

Time-resolved luminescence spectroscopy study of CsI:Eu crystal

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This paper studies the spectral-kinetic properties of CsI:0.8·10⁻⁴ % Eu, CsI:1·10⁻² % Eu and CsI:3.9·10⁻¹ % Eu crystals. It has been found that spectrum and decay kinetics of photoluminescence depend on concentration of an activator and degree of thermal-dynamic disbalance of CsI:Eu. The emission of all the crystals decays exponentially, but each crystal differs from each other in temperature behavior of the emission decay kinetics. Possible types of the emission centers have been suggested such as single dipole Eu²⁺-v_c⁻, two- and three-dipole clusters of Eu²⁺-v_c⁻ which are responsible for the bands with maxima at 2.69, 2.78 and 2.67 eV, respectively. Criterion for discrimination of the emission centers in CsI:Eu is the temperature behavior of their emission decay kinetics.

Исследованы спектрально-кинетические свойства кристаллов CsI:0,8·10⁻⁴ % Eu, CsI:1·10⁻² % Eu и CsI:3,9·10⁻¹ % Eu. Установлено, что спектр и кинетика затухания фотолуминесценции зависят как от концентрации активатора, так и от степени отклонения состояния кристалла CsI:Eu от термодинамически равновесного. Свечение всех кристаллов затухает экспоненциально, а кинетические параметры затухания по-разному изменяются с температурой. Предложена модель, согласно которой центрами свечения являются одиночные диполи Eu²⁺-v_c⁻, а также их двух- и трех- дипольные кластеры, которые ответственны за полосы с максимумами 2,69, 2,78 и 2,67 эВ соответственно. Критерием дискриминации активаторных центров в CsI:Eu может служить температурное поведение кинетики затухания свечения.

Дослідження кристала CsI:Eu методом люмінесцентної спектроскопії з часовим розділенням. В.Яковлев, Л.Трефілова, Г.Карнаухова, Н.Овчаренко, О.Кісіль.

Досліджено спектрально-кінетичні властивості кристалів CsI:0,8·10⁻⁴ % Eu, CsI:1·10⁻² % Eu і CsI:3,9·10⁻¹ % Eu. Встановлено, що спектр і кінетика загасання фотолумінесценції залежать як від концентрації активатора, так і від ступеня відхилення стану кристала CsI:Eu від термодинамічно рівноважного. Свічення всіх кристалів загасає експоненційно, а кінетичні параметри загасання по-різному змінюються з температурою. Запропоновано модель, відповідно до якої центрами свічення є одиночні диполі Eu²⁺-v_c⁻, а також їхні двох-і трьох-дипольні кластери, що є відповідальними за смуги з максимумами 2,69, 2,78 і 2,67 еВ відповідно. Критерієм дискримінації активаторних центрів у CsI:Eu може бути температурна поведінка кінетики загасання свічення.

1. Introduction

Eu^{2+} ions owing to their aggregation ability can form emission centers of many different types in alkali halide crystals [1, 2]. A lot of investigations have been done to determine spectral-kinetic properties of the emission centers for Eu doped alkali halide crystals with face-centered cubic (f.c.c.) lattice. However, there are few papers dealing with the emission centers in CsI:Eu crystal with simple cubic (s.c.) lattice. This paper aims at identification of the activator emission centers of CsI:Eu and understanding the effect of the activator concentration on aggregation processes of Eu^{2+} ions in CsI lattice.

2. Materials and methods

CsI:Eu boules were grown by the Stockbarger technique in evacuated quartz ampoules at crystallization rate of 3.5 mm/h. Three samples with dimension $\varnothing 13 \times 2 \text{ mm}^3$ were cut from the boules. The samples were kept in a lightless place for six months at room temperature in order to let them reach thermal-dynamic balance. After spectral-kinetic investigation of these samples, they were heated at 650 K in a muffle furnace for one hour and then cooled down to the room temperature at rate 10 K/min, which caused thermal-dynamic disbalance. Hereinafter these samples will be referred to as untreated and treated crystals, respectively.

