

Afterglow suppression in CsI crystal by Eu^{2+} doping

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The influence of europium addition on absorption, luminescence and scintillation properties of CsI crystals is studied. It is shown the important role of europium as a scavenger allowing the melt purification before crystal growth. In its turn, this leads the IR-transparency improving of crystals, as well as suppressing of slow scintillation pulses. Reducing the prolonged emission in the range of 410-580 nm results in evident increase of the F/T ratio, which is important for the CsI application as a fast scintillator. At the same time, the excess scavenger's concentration above the crucial leads to the quenching of intrinsic UV emission and appearance of typical for Eu^{2+} ions luminescence.

Исследовалось влияние европия на абсорбционные, люминесцентные и сцинтилляционные характеристики кристаллов CsI. Показана важная роль европия как скавангера, позволяющего очистить расплав перед началом роста. Результатом является улучшение прозрачности в ИК-диапазоне и снижение вклада затянутых сцинтилляционных импульсов. Подавление медленной люминесценции в области 410-580 нм приводит к увеличению отношения F/T , важного при использовании CsI как быстрого сцинтиллятора. В то же время избыточное содержание скавангера вызывает тушение собственного УФ свечения и появление характерной для ионов Eu^{2+} люминесценции.

1. Introduction

CsI crystals are used as fast radiation stable scintillators [1, 2], electromagnetic calorimeter [3], IR-transparent optics for power CO_2 -lasers [4], and photocathodes for gaseous detector [5]. Maximal crystal purity is the general requirement for all these cases. In respect to CsI crystals as scintillators, high intensity of the fast UV emission (~ 307 nm, ~ 10 ns) and the minimal contribution of the slow (microseconds) component in the range of 410–580 nm is considered to be the quality criteria [1]. At the same time, for scintillator' perfection estimation the ratio of the fast component signal (*Fast*), to the total emission (*Total*), so called F/T ratio, is often used [1]. Ideally, F/T ratio should be closed to 1, nevertheless, even in the best samples it does not

exceed ~ 0.7 due to the presence of structure defects and contaminations. The list and the influence of undesirable impurities in CsI crystals are varied [2], but in general they are related to different oxygen-containing anions. Such kind of admixtures deteriorates functional parameters of pure and Tl doped scintillators considerably, which leads to the reduction of their radiation stability and afterglow increase [5, 6].

Elimination of the residual contaminations is a very complicated technological task, which is usually solved by deep purification of the initial salt and the reactive atmosphere application during growing process. Introduction of europium is one of the ways to solve this problem as applied to CsI:Tl scintillators [8, 9]. In co-doped CsI(Tl, Eu) scintillators the suppression of the undesirable millisecond afterglow was discovered. Currently two

models explaining this positive effect, are dominating. The former is based on the idea that of Eu^{2+} ions introduce deep electron traps which alter the decay kinetics [9]. The theoretical estimations allow describing such kind of effect, but there is no direct evidence of exactly this mechanism. The latter idea is connected with europium application as scavenger — melting cleaner [7]. It is expected that europium admixture links oxygen-containing compounds with high-melting oxides (such as EuO and Eu_2O_3) formation, which are not included into the solid solution and stimulate crystal purification. The similar experiments were carried out earlier to improve IR-transparency of optical windows made from Csl crystals [4].

This work is devoted to discuss the role of Eu^{2+} ions introduced into Csl melt from the point of determination of the dominating mechanisms for crystals purification and improvement of their functional characteristics.

2. Experiment

Pure and europium activated Csl crystals were grown by Bridgman method in evacuated sealed quartz ampoules, and by Czochralski method in the platinum crucibles in argon atmosphere. Initial Csl salt contained $\sim 10^{-4}$ wt. % of oxygen-related impurities. Preliminary dehydration of raw material was carried out by heating up to 350°C in vacuum. Dehydrated EuI_2 used as admixture was loaded into cesium iodide with concentrations in a range of 0.01–7 %. The content of Eu^{2+} in obtained crystals was varied from $<10^{-5}$ to $2 \cdot 10^{-1}$ %.

