

Specific features of photoluminescence centers in CsBr:Eu²⁺ crystals grown from melt

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Specific formation features of isolated dipole centers (IDC) Eu²⁺-V_{Cs} (impurity-cationic vacancy) and aggregate centers (AC) of photoluminescence (PL) in CsBr:Eu²⁺ crystals have been studied. These centers provide the PL with maxima in 435–450 nm and 490–520 nm regions. The centers causing the PL peaked at 490–520 nm have been found to be formed within a narrow Eu²⁺ concentration range (0.01 to 0.1 mol.%) and at temperatures up to 180–200°C. It has been supposed that in the CsBr:Eu²⁺ crystals, besides of the IDC responsible for the PL peaked at 440 nm, several AC types can be observed, in particular, CsEuBr₃ and Cs₄EuBr₆ nanocrystals as well as EuBr₂ precipitates.

Исследованы особенности образования изолированных дипольных центров (ИДЦ) типа Eu²⁺-V_{Cs} ("примесь-катионная вакансия") и агрегатных центров (АЦ) фотолуминесценции (ФЛ) в кристаллах CsBr:Eu²⁺, обуславливающих ФЛ в спектральной области с максимумами при 435–450 нм и 490–520 нм. Установлено, что центры ФЛ с максимумами при 490–520 нм образуются в узкой области концентраций Eu²⁺ (0,01–0,1 мол.%) при температурах до 180–200°C. Высказано предположение, что помимо ИДЦ отвечающих за ФЛ с максимумом при 440 нм, в кристаллах CsBr:Eu²⁺ могут наблюдаться несколько типов АЦ, в частности, нанокристаллы соединений CsEuBr₃, Cs₄EuBr₆ и осадки EuBr₂.

CsBr:Eu²⁺ single crystals are believed to be a material of promise as memory lumino-phors in digital luminescent roentgenography [1]. A specific feature of Eu²⁺ impurity entering into CsBr and other AHC consists in formation of isolated dipole centers (IDC) of Eu²⁺-V_{Cs} type, where cesium vacancies act to compensate the excess charge of Eu²⁺ ions. At the same time, along with the IDC, various aggregate centers (AC) are formed in CsBr crystals [2 – 4]. In particular, we have found the AC responsible for a photoluminescence (PL) band peaked at $\lambda_{max} = 516$ nm (300 K) [4]. The purpose of this work is to study the specific features of IDC and AC formation processes in CsBr:Eu²⁺ depending on the crystal growing conditions, the introduced impurity concentration, as well as on heat treatment of the crystals.

The CsBr:Eu²⁺ crystals of up to 38 mm in dia. and up to 80 mm height were grown in evacuated quartz ampoules using the Bridgman technique. Europium impurity was entered into the raw material as EuOBr, EuO, and Eu metal in the amounts of 0.1 to 0.4 mol.%. The Eu²⁺ impurity content in various crystals was controlled in arbitrary units using the PL intensity of Eu²⁺ centers. The PL spectra were excited by an LGI-21 N₂ laser ($\lambda_{ex} = 337.1$ nm) at room temperature.

The study of absorption and luminescence spectra of the grown crystals has shown that, independent of the chemical nature of the impurity compound (EuOBr, EuO, or Eu metal) introduced into the CsBr melt, the impurity in the crystal is in its divalent state. In the absorption spectra, broad bands are observed peaked at 250 and 350 nm due to inter-configuration

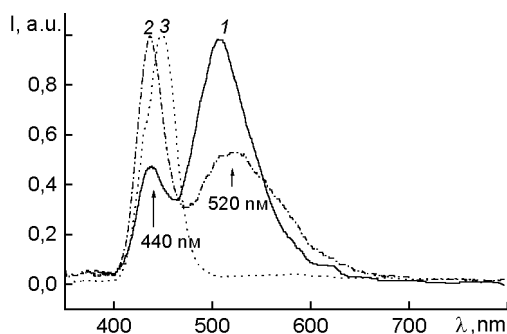


Fig. 1. PL spectra of CsBr:EuOBr single crystals at different activator concentrations (mol.%): 0.1 (1), 0.2 (2), 0.4 (3). $T = 300$ K.

