

Suppression mechanism of millisecond afterglow in CsI:Tl crystals by Eu^{2+} impurity

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The causes of millisecond afterglow in CsI:Tl crystals have been considered. The two afterglow components with about 5 ms and about 60 ms characteristic time at RT have been shown to be related to the trap disruption at 190 and 215 K. The thermostimulated luminescence peak at 215 K is of extrinsic nature and is associated most probably with barium cations in the form of single dipoles $\text{Ba}^{2+}-\text{V}_\text{C}^-$. In contrast to Ba^{2+} , introduction of Eu^{2+} cations results in the afterglow attenuation. The aggregation of $\text{Eu}^{2+}-\text{V}_\text{C}^-$ dipoles in a quenched sample has been found to occur during almost 10 min at RT. The afterglow suppression mechanism in CsI:Tl,Eu crystals consists in that not only europium ions but also other Me^{2+} type impurities are involved in the aggregation process. After the solid solution decomposition and metastable aggregate formation, not millisecond but more durable afterglow is observed in the crystals within the second and minute time ranges.

Рассмотрены причины миллисекундного послесвечения кристаллов CsI:Tl. Показано, что два компонента послесвечения с характерными временами ~6 и ~60 мс при комнатной температуре связаны с разрушением ловушек при 190 и 215 К. Пик термостимулированной люминесценции при 215 К имеет примесную природу и наиболее вероятно связан с катионами бария в виде одиночных диполей $\text{Ba}^{2+}-\text{V}_\text{C}^-$. В отличие от Ba^{2+} , введение катионов Eu^{2+} приводит к снижению послесвечения. Показано, что агрегация диполей $\text{Eu}^{2+}-\text{V}_\text{C}^-$ в закаленном образце занимает не более 10 мин при комнатной температуре. Механизм подавления послесвечения в кристаллах CsI:Tl,Eu состоит в том, что в процесс агрегации вовлекаются не только ионы европия, но другие примеси типа Me^{2+} . После распада твердого раствора и образования метастабильных агрегатов в кристаллах наблюдается не миллисекундное, а более длительное послесвечение в секундном и минутном диапазоне времен.

The CsI:Tl crystals are used with success in visualization systems, such as tomographs, introsopes, etc. [1]. A high afterglow (AG) level of those crystals is extremely undesirable for such applications, because AG deteriorates considerably the image quality [2]. Recently, numerous publications are appeared (e.g., [2–5]) dedicated to the AG attenuation in CsI:Tl crystals. In particular, crystals doped additionally with Eu^{2+} [3–5] or Sm^{2+} [2] are considered. The introduction of those dopants provides a considerable reduction of the AG level.

However, the conclusions made in those works are in contradiction with the known concepts of the effect of divalent dopants on the AG of CsI:Tl crystals. The same authors stated before [6] that cations such as Ca^{2+} or Ba^{2+} cause a noticeably increased AG. A similar conclusion was drawn in some previous works [7, 8]. The TSL curves presented in those works show clearly that Cd^{2+} or Ba^{2+} cations favor the V_F type hole color center formation about 215 K, that is, just in the temperature region which is associated with the millisecond AG [9].

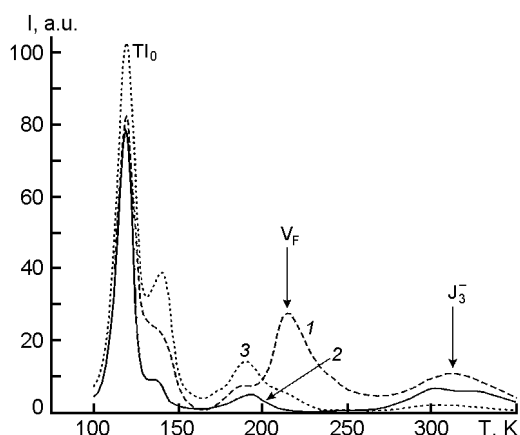


Fig. 1. TSL curves for CsI:Tl,Ba (1) and CsI:Tl,Eu (2) crystals. Irradiation with γ source ^{241}Am (60 keV, 1.8 Ci) at 77 K for 15 min. The heating rate $\beta = 0.04$ K/s. For comparison, TSL of a conventional CsI:Tl crystal is shown (3).