Optical absorption spectra in UV-VIS range were registered by Specord M40 spectrophotometer. IR-absorption spectra were measured by Spectrum One FT-IR spectrometer. Since the fluorescent methods are most sensitive to reveal the presence of oxygen impurities in the crystals, in this research crystals' photoemission characteristics were defined using FLS 920 fluorescence spectrometer. Radioluminescence spectra were measured using X-ray excitation (Cu, 40 mA, 40 kV).

To estimate the scintillation suitability of crystals, integral emission output was determined as purification criteria, including slow and fast luminescence components' contribution. Ratio F/T in the samples was ascertained using pulse method with the cosmic muons excitation.

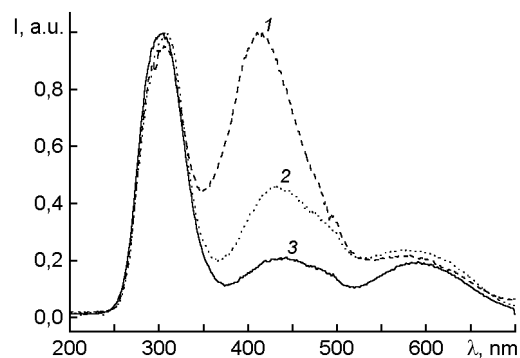


Fig. 1. X-ray luminescence spectra of undoped Csl crystals with total admixtures contents' $\sim 5 \cdot 10^{-3}$ (1), $5 \cdot 10^{-4}$ (2); $1 \cdot 10^{-4}$ (3), %.

3. Results and discussion

IR spectra of undoped Csl crystals, grown by Bridgman method, demonstrate weak bands corresponding to trace amounts of CO_3^{2-} , SO_4^{2-} , OH^- , H_2O^- , CNO^- ions. At the same time, the intensity of these bands is much higher for crystals obtained by the Czochralski method, and the total content of oxygen radicals may reach $\sim 5 \cdot 10^{-3}$ %.

X-ray luminescence spectra of "pure" Csl crystals with different total contents of oxygen-containing impurities ($1 \cdot 10^{-4}$; $5 \cdot 10^{-4}$ and $\sim 5 \cdot 10^{-3}$ %) are presented in Fig. 1. The band with the maximum at 307 nm, corresponding to the intrinsic fast emission, is notable for all crystals. The presence and contribution of additional bands in the range of 410–580 nm with slow decay defines crystals contamination level by oxygen-containing radicals.

Radioluminescence spectra of "pure" and Eu-doped crystals are shown in Fig. 2. Total impurity content in undoped sample is close to $\sim 5 \cdot 10^{-3}$ %. Dopant concentration in activated crystals was $2 \cdot 10^{-4}$ and $2 \cdot 10^{-2}$ % Eu^{2+} (3 and 7 % Eu^{2+} in the melt, correspondingly). The nominally pure crystal is characterized by approximately equal contribution of UV and blue luminescence, whereas for Eu-doped samples the ratio of these bands (and, hence, the F/T ratio) depends on the activator content. Small additions ($\leq 2 \cdot 10^{-4}$ % Eu) lead to a significant reduction in the contribution of the slow emission component. The ratio of F/T turns out to be rather high, i.e. close to 1. It has to be noted that the typical bands corresponding to oxygen radicals, are absent in IR spectra of these samples.