$4f^7 \rightarrow 4f^65d$ transitions in Eu^{2+} ions. The PL spectra of CsBr:Eu $^{2+}$ excited in the Eu^{2+} absorption bands vary depending on the impurity concentration, heat treatment of the crystal samples, and on the crystal growing conditions. Let us consider the luminescence features of CsBr:Eu crystals obtained using the impurity in the form of various chemical compounds.

In the PL spectra of CsBr:0.1 mol.% EuOBr crystals ($\lambda_{ex} = 337.1$ nm), two emission bands are observed, a predominant one peaked at 520 nm ("green" component) and a lower intensity band peaked at 440 nm ("blue" component) (Fig. 1, curve 1). As the impurity content increases, the 440 nm emission intensity rises (Fig. 1, curve 2) while that at 520 nm drops down to its complete disappearance at 0.4 mol.% EuOBr (Fig. 1, curve 3). It has been shown [5] that the CsBr:Eu $^{2+}$ emission in the blue spectral region is due to the radiation of single dipoles $\text{Eu}^{2+}-V_{\text{Cs}}$ (impurity-cationic vacancy) while that in the green region, according to [2], could be explained by formation of aggregates of those dipoles, in particular, of $3(\text{Eu}^{2+}-V_{\text{Cs}})$ trimers. At the same time, our results evidence the decrease of the "green" PL center concentration as that of the single dipoles increases. This is hard to explain in the concept of the "green" PL centers as aggregated dipoles.

In the as-grown CsBr:0.3 mol.% EuO crystal, the Eu^{2+} impurity is distributed over the crystal height nearly homogeneously (Fig. 2, curve 1). In the PL spectrum of the crystal, the 440 nm emission predominates. After the crystal grinding and the repeated growing from the melt, the Eu^{2+} impurity distribution over the crystal height and its PL spectrum change considerably. Now, it is just the PL of AC peaked at 520 nm that is predominant, it

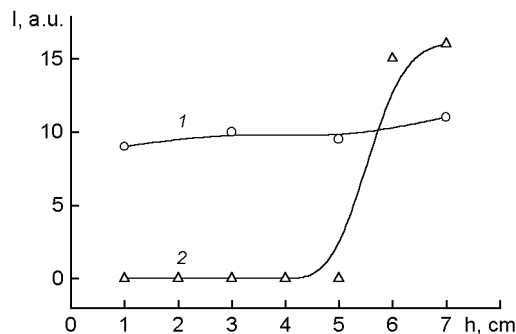


Fig. 2. Distribution of Eu^{2+} impurity over the CsBr:0.3 mol.% EuO crystal height after the initial growing (1) and repeated growing (2).

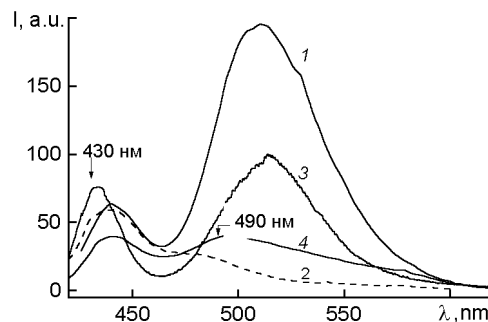


Fig. 3. PL spectra of CsBr:Eu metal (0.3 mass.%) single crystals: as-grown (1), quenched from 500°C to room temperature (2), annealed at 180°C for 70 h (3) and at 200°C for 140 days (4).

being observed only in the crystal upper part (Fig. 2, curve 2).

As to the CsBr:0.3 mol.% Eu metal crystal, the Eu^{2+} impurity is distributed over the crystal height nearly homogeneously and the component due to AC PL peaked at 520 nm predominates (Fig. 3, curve 1). After the crystal quenching from 500°C to room temperature, the AC PL intensity drops by about one decimal order, so the component due to the IDC becomes predominant (Fig. 3, curve 2). As the crystals are heated gradually to 180°C for 70 h, the initial AC PL intensity becomes recovered, while as those are annealed at 200°C for 140 days, the AC are decomposed (Fig. 3, curve 3). In this case, the AC emission components peaked at 490, 520, and 570 nm can be distinguished, thus evidencing the plurality of the centers.

