

# Energy transfer in co-doped NaI:(Tl,Eu) crystals

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The energy transfer mechanism in Eu doped and Tl, Eu co-doped NaI crystals is discussed. The self-trapped exciton emission band overlaps stronger with  $\text{Eu}^{2+}$  excitation bands rather than with  $\text{Tl}^+$ . This suggests that transfer  $\text{STE} \rightarrow \text{Activator}$  can be more efficient in  $\text{Eu}^{2+}$  co-doped NaI:Tl crystals. Theoretical estimation of energy transfer efficiency was done based on the Forster model. It is shown that Europium concentration of 1 mass% or above is required for efficient dipole-dipole energy transfer. However, this concentration is not reachable in NaI:(Tl,Eu) due to the solubility limit of  $\text{Eu}^{2+}$  in NaI crystal.

Обсуждается механизм передачи энергии в активированных Eu и соактивированных Tl и Eu кристаллах NaI. Полоса излучения автолокализованного экситона (АЛЭ) перекрывается сильнее с уровнями возбуждения  $\text{Eu}^{2+}$ , чем в случае  $\text{Tl}^+$ . Это говорит о том, что передача АЛЭ  $\rightarrow$  Активатор может быть более эффективной в  $\text{Eu}^{2+}$  соактивированных кристаллах NaI:Tl. Теоретическая оценка эффективности переноса энергии осуществлялась на основе модели Фостера. Показано, что для эффективного диполь-дипольного переноса энергии необходима концентрация европия 1 масс% или выше. Однако, эта концентрация не достижима в NaI:(Tl,Eu) из-за пределов растворимости  $\text{Eu}^{2+}$  в кристалле NaI.

**Перенос енергії в соактивованих кристалах NaI:(Tl,Eu).** С.Грідін, С.Васюков, Н.Шіран, А.Гектін

Обговорюється механізм передачі енергії в активованих Eu і соактивованих Tl та Eu кристалах NaI. Смуга випромінювання автолокалізованого екситону (АЛЕ) перекривається сильніше з рівнями збудження  $\text{Eu}^{2+}$ , ніж у випадку  $\text{Tl}^+$ . Це говорить про те, що передача АЛЕ  $\rightarrow$  Активатор може бути більш ефективною в  $\text{Eu}^{2+}$  соактивованих кристалах NaI:Tl. Теоретична оцінка ефективності переносу енергії здійснювалася на основі моделі Фостера. Показано, що для ефективної диполь-дипольної передачі енергії необхідна концентрація европію 1 мас% або вище. Однак, така концентрація не досяжна в NaI:(Tl,Eu) у зв'язку з межами розчинності  $\text{Eu}^{2+}$  в кристалі NaI.

## 1. Introduction

As it was shown in our previous works, co-doping of NaI:Tl and CsI:Tl classical scintillators with  $\text{Eu}^{2+}$  can improve some scintillation properties. In case of CsI:(Tl,Eu) europium halides added into the melt during the crystals growth as scavengers [1]. This ef-

fect results in suppression of the scintillation afterglow. In case of NaI scintillator presence of  $\text{Eu}^{2+}$  ions in the crystal lattice was found to significantly change its luminescent properties [2]. Besides, the light yield improvement was found in Eu co-doped NaI:Tl crystals [3].

Goal of the present work is to investigate possible mechanisms of the light yield improvement in NaI:(Tl,Eu) crystals. Fluorescent spectroscopy methods were used to study the interaction between the intrinsic and activator-induced emission centers.

## 2. Experimental

The series of NaI:Eu, NaI:Tl and NaI:(Tl, Eu) single crystal boules 25-35 mm in diameter and 100-200 mm in height were grown by the Czochralski method of automated pulling from the melt in controlled reactive atmosphere. Due to the crystals' high hygroscopicity all the processing was performed in the dry boxes only. The Europium concentration in samples was varied from 10-5 to 0.5 mass%  $\text{Eu}^{2+}$  and determined by chemical and absorption methods.

The absorption spectra were measured by means of SPECORD 40 spectrophotometer. Spectral and kinetic characteristics of photoemission were studied using FLS920 combined steady state and fluorescence life-time spectrometer manufactured by Edinb. Instr. Ltd. A Xe900 steady state xenon lamp was used in the continuous mode for UV spectroscopy. The spectroscopic investigation of crystals emission was performed at the SUPERLUMI setup of HASYLAB at DESY (Hamburg, Germany) under synchrotron radiation excitation.

