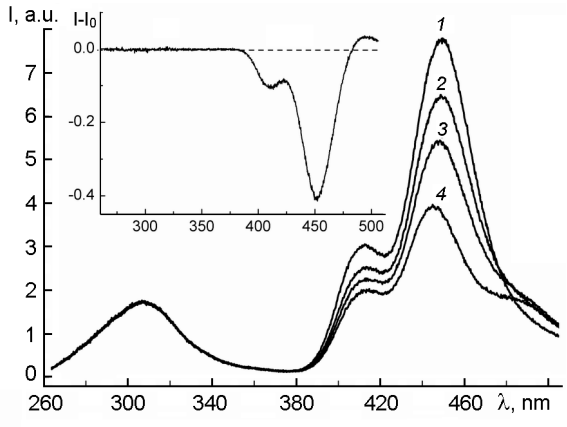

Fig. 2. Radioluminescence of CsI: 10^{-3} % Eu^{2+} crystal: initial (*1*) and preliminary X-ray irradiated during 3 min (*2*), 11 min (*3*), 39 min (*4*). Insert – difference between (*1*) and (*4*) spectra. X-ray irradiation 1 Gy/min (tube Cu, 30 mA, 40 kV). 300 K.

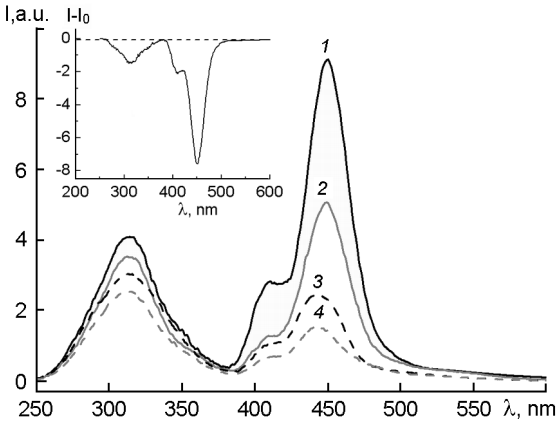

Fig. 3. Radioluminescence of CsI: 10^{-3} % Eu^{2+} crystal: initial (*1*) and preliminary X-ray irradiated during 2.5 (*2*), 10 (*3*), 25 (*4*), 50 (*5*) minutes. Insert — difference between (*1*) and (*5*) spectra. X-ray irradiation 10 Gy/min (W, 10 mA, 150 kV). 300 K

Radioluminescence spectra of the initial and exposed to X-ray CsI:Eu crystal (10^{-3} % Eu^{2+}) with the use of low and high dose rates (1 and 10 Gy/min) are presented in Fig. 2 and 3. Under impact X-ray irradiation, the emission intensity decreases, notably more considerably at the initial (less than 100 Gy) irradiation stages. Intrinsic

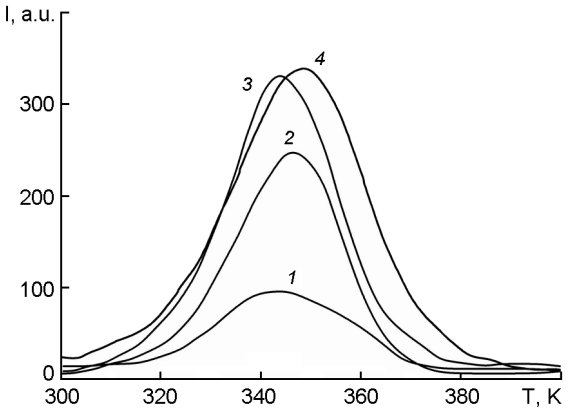

Fig. 4. Glow curves of CsI: 10^{-3} % Eu crystal irradiated at 300 K by doses of 5 (*1*), 30 (*2*), 250 (*3*) and 500 Gy (*4*).