A nitrogen laser was used to excite luminescence with UV light pulses ($\lambda = 337.1 \text{ nm}$; $t_{1/2} = 5 \text{ ns}$; $Q = 1 \text{ mJ}$). The photoluminescence pulse was registered with an optical spectrometer consisting of MDR-3 monochromator, FEU-106 photomultiplier and GDS-2204 digital oscilloscope. Oscillograms of the luminescence for optical photons with certain energy within the range of 5.0–2.0 eV were obtained at certain temperatures within the range of 80–300 K. The oscillograms were converted into luminescence kinetics curves in order to determine kinetics parameters of the luminescence pulse, as well as to plot its luminescence spectrum at any time delay with 5 ns resolution. The measurement was carried out at temperatures within 78–400 K.

Concentration of Eu in CsI crystals was determined by voltammetry. The classic polarographic method provides the limit quantification of Eu concentration $1 \cdot 10^{-3} \text{ wt. \%}$ evaluated directly for alkali halide crystals [3] and $5 \cdot 10^{-4} \text{ wt \%}$ evaluated indirectly for LiI:Eu [4]. However the obtained level for evaluation of Eu concentration is not

enough to study segregation of Eu in CsI crystals. We used the alternating current voltammetry [5] with the hanging mercury drop electrode in order to increase the sensitivity of Eu determination. Our method provides the limit quantification of $5 \cdot 10^{-5} \text{ wt. \%}$. We measured the Eu anode oxidation current at linear sweep voltage in the range of $-1.25 \dots -0.70 \text{ V}$ (vs. silver chloride electrode) in acetate buffer (pH 5.2) containing ethylenediaminetetraacetic acid. It was revealed that the analysis is not burdened with systematic errors. As for random errors they are characterized by the values of relative standard deviation S_r of $0.03 \dots 0.17$ for europium contents: $4.32 \cdot 10^{-1} \dots 7 \cdot 10^{-5} \text{ wt. \%}$, respectively.

3. Discussion and results

Comparison of $\text{CsI:}8 \cdot 10^{-4} \text{ \%Eu}$, $\text{CsI:}1 \cdot 10^{-2} \text{ \%Eu}$ and $\text{CsI:}3.9 \cdot 10^{-1} \text{ \%Eu}$ samples before and after thermal treatment shows that emission spectra of the samples with low and medium concentration of Eu have dramatically changed, whereas the sample with high concentration has not undergone any material change. Thus, $\text{CsI:}8 \cdot 10^{-4} \text{ \%Eu}$ sample has one band spectrum with maximum at 2.69 eV (461 nm) before thermal treatment and gets two band spectrum with maxima at 2.83 (438 nm) and 2.64 eV (470 nm) after it (Fig. 1a). The sample with $1 \cdot 10^{-2} \text{ \%Eu}$ has one band spectrum with maximum at 2.78 eV (446 nm) before thermal treatment and gets one band spectrum with maximum at 2.69 eV after it (Fig. 1b). The thermal treatment does not affect the spectrum with maximum at 2.67 eV (464 nm) of $\text{CsI:}3.9 \cdot 10^{-1} \text{ \%Eu}$ (Fig. 1c).

Two-week observation shows that the luminescence spectrum of the sample with $8 \cdot 10^{-4} \text{ \%Eu}$ after thermal treatment slowly resumes its initial shape, i.e. the low energy band at 2.64 eV shifts to 2.69 eV, whereas the high energy band at 2.83 eV decays (Fig. 2). The spectra of $\text{CsI:}1 \cdot 10^{-2} \text{ \%Eu}$ and $\text{CsI:}3.9 \cdot 10^{-1} \text{ \%Eu}$ samples remain unchanged during the same period of time.

The analysis of oscillograms (Fig. 3) reveals that the photoluminescence decay kinetics of all the samples before and after thermal treatment fits the following expression

$$I(t) = I_0 \cdot \exp(-t/\tau), \quad (1)$$

where I_0 — emission intensity immediately after excitation pulse depletion, τ — decay constant.