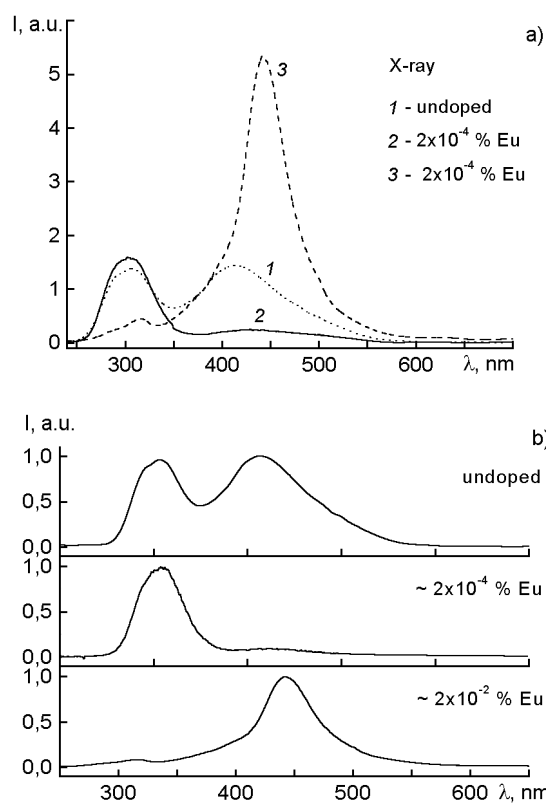


Fig. 2. Radioluminescence spectral patterns depending on Eu contents in Csl crystals (a), normalized spectra (b).

Thus, growth of the europium content in crystals leads to a gradual reduction of the blue emission as it can be seen from the spectra, presented in Fig. 2. However, the effect has concentration limit, above of which the situation changes. Concentration increase higher than $2 \cdot 10^{-4}$ % Eu^{2+} (3 % Eu^{2+} in the melt) results in intensity decrease of the intrinsic UV luminescence, and a narrow band at 445 nm (0.2 eV) appearance. The latter has emission spectra and microsecond decay kinetics typical for $4f^6 5d^1 - 4f^7$ transition in Eu^{2+} ion [10]. It is important to note that at any concentration in crystals, europium is in the divalent state (even in case of phase precipitation EuI_2 and CsEuI_3 [11]).

Concentration dependence of X-ray luminescence spectra of Csl:Eu can be connected with the fact of low activator's segregation coefficient in solid solution ($K \sim 0.002$). Due to this the interaction between europium and oxygen residuals is limited as far as dopant gradually accumulates directly in the crystal and gives the typical Eu^{2+} emission.

It should be noted the role of the europium in the other stages of crystal growth. The active interaction of europium with oxygen-containing radicals, leading to the

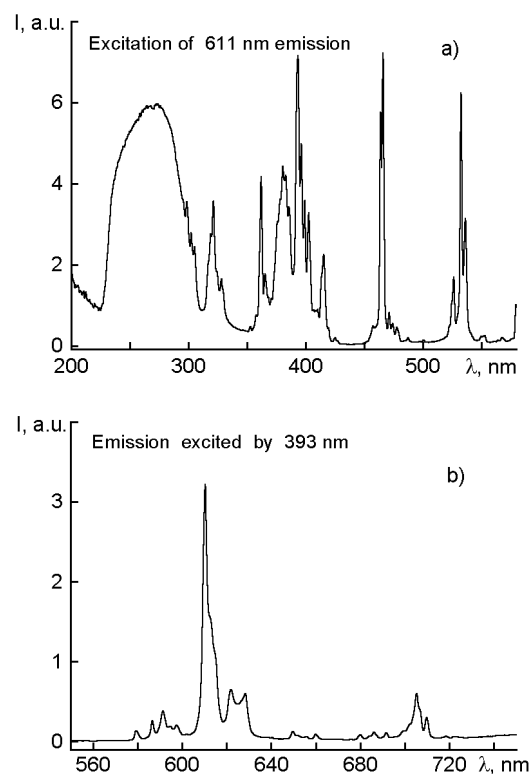


Fig. 3. Eu^{3+} ions luminescence in the crystallized melt of Csl:Eu: emission excitation spectrum of 611 nm (a) and emission spectrum under excitation of 393 nm (b).