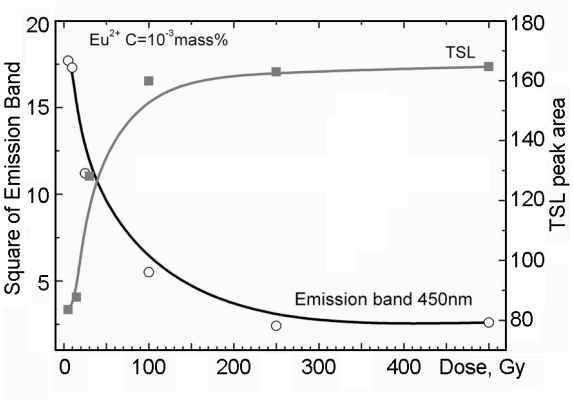

Fig. 5. Dependences of TSL (peak 350 K) and X-ray luminescence band (450 nm) on the irradiation dose of CsI:Eu crystal (irradiation rate 10 Gy/min).

UV (308 nm) luminescence and the narrow activator peak ~450 nm, overlapping with the band of ~410 nm, are revealed in the spectrum. When the activator concentration increases up to 10^{-1} % Eu^{2+}, the maximum of the main band (~450 nm) shifts up to 460 nm, which is, apparently, connected with formation of aggregates an activator centers.

If the dose rate is 1 Gy/min, the intensity of the main band and peak at 410 nm reduces (Fig. 2). Moreover, the weak emission in the range of $\lambda > 500$ nm slightly increases. It is important to mention that the own UV luminescence remains unchanged.

When the irradiation rate increases up to 10 Gy/min, then quite another picture is observed (Fig. 3). The area of main peak 450 nm sharply falls at a dose of 100 Gy, and it does not change for the future dose accumulation. The intensity of 410 nm peak decreases and totally disappears at $D \approx 250$ Gy. Yield of the intrinsic UV-luminescence decreases as well.

Thermostimulated luminescence of Eu doped CsI crystals irradiated at room temperature indicated the presence of a broad peak around 350 K ($H_{1/2}$ = 30 K) (Fig. 4). The peak position is consistent with that for pure and In, Cd, Ba doped cesium iodide crystals previously described in [12–15]. According to the existing conception, exactly at this temperature annihilation of I_3^- — centers and relaxation of CsI lattice take place [12, 13].

Dynamics of radiation defects accumulation and decrease of luminescence efficiency of CsI:Eu crystal are shown in Fig. 5.

4. Discussion

The most important result is the reducing of Eu^{2+} luminescence intensity with the accumulating of radiation dose. The luminescence quenching of Eu^{2+} ions (in case of the permanent europium concentration) directs to modification of the luminescence center structure. The absence of Eu^{3+} ions typical line structure emission indicates that hole capture does not occur. It is possible to assume that in this case the activator center (like Eu^{2+} — v_c^-) can be an electron traps only.

The structure of the radiation-induced activator center cannot be determined definitively, however the following facts should be taken into account for the appropriate model development.

Change of TSL peak at ~350 K, with the irradiation increasing, demonstrates the first relatively fast stage (up to 250 Gy) followed by more slow stage (Fig. 5). In general, this dependence is similar to the well known radiation induced defects accumulation in alkali-halide crystals [16, 17]. In these cases the first stage and saturation usually correspond to carriers capture by pre-radiation defects. In the case of CsI:Eu crystal, this kind of defects are connected with equilibrium vacancies and cation vacancies compensating the excess charge of Eu^{2+} ions.

It should be noted that in glow curves of pure and Ga, Tl, In doped CsI crystals reveal TSL peaks at 210 and 350 K, connected with radiation defects like V_F and/or I_3^- —centers, respectively [12]. Similar defects were found for CsI:Cd and CsI:Ba crystals [15].

Dose dependence of the TSL peak and output of radio-luminescence 450 nm band,

shown in Fig. 5, demonstrates that at the first stage an increase of TSL is accompanied by reduction of the luminescence intensity, and the saturation occurs near 250 Gy. The further increase of dose practically does not influence on the activator luminescence intensity. Such behavior of course indicates the correlation between luminescence intensity and radiation defects modification dynamics.

The additional luminescence bands may be associated with a distortion of the crystal lattice near Eu^{2+} ions. However, the exact identification of the defect types is not possible yet.

Thus, the obtained data, undoubtedly prove the luminescence degradation with irradiation CsI:Eu crystals, however, the transformation mechanism of the luminescence center structure needs further study.