It follows from the results obtained that, independent of the chemical nature of the impurity compound, in the PL spectra of CsBr:Eu $^{2+}$ crystals, along with isolated dipole centers emitting in the 440 nm band, three AC types are manifested containing Eu^{2+} ions and causing the PL peaked near

430 nm ("violet" component), 440 nm and 490–520 nm ("blue" and "green" components, respectively). The AC responsible for the above-mentioned PL components exhibit a complex structure that depends on the introduced impurity concentration and on the center formation temperature. It is difficult to consider the AC structure, since there is no phase diagram of the Cs–Br–Eu system. Some conclusions, however, are possible to be drawn basing on the luminescence characteristics of CsBr crystals containing different activator concentrations. In particular, it can be stated that in the crystals CsBr:(0.1–0.4 mol.% EuOBr), besides of $\text{Eu}^{2+}-V_{\text{Cs}}$ IDC responsible for the 440 nm PL band, several other center types are formed answering to 430, 490, and 520 nm PL maxima. The 520 nm PL band is shifted considerably (up to 70 nm) towards longer wavelengths as compared to the IDC emission spectrum. This fact evidences that Eu^{2+} ions in those centers are arranged in the crystal lattice sites at a different symmetry than in the IDC.

Consideration of PL spectra of lumino-phors containing europium ions and luminescent in the "green" spectral region shows that such a luminescence is observed only in the perovskite-like structure crystals, in particular, in EuAlO_3 [6]. According to [7, 8], in CsCl–PbCl₂ and CsBr–CdBr₂ at Pb²⁺ and Cd²⁺ concentrations of 0.05 to 0.1 mol.%, nanocrystals of perovskite-like phases (CsPbCl₃ and CsCdBr₃) of 20 to 50 nm size are formed. By analogy, the formation of similar nanocrystals of CsEuBr₃ type could be expected in CsBr single crystals activated with EuOBr or Eu metal. In our opinion, it is just such precipitates that are the "green" luminescence centers in CsBr:Eu²⁺ while the PL at 430 nm is due

most likely to stable and metastable precipitates of EuBr₂ type. The luminescence of similar AC was observed in the mentioned spectral region in ABr:Eu crystals (A = Na, K, Rb) [9]. It is not impossible that one AC type, apparently to the "blue" luminescence (near 490 nm) one, may be associated with formation of Cs₄EuBr₆ nanocrystals, like to formation of the similar Cs₄PbBr₆ in CsBr:Pb [8].

An alternative to the above-discussed types of luminescence AC in CsBr:Eu²⁺ is the formation of dual $\text{Eu}^{2+}-\text{O}^{2-}$ centers [10] where the excess charge of Eu^{2+} ions is compensated by oxygen impurity. At the same time, however, such a model does not explain the complex dependences of the PL spectra on the activator concentration and formation of plural luminescence AC in CsBr:Eu²⁺.

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Особливості утворення центрів фотолюмінесценції у кристалах CsBr:Eu²⁺, вирощених з розплаву

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Досліджено особливості утворення ізольованих дипольних центрів (ІДЦ) типу $\text{Eu}^{2+}-V_{\text{Cs}}$ ("домішка-катионна вакансія") і агрегатних центрів (АЦ) фотолюмінесценції (ФЛ) у кристалах CsBr:Eu²⁺, що обумовлюють ФЛ у спектральній області з максимумами при 435–450 нм і 490–520 нм. Встановлено, що центри ФЛ з максимумами при 490–520 нм утворюються у вузькій області концентрацій Eu^{2+} (0,01–0,1 мол.%) при температурах до 180–200°C. Висловлено припущення, що крім ІДЦ, що відповідають за ФЛ з максимумом при 440 нм, у кристалах CsBr:Eu²⁺ можуть спостерігатися декілька типів АЦ, зокрема, нанокристали сполук CsEuBr₃, Cs₄EuBr₆ і преципітати EuBr₂.