## 3. Results and discussion

Europium concentration in NaI:(Tl,Eu) was varied to obtain a set of samples with different  $\text{Eu}^{2+}$  content. It was found that the increase of europium leads to a significant change in the emission spectrum (Fig. 1). At higher europium concentration than thallium or neighbour concentration the emission spectrum of NaI:(Tl,Eu) crystals contains mostly the  $\text{Eu}^{2+}$  related emission band peaking around 440 nm (Fig. 1, b). Thallium characteristic emission which is normally peaking around 410 nm in NaI:Tl (Fig. 1, a) is strongly suppressed by Eu. Measurements of excitation spectra for  $\text{Eu}^{2+}$  emission (440 nm band) in NaI:(Tl,Eu) reveal the overlap of  $\text{Tl}^+$  emission band with Eu absorption. This overlapping suggests the energy transfer between the activator centers.

Apart the overlapping between  $\text{Tl}^+$  emission and  $\text{Eu}^{2+}$  absorption, the overlap between self-trapped excitons (STE) emission band should be also noted. Low temperature emission of STE is peaking around 300 nm in NaI crystals (Fig. 2). Even though STE

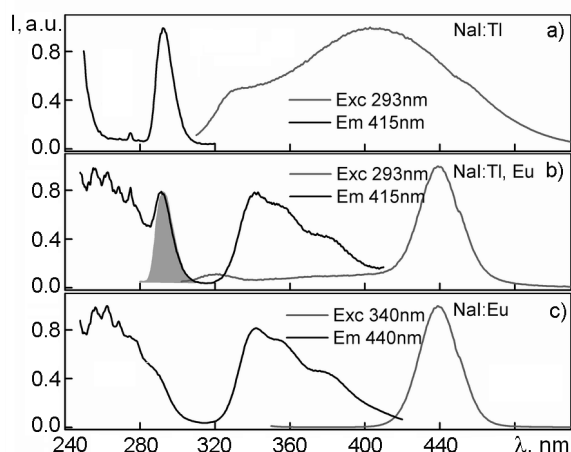


Fig. 1. Excitation and emission spectra of NaI:Tl (a), NaI:(Tl,Eu) (b) and NaI:Eu (c) crystals measured at 300K.

luminescence is quenched at room temperature, non-radiative resonance energy transfer from exciton to activator is still possible. According to Fig. 2, the STE emission band overlaps stronger with  $\text{Eu}^{2+}$  excitation bands rather than with  $\text{Tl}^+$ . This suggests that transfer  $\text{STE} \rightarrow \text{Activator}$  can be more efficient in  $\text{Eu}^{2+}$  co-doped NaI:Tl crystals.

In general, energy from donors to acceptors can be transferred by the non-radiative Forster resonant energy transfer mechanism or by re-absorption of the donors' emission by acceptors. The former mechanism is required for improvement of scintillation properties.

Resonance energy transfer occurs due to multipole Coulomb interaction of the impurity ions in case of overlapping donor luminescence and acceptor absorption lines [4]. Probability of the Forster resonance energy transfer (FRET) can be estimated using the following expression:

$$W = \frac{3\pi\hbar e^4 f_1 f_2}{n^4 m^2 w^2 R^6} \int g_1(E) g_2(E) dE, \quad (1)$$

where  $n$  – refractive index;  $m$  – mass of the electron;  $e$  – electron charge;  $R$  – distance between interacting ions;  $\int g_1(E) g_2(E) dE$  – the overlapping integral of the luminescence spectrum of the donor  $g_1(E)$  and the absorption spectrum of the acceptor  $g_2(E)$  in case of  $\int g_1(E) dE = 1$  and  $\int g_2(E) dE = 1$ ;  $w$  – the average frequency overlap;  $f_1$  and  $f_2$  – the oscillator strengths of the transitions donor and acceptor ions corresponding.

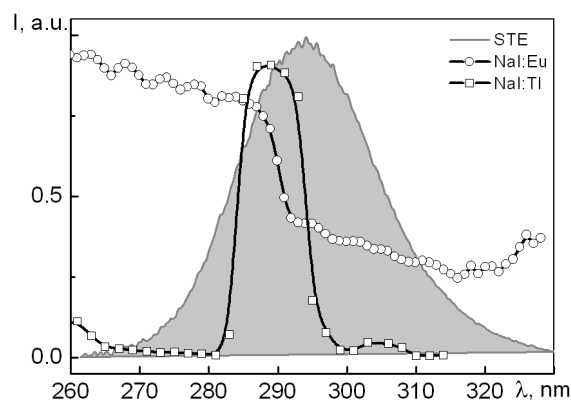


Fig. 2. Emission spectrum of self-trapped excitons in NaI, overlapping with  $\text{Eu}^{2+}$  and  $\text{Tl}^+$  excitation spectra measured at 10K.