Consideration of TSL curves from [3, 7, 8] has shown that the absence of the TSL peak near 215 K is typical of CsI:Tl,Eu crystals. This statement is confirmed fully by our results. In Fig. 1, presented are the TSL data for CsI:Tl crystals with the same Tl concentration ($C_{\text{Tl}} = 0.09$ % mol.), but with different co-dopants: Ba^{2+} (curve 1) and Eu^{2+} (curve 2). The doping admixtures BaI_2 or EuI_2 were added to the raw materials in an amount providing the concentration of the corresponding ions in the crystal of the order of $(2-4) \cdot 10^{-4}$ % mol. A special purified salt containing the above impurities in amounts lower than the detection limit thereof by chemical analysis has been used for crystal growth. It is seen from Fig. 1 that Me^{2+} ions stimulate an intense 215 K peak in one case while in the other one (Eu^{2+}) this peak is absent; instead, a rather intense peak is observed near 295 K.

It follows from Fig. 1 and the conclusions from [9] that the millisecond afterglow is connected with 190 and 215 K TSL peaks deterioration. Since the AG decay for those crystals in the 2 to 100 ms shows two components with $\tau_1 \sim 5$ ms and $\tau_2 \sim 60$ ms, it is logical to associate τ_1 with the 190 K peak deterioration while τ_2 , with the 215 K peak.

The mentioned behavior difference of Me^{2+} impurities can be explained basing on [10] aimed at aggregation of $\text{Eu}^{2+}-\text{V}_{\text{C}}^-$ centers in alkali halide crystals, including CsI. It is stated in the work cited that Eu^{2+} ions show a trend to aggregation, especially within the CsI lattice. The aggregation goes efficiently even at temperatures lower than

the room one and results in formation of so-called trimers $3(\text{Eu}^{2+}-\text{V}_{\text{C}}^-)$, see Fig. 2a. According to EPR data, the number of individual dipoles at room temperature is negligible, substantially all the Eu^{2+} are gathered in complexes.

The conclusions given in [10] can be checked in experiment also for CsI:Tl crystals. Following the guidelines from [10], we have quenched a CsI:Tl,Eu crystal from 800 K. The AG level was measured using a Heimann NPG3 unit. The anode current of a X-ray tube was 0.6 mA at 140 kV voltage. The AG_{100} was determined 100 ms after the 1 s long exciting X-ray was over; the samples were shaped as $20 \times 20 \times 4$ mm³ plates. The AG measurement results prior to and after the quenching are presented in Fig. 3. The AG value amounted 0.3 % for the unquenched sample and increased up to 2.6 % immediately after the quenching. It is notable that the relaxation of the quenched sample was very fast, the AG was reduced to the practically initial level during 9 min. This result agrees well with the statement [10] that the Eu dimers aggregation occurs even at $T < 300$ K. The quenching from lower temperatures (550 and 650 K) does not result in any substantial AG increase, only its insignificant amplification by 0.2–0.4 % being observed. It is just the crystals with TSL corresponding to the curve 2 in Fig. 1 that were subjected to quenching.