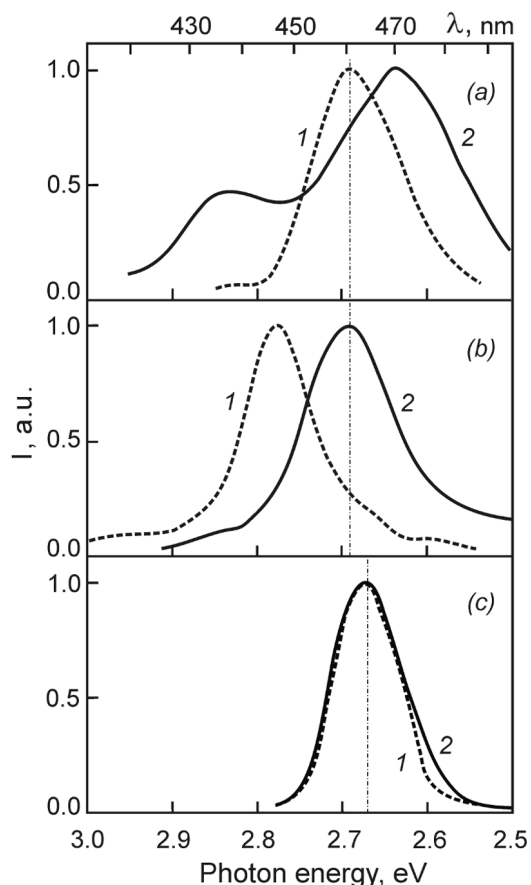


Fig. 1. Luminescence spectra of untreated (1) and treated (2) CsI:Eu. Concentration of Eu (wt. %): *a* — $8 \cdot 10^{-4}$, *b* — $1 \cdot 10^{-2}$, *c* — $3.9 \cdot 10^{-1}$. $T = 78$ K.

We have found that photoluminescence of all the samples decays exponentially in microsecond time scale within temperature interval of 78–400 K which can be resulted by partly allowed electron transitions in Eu^{2+} ion. Fig. 3 verifies this fact for CsI:Eu samples which were subjected for the thermal treatment.

Here we shall try to explain why the untreated crystal with low activator concentration and the treated crystal with medium concentration are similar in luminescence spectra and temperature behavior of the decay kinetics. First of all it is important to determine the emission centers of CsI with low Eu concentration. The studies on $\text{Kl}:1 \cdot 10^{-3}$ %Eu [6] and $\text{KCl}:8 \cdot 10^{-4}$ %Eu [2] show that the emission center is a single dipole $\text{Eu}^{2+}-\text{v}_c^-$, and after thermal treatment of $\text{KCl}:8 \cdot 10^{-4}$ %Eu at 500 K this dipole dissociates into Eu^{2+} ion and cation vacancy v_c^- , and the spectrum of this crystal shifts towards short-wave length region [2].

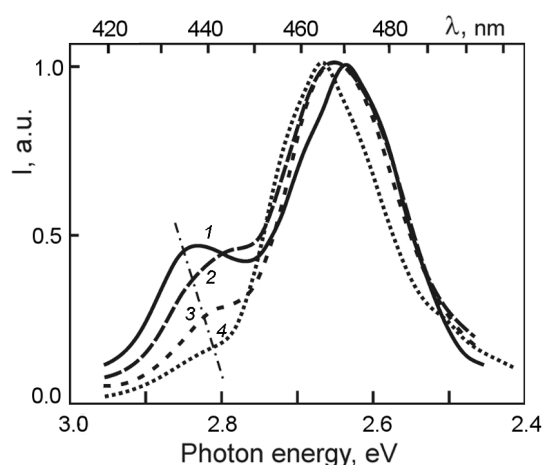


Fig. 2. Luminescence spectra of CsI: $8 \cdot 10^{-4}$ %Eu measured at $T = 78$ K after thermal treatment in 2 (1), 40 (2), 70 (3) and 170 (4) hours.

Therefore, based on the results of these studies we assume that the emission center in CsI: $8 \cdot 10^{-4}$ %Eu is a single dipole $\text{Eu}^{2+}-\text{v}_c^-$. After the thermal treatment of CsI: $8 \cdot 10^{-4}$ %Eu at 650 K its spectrum gets two bands peaking at 2.83 eV and 2.64 eV which can be caused by thermal dissociation of single dipoles $\text{Eu}^{2+}-\text{v}_c^-$ into Eu^{2+} -ions and cationic vacancies which spread throughout the lattice. We think that Eu^{2+} ion unperturbed and perturbed with more than one cationic vacancy causes 2.83 eV and 2.64 eV bands, respectively.