formation of europium oxides and oxy-iodides, takes place during preliminary heat treatment of the initial raw material. Considering the possible europium oxygen compounds, it should be noted that europium has valence (2+) in EuO , Eu_2O_2 , Eu_4O_6 whereas in Eu_2O_3 , EuOI , $\text{Eu}_2\text{O}_2\text{I}$ the europium valence is (3+). As is well known [12], the spectral-kinetic luminescence parameters of europium ions with different valences are clearly distinguished. Spin-allowed $d f$ transitions with specific narrow emission band in the blue region with microsecond emission are typical for Eu^{2+} ions, whereas spin-forbidden $f f$ transitions line spectrum in the red region and millisecond decay are typical for Eu^{3+} ions. From the above mentioned compounds, only EuO and Eu_2O_3 oxides are rather thermally stable at Csl melting temperature (621°C).

One more stage is the interaction between europium and oxygen admixtures directly in the melt. Fig. 3 shows excitation and luminescence spectra of the frozen melt which remained in the platinum crucibles bottom after Csl:Eu crystal growth by Czochralski method. Intense line luminescence in the red region is revealed, which is typical for $f f$

transitions in Eu^{3+} ions, whereas the blue band of Eu^{2+} ions is absent. It indicates the precipitation formation of oxide (Eu_2O_3) during decomposition of CsI– EuI_2 solid solution. Typical for oxygen radicals IR bands are practically absent for single crystals; whereas the crystallized melt demonstrates the peak at $\sim 540\text{ cm}^{-1}$ caused by Eu_2O_3 . The obtained data confirm that trivalent europium compounds are products of interaction between europium and oxygen ions in CsI melt. Elucidation of their nature requires detailed research, but in principle not only europium oxides but also oxy-iodides (EuOI , $\text{Eu}_2\text{O}_2\text{I}$) can be the interaction products.

In analysis of the solid solution CsI:Eu production, it should be taken into account that the phase diagram of CsI– EuI_2 binary system belongs to eutectic type [13]. The lattice structure of EuI_2 is orthorhombic and for CsI is body-centered cubic. Eu^{2+} and Cs^+ ions differ not only by valence but also by sizes ($\Delta R/R \approx 28\%$). This discrepancy can explain the low segregation coefficient of europium in CsI solid solution ($K \approx 0.002$). The presented data indicate that activator's precipitates can appear in CsI:Eu crystals with a high probability. These inclusions contain europium ions mainly in the divalent state. Introduction of the small and strictly controlled europium iodide admixtures ($< 1 \cdot 10^{-4}\%$) allows to increase the IR-transparency and scintillation efficiency of pure CsI. The effect is determined mainly by interaction between europium and oxygen admixtures deteriorating optical and scintillation crystal's properties, and their elimination off the melt during the crystals growth process.

4. Conclusions

Thus, it is shown the important role of europium as a scavenger allowing the melt

purification before CsI crystal growth. In its turn, this results in the IR-transparency improving of crystals, as well as suppressing of slow scintillation pulses. Reducing the prolonged emission in the range of 410–580 nm leads to increase of F/T ratio, which is important for the CsI application as a fast scintillator. At the same time, the increase of scavenger's crucial concentration give rise to the luminescence peak at 445 nm, typical for Eu^{2+} ions, and leads to the quenching of intrinsic fast UV emission in CsI crystal.

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Заглушення післясвітіння в Eu^{2+} активованих кристалах CsI

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Досліджувався вплив європію на абсорбційні, люмінесцентні та сцинтиляційні характеристики кристалів CsI. Показано важливу роль європію як скавангера, що дозволяє очистити розплав до початку росту. Пригнічення повільної люмінесценції в діапазоні 410-580 нм призводить до підвищення співвідношення F/T , важливого в разі використання CsI як швидкого сцинтилятора. В той же час збитковий вміст скавангера спричинює загасання власного УФ світіння та виникнення характерної для іонів Eu^{2+} люмінесценції.