Let the results obtained be considered from another viewpoint. The initial "special purity for crystal growth" ("spcg") grade CsI is known to contain always a certain amount of Me^{2+} impurities [11], the Ba^{2+} (up to $1 \cdot 10^{-3}$ wt%) and Ca^{2+} (up to $5 \cdot 10^{-4}$ %) being ones of most importance. It is appropriate to mention that $\text{Ba}(\text{OH})_2$ is used to precipitate sulfates in the mother liquors during the salt synthesis. Our experience in CsI:Tl crystal growing from the "spcg" grade salt evidences that the grown samples show always a rather intense AG_{100} and a clear storage near 215 K although causing no pronounced peak (cf. Curves 1 and 3 in Fig. 1). An obvious way to reduce AG_{100} is a deep purification of the raw salt. An additional purification of the melt [12] is well known to provide the AG_{100} reduction by several times [13]. Basing on those considerations, the initial salt contamination with Me^{2+} cations can be suggested to be a substantial factor worsening the AG_{100} characteristic. Among those cations, Ba^{2+} ones are most isomorphic to the CsI lattice [14] and

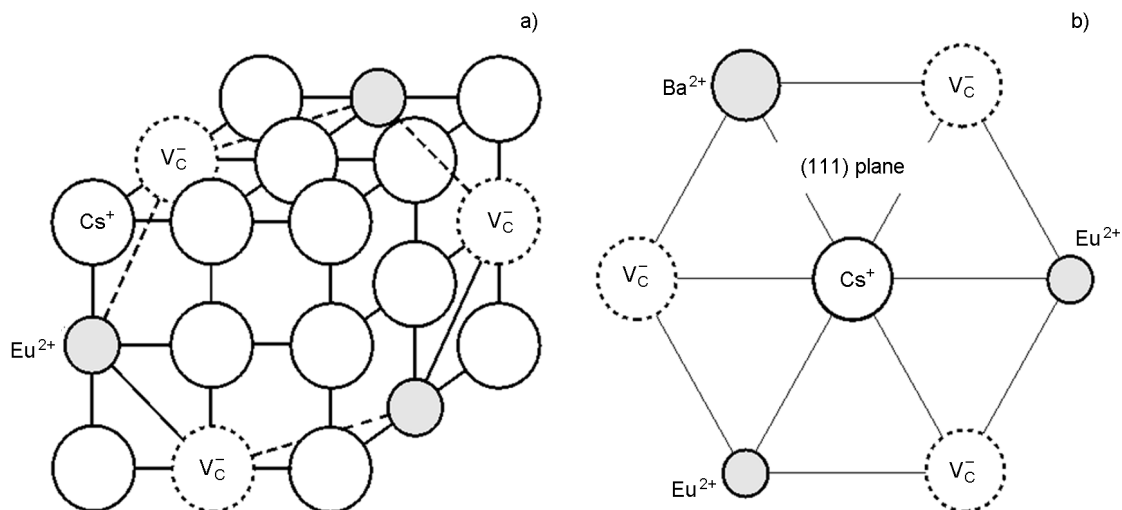


Fig. 2. A model of trimer (a) in the CsI lattice according to [10]. A schematic image of a mixed trimer (b) consisting of two Eu²⁺ and one Ba²⁺ cations.

least tending to aggregation, because Ba²⁺ ionic radius ($r = 1.56 \text{ \AA}$ for coordination number 8) is close to that for Cs⁺ ($r = 1.74 \text{ \AA}$). The luminescence of Ba²⁺-V_C⁻ dipoles was studied in [15], the results show that the dipole decomposition is slow, since the gradual evolution of luminescence spectrum can be observed during several months. In contrast, as it follows from Fig. 3 and data from [10], the Eu²⁺-V_C⁻ dipoles are decomposed during several minutes. The decomposition products are trimers shown schematically in Fig. 2a. The decomposition is caused by a considerable difference between Cs⁺ and Eu²⁺ ($r = 1.39 \text{ \AA}$) ionic radii, that is pointed in numerous works (see, e.g., [10, 14]).