Having cleared up the question with the emission centers in CsI: $8 \cdot 10^{-4}$ %Eu we can now look into similarity in the spectra of CsI: $8 \cdot 10^{-4}$ %Eu before thermal treatment and CsI: $1 \cdot 10^{-2}$ %Eu after thermal treatment. Based on the results shown in Fig. 1, it is logical to assume that single dipole $\text{Eu}^{2+}-\text{v}_c^-$ is responsible for the emission of CsI: $1 \cdot 10^{-2}$ %Eu after thermal treatment. Why does a single dipole arise in CsI: $1 \cdot 10^{-2}$ %Eu sample after the thermal treatment? A possible answer to this question is that Eu concentration in the sample is high enough to give rise only to two-dipole cluster (a simple aggregate) which is responsible for 2.78 eV band. After thermal treatment the two-dipole cluster splits into two single dipoles which are responsible for 2.69 eV band. There is also more evidence that our assumption is sound, namely about the similarity of temperature dependences of emission decay constant for the untreated CsI: $8 \cdot 10^{-4}$ %Eu and the treated CsI: $1 \cdot 10^{-2}$ %Eu (Fig. 4a (curve 1) and Fig. 4b (curve 2), respectively).

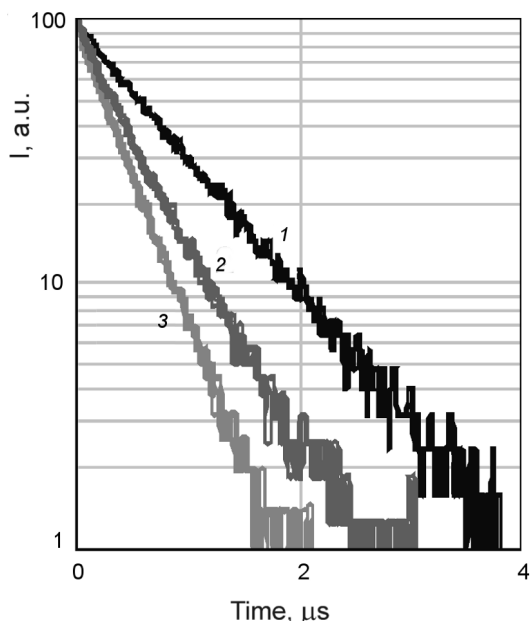


Fig. 3. Oscillograms of luminescence pulse registered at $E_{max} = 2.69$ eV (1), 2.64 eV (2) and 2.67 eV (3) for treated CsI:Eu samples. Concentration of Eu (wt. %): $1 \cdot 10^{-2}$ % (1), $8 \cdot 10^{-4}$ % (2) and $3.9 \cdot 10^{-1}$ % (3). $T = 78$ K.

Fig. 4 shows that the thermal treatment does not affect significantly the decay kinetics of the samples with low and high concentrations of Eu, however it affects dramatically the decay kinetics of the sample with medium concentration of Eu. The emission decay constant of CsI:1·10⁻² % Eu before thermal treatment goes down with temperature according to the Mott's law:

$$\tau(T) = \left[v_i + \omega \cdot \exp\left(-\frac{E_a}{kT}\right) \right]^{-1}, \quad (2)$$

where v_i — frequency of spontaneous radiative transition, ω — frequency factor, E_a — thermal activation energy of non-radiative transition, k — Boltzman constant. The value of these fitting parameters is shown in Table.

The emission decay constant of the treated CsI:1·10⁻² % Eu sample does not undergo any material change at temperatures from 78 to 380 K. Thus, our model of two-dipole cluster is well supported by the likeness of both spectral and kinetics parameters of the emission for the treated CsI:1·10⁻² % Eu sample and the untreated CsI:8·10⁻⁴ % Eu sample.

As mentioned above, cation vacancy v_c^- shifts the emission of Eu^{2+} ion towards the