4. Conclusions

The present work shows that irradiation leads to suppression of the activator luminescence in CsI:Eu crystals. The effect is quite considerable even at small doses (less than 100 Gy) and it is observed in a wide range of Eu ions concentration and irradiation dose rates. Changes in the absorption spectra were not detected in crystals up to 500 Gy irradiation. Intensity of the 450 nm emission band correlating with 350 K glow peak, ascribed to I_3^- centers, with irradiation dose of CsI:Eu crystal. The analysis of irradiation-stimulated changes in the activator centers structure shows that the activator centers are efficient centers of electron capture. At the same time, formation of the hole type centers (I_3^-) can lead to a partial decrease in intrinsic UV and activator luminescence of CsI:Eu crystals.

References

1. Inorganic Scintillators for Detector Systems, ed. by P.Lecoq, A.Annenkov, A.Gektin, M.Korzhik, C.Pedrini, Springer (2006).
2. A.V.Gektin, N.V.Shiran, in: Proc. "Scint. Materials: Engineering, Devices and Application", Kharkov, ISMA (2011), p.6.
3. T.Berger-Hrynova, in: Proc. "Scint. Materials: Engineering, Devices and Application", Kharkov, ISMA (2011), p.40.
4. A.Gektin, N.Shiran, A.Vasil'ev, A.Belsky, Functional Materials for Scintillation Technique and Medical Application, Kharkov, ISMA, 2012, 428 (in Russian)
5. A.Gektin, N.Shiran, in: Proc. Int. Conf. SCINT'97, Shanghai, China (1997), p.115.
6. N.Shiran, A.Gektin, S.Vasyukov et al., *Functional Materials*, **18**, 438 (2011).
7. A.Gektin, N.Shiran, A.Belsky, S.Vasyukov, *Opt. Mater.*, **34**, 2017 (2012).
8. A.M.Lebedynskiy, S.A.Vasyukov, A.V.Gektin et al., *J. Appl. Spectrosc.*, **79**, 583 (2012).
9. H.J.Seo, W.S.Zhang, T.Tsuboi, *J. Alloys and Comp.*, **344**, 268 (2002).
10. H.Vrielinck, D.G.Zverev, P.Leblans, *Phys. Rev.*, **B 85**, 144119 (2012).
11. N.V.Shiran, *Functional Materials*, **4**, 35 (1997).
12. V.V.Kolotilin, V.I.Shtanko, *Sol. State Phys.*, **26**, 236 (1984).
13. G.O.Amolo, J.D.Comins, R.M.Erasmus, T.E.Derry, *Nucl. Instr, Meth. Phys. Res.*, **B 250**, 359 (2006).
14. A.Gektin, N.Shiran, A.Belsky, A.Vasiliev, *Nucl. Tracks Rad. .Meas.*, **21**, 11 (1993).
15. I.V.Garapyn, I.Z.Hud, B.V.Pavlyk, *Ukr. Zh. Fiziki.*, **51**, 287 (2006).
16. C.R.A.Catlow, K.M.Diller, L.W.Hobbs, *Philos. Mag.*, **A 42**, 123 (1980).
17. A.V.Gektin, V.Ya.Serebryanny, N.V.Shiran, *Phys. Stat. Sol.*, **A134**, 351 (1992).

Радіаційна стійкість кристалів CsI:Eu

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В роботі обговорюються проблеми радіаційної стійкості та природи післясвітіння кристалів CsI:Eu. Встановлено, що параметри свічення залежать від умов рентгенівського впливу. Опромінення призводить до падіння свічення при дозах, менших за 100 Gy, коли наведене поглинання ще не спостерігається. Утворення діркових (V_F^- і I_3^-) та активаторних центрів забарвлення може призвести до часткового зниження власної УФ та активаторної люмінесценції, проте це не є домінуючим процесом радіаційно-наведених явищ. Виявлена зворотну залежність післясвічення та люмінесценції Eu^{2+} іонів від дози опромінення. Радіаційно-наведене тушіння люмінесценції обумовлено змінами структури активаторних центрів.