It is rather reasonable to suppose that not only Eu²⁺ but also other Me²⁺ cations are included in the trimers. Fig. 2b shows schematically a mixed trimer consisting of two europium and one barium ions. In our opinion, it is just the migration process of mobile Eu²⁺-V_C⁻ dipoles to stable Ba²⁺-V_C⁻ complex that results in disappearance of energy storage near the 215 K peak and the AG₁₀₀ reduction. After the solid solution decomposition and formation simple and mixed aggregates in the crystals, not the millisecond afterglow but a more prolonged one (in second and minute ranges) associated with the deterioration of 295 K TSL peak that was observed in [5], see the curve 2 in Fig. 1, too. It is to note that our results refer to the second component of the AG decay ($\tau_2 \sim 60 \text{ ms}$). To elucidate the nature of the $\tau_1 \sim 5 \text{ ms}$, that is connected, in

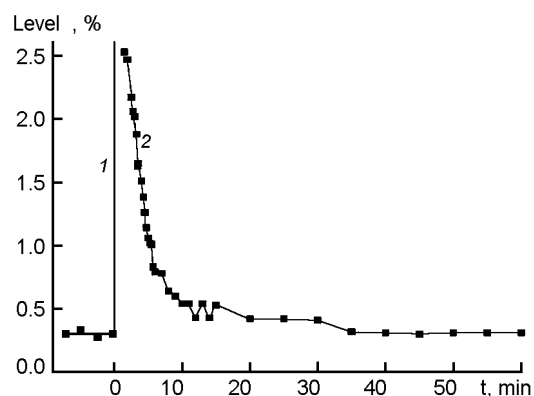


Fig. 3. Afterglow level of a CsI:Tl,Eu crystal prior to and after quenching from 800 K.

our opinion, with the intrinsic lattice structure defects, additional studies are necessary.

The conclusions can be formulated briefly as follows. The CsI:Tl crystal afterglow is increased due to Eu²⁺ ions, similar other Me²⁺ impurities. If the impurity is in the Eu²⁺-V_C⁻ state (single dipoles), such crystals show a substantial millisecond afterglow associated with decomposition of VF type hole color center near 215 K. After the solid solution decomposition and formation of metastable aggregates, the afterglow in second and minute range is observed in the crystals. A distinctive feature of Eu²⁺ ions in the CsI lattice is a high aggregation rate that occurs even at temperatures lower than room one. The trimer formation process from single dipoles at RT lasts maximum 10 min. The proposed afterglow suppression mechanism in CsI:Tl,Eu crystals consists in

that not only europium ions but also other Me^{2+} impurities are involved in the aggregation process. For example, the trimer core may be formed by low-mobility $\text{Ba}^{2+}-\text{V}_{\text{C}}^{-}$ dipoles. The Eu^{2+} concentration exceeding considerably the background level of Me^{2+} impurity ion content is the indispensable condition for reduced millisecond AG. It is to take into account that a fraction of Eu^{2+} interacts with oxygen-containing impurities in the melt with europium oxide formation [16].

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Механізм пригнічення мілісекундного післясвітіння домішкою Eu^{2+} у кристалах CsI:Tl

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Розглянуто причини мілісекундного післясвітіння кристалів CsI:Tl . Показано, що два компоненти післясвітіння з характерними часами ~ 5 та ~ 60 мс при кімнатній температурі пов'язані з руйнуванням пасток при 190 та 215 К. Пік термостимульованої люмінесценції при 215 К має домішкову природу та пов'язаний найімовірніше з катіонами барію у формі окремих диполів $\text{Ba}^{2+}-\text{V}_{\text{C}}^{-}$. На відміну від Ba^{2+} , введення катіонів Eu^{2+} призводить до зниження післясвітіння. Показано, що агрегація диполів $\text{Eu}^{2+}-\text{V}_{\text{C}}^{-}$ у загартованому зразку триває не більше 10 хв при кімнатній температурі. Механізм пригнічення післясвітіння в кристалах CsI:Tl:Eu полягає в тому, що до процесу агрегації залучаються не тільки іони европію, але й інші домішки типу Me^{2+} . Після розпаду твердого розчину та утворення метастабільних агрегатів у кристалах спостерігається не мілісекундне, а більш тривале післясвітіння у секундному та хвилинному діапазонах часу.