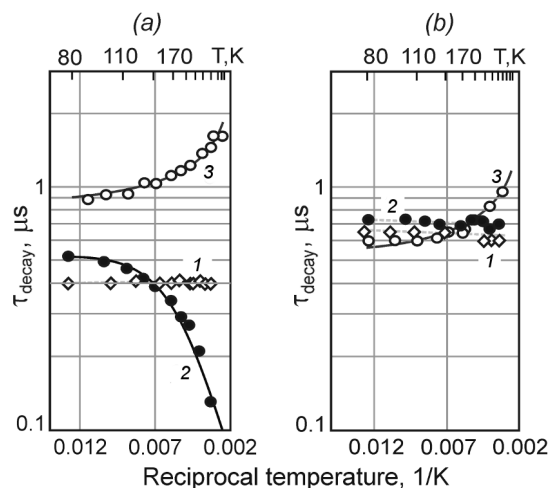


Fig. 4. Photo-scintillation decay constant vs. reciprocal temperature for untreated (a) and treated (b) CsI:Eu samples. Concentration of Eu (wt. %): $8 \cdot 10^{-4}$ % (1), $1 \cdot 10^{-2}$ % (2) and $3.9 \cdot 10^{-1}$

long wavelength region. Since the single dipole and the two-dipole clusters are responsible for 2.69 eV and 2.78 eV emission bands, respectively, we can suggest that cation vacancy has a weaker effect on Eu^{2+} ion in the two-dipole cluster than in the single dipole $\text{Eu}^{2+}-v_c^-$. It means that the distance between Eu^{2+} and v_c^- in the two-dipole cluster determines the energy of radiative transition in Eu^{2+} ion.

Fig. 5 demonstrates all possible configurations of the two-dipole cluster. It is obvious that the configurations C, D and E have the longest distance between Eu^{2+} and v_c^- , therefore we believe that the two-dipole cluster can have either of the configurations suggested. However, our conclusion about the structure of the two-dipole cluster in CsI lattice contrasts with the idea of the authors [7] who state that the plane configuration (A) of the two-dipole cluster is energy efficient in f.c.c. lattice of alkali halide crystals.

The photoluminescence spectrum of the heavily doped sample (Fig. 1c, curves 1,2) is almost similar to the spectrum of the slightly doped sample (Fig. 1a, curve 1). However, in spite of the similarity of the emission spectra, these samples drastically differ in temperature behavior of the emis-

Table. Values of the decay kinetics parameters for expression (2)

v_i, s^{-1}	ω, s^{-1}	E_a, eV
$1.9 \cdot 10^6$	$3.3 \cdot 10^7$	0.048 ± 0.002

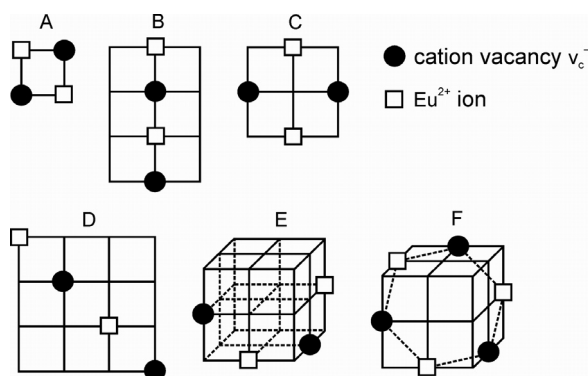


Fig. 5. Possible configurations of a cluster consisting of two dipoles $\text{Eu}^{2+}-\text{v}_c^-$.

sion decay kinetics (curves 1,3 in Fig. 4a,b). The emission decay constant of either treated or untreated $\text{CsI:3.9}\cdot 10^{-1} \% \text{Eu}$ sample defies logical expectations: instead of coming down, it goes up! Such temperature behavior of the emission decay kinetics disagrees with the law of formal kinetics [8]. This anomaly has already been covered in our previous paper [9]. So here we are obliged to refer to our investigation in order to give the explanation of this phenomenon.

According to [10] the exchange interaction governs the spin states of Eu^{2+} ions in the cluster of $(\text{Eu}^{2+}-\text{v}_c^-)$ dipoles. We suggest that owing to the exchange resonance, the energy passes from excited Eu^{2+} ion (donor) to non-excited Eu^{2+} ion (acceptor) in the cluster. The emission decay kinetics of the cluster depends more on the energy exchange rate, rather than on the probability of radiative transition in Eu^{2+} ion itself. The overlap of donor-acceptor wave functions determines the energy exchange rate which exponentially decreases when the distance between the donor and acceptor grows. Probability of the energy exchange can be expressed as:

$$p = \tau^{-1} \sim \exp(-r/a_B) \quad (3)$$

where a_B is half of the Bohr radius.

According to (3) the decay constant grows with the interdipole distance in the cluster of $(\text{Eu}^{2+}-\text{v}_c^-)$ dipoles. In our case the decay constant of 2.67 eV emission grows with temperature, which is probably due to thermal expansion of the crystal. The temperature dependence of the lineal expansion coefficient within 77–400 K fits the lineal function with a proportion coefficient 1.25 [11]. The lattice constant is a minimal distance separating $\text{Eu}^{2+}-\text{v}_c^-$ dipoles from each

other in the cluster. The temperature dependence of emission decay time constant can be expressed as:

$$\tau(T) = A \cdot \tau_0 \cdot \exp\left[\frac{r_0 \cdot (1 + \beta T)}{a_B}\right], \quad (4)$$

where $A = 0.075$ – proportion coefficient, τ_0 – time decay constant, r_0 – lattice parameter at $T = 78 \text{ K}$, $\beta = 0.0035 \text{ K}^{-1}$ – gradient of the temperature dependence in [8], $a_B = 0.15 \text{ nm}$ – half of Bohr radius.

Fig. 4a (curve 3) shows a perfect match of experimental and fitting curves $\tau(T)$, which testifies the soundness of our interpretation. Thus, we can claim that 2.67 eV emission band of $\text{CsI:3.9}\cdot 10^{-1} \% \text{Eu}$ is caused by the cluster in which the exchange interaction of Eu^{2+} ions takes place.

According to the literature, single dipoles aggregate in two- and three-dipole clusters and the higher concentration the more three-dipole clusters arise. We are sure that $\text{CsI:3.9}\cdot 10^{-1} \% \text{Eu}$ has clusters consisting of more than two dipoles since their decay kinetics does not abide by the Mott's quenching law, whereas $\text{CsI:1}\cdot 10^{-2} \% \text{Eu}$ consisting of the two-dipole clusters, as we proved above, abides by this law.

The authors [12] found by means of ionic thermo-currents method that the number of single dipoles $\text{Eu}^{2+}-\text{v}_c^-$ decreases according to the third order kinetics in the aging quenched crystal which means that they aggregate in three-dipole clusters. According to [10], this three-dipole cluster has hexagon configuration which fits our results. This hexagonal configuration (Fig. 6) allows the excitation energy to cycle from one dipole to another one in the cluster.

4. Conclusions

Having investigated spectral-kinetic properties of $\text{CsI:0.8}\cdot 10^{-4} \% \text{Eu}$, $\text{CsI:1}\cdot 10^{-2} \% \text{Eu}$ and $\text{CsI:3.9}\cdot 10^{-1} \% \text{Eu}$ in the balanced and disbalanced thermal-dynamic states, we can sum up our experimental results:

in the balanced thermal-dynamic state all the crystals have one-band spectra with maxima at 2.69, 2.78 and 2.67 eV, respectively and their emission decays exponentially, but each crystal differs from each other in temperature behavior of their decay constant;

in the disbalanced thermal-dynamic state $\text{CsI:0.8}\cdot 10^{-4} \% \text{Eu}$ has two-band spectrum with maxima at 2.83 and 2.64 eV, and

CsI:1·10⁻² %Eu as well as CsI:3.9·10⁻¹ %Eu have one-band spectra with maximum at 2.69 eV and 2.67 eV, correspondingly. The emission of all the crystals decays exponentially. CsI:0.8·10⁻⁴ %Eu and CsI:1·10⁻² %Eu have similar temperature behavior of the decay constant, whereas CsI:3.9·10⁻¹ %Eu has an anomalous temperature dependence of the decay constant, like in the balanced thermal-dynamic state.

Having analyzed the results, we suggest possible types of the emission centers, namely single dipole Eu²⁺-v_c⁻, two- and three-dipole clusters of Eu²⁺-v_c⁻. The bands at 2.69 eV and 2.67 eV are caused by the single dipoles and their three-dipole clusters, respectively. As for the band at 2.78 eV, it is associated with the two-dipole clusters of Eu²⁺-v_c⁻. Although the single dipoles and their three-dipole clusters are responsible for rather similar emission spectrum, they differ in decay time: it remains the same for the single dipoles and grows for three-dipole clusters with temperature.

Thus, the difference in the temperature behavior of decay kinetics can be used as a criterion for discrimination of the emission centers in CsI:Eu and possibly in other alkali-halide crystals doped with Eu.

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