FRET efficiency in NaI:(Tl, Eu) can be estimated based on the equation (1) using FRET efficiency in NaI:(Tl, Eu) can be estimated based on the equation (1) using Photochem CAD simulation software. Estimation of dipole-dipole energy transfer efficiency and average distance between ions as function of activators content is shown in Fig. 3. Based on the spectral overlap method used, non-radiative dipole-dipole transfer is possible in case of short donor-acceptor distance  $D$ , less than 3-4 nm (Fig. 3, a). Based on Fig. 3, b europium concentration of  $10^{-1}$  mass% or higher is required to make sure the average distance between the acceptors is 4-5 nm. However, aggregation of europium ions in NaI was observed at Eu concentrations above  $10^{-2}$ – $10^{-1}$  mass% and higher [2]. This suggests that dipole-dipole transition  $\text{Tl} \rightarrow \text{Eu}$  is limited due to poor solubility of  $\text{Eu}^{2+}$  in NaI.

Anyway, energy transfer mechanism  $\text{Tl} \rightarrow \text{Eu}$  is not expected to cause any improvement of light yield observed in [3]. On the other hand, gain in NaI:(Tl, Eu) scintillation efficiency can be explained by the energy transfer from STE to  $\text{Eu}^{2+}$  emission centers. As it was suggested in [5, 6], quenching of STE excited states can be the major reason of energy losses in alkali halide scintillators at RT. In this respect, the energy transfer of exciton to emission centers can be the source of the light yield increase at RT. Since  $\text{Eu}^{2+}$  excitation energy levels coincide with STE emission in NaI (Fig. 2), energy transfer from excitons to Eu emission center is possible. However, efficiency of  $\text{STE} \rightarrow \text{Eu}^{2+}$  transfer is limited by the concentration of activator as shown in Fig 3. In order to fully benefit from this transfer,

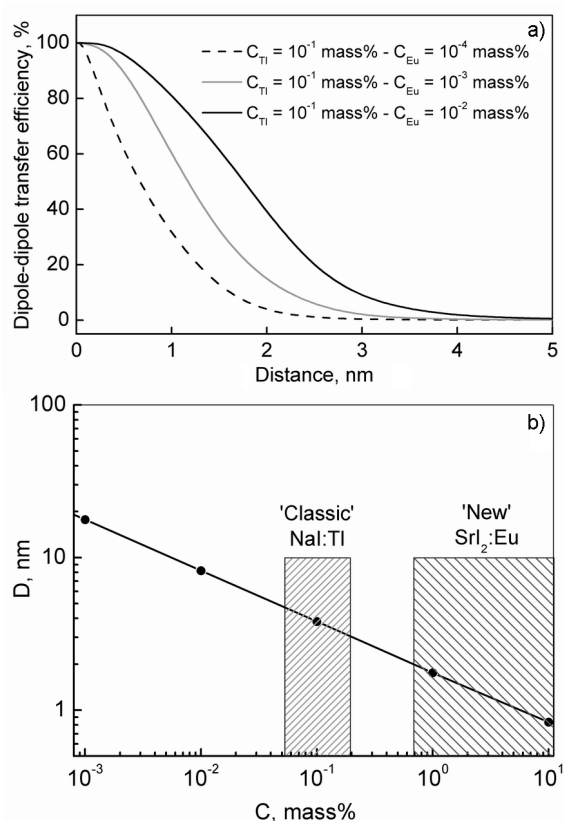


Fig. 3. *a* – Efficiency of dipole-dipole energy transfer mechanism versus distance between ions; *b* – average distance between activator ions as a function of activator concentration. Rectangles marked concentration which achieves good scintillation efficiency for 'Classic' and 'New' materials. The value  $D$  estimated using the following expression:

$$D = \frac{1}{\sqrt[3]{N}}, \text{ where } N - \text{activator ions per cm}^3.$$

Europium concentration about 1 mass% is required (Fig. 3, b). This can be the case for many Eu-doped alkali-earth halide scintillators such as  $\text{SrI}_2:\text{Eu}$ ,  $\text{BaBrI}:\text{Eu}$  etc [7, 8].

#### 4. Conclusions

Improvement of NaI:Tl scintillation yield by europium co-doping is considered. We suggest that emission centers created by  $\text{Eu}^{2+}$  in NaI can benefit from excitonic energy transfer from the crystal matrix. Probability of this transfer is estimated for the case of Forster resonance mechanism. It is shown that europium concentration of 1 mass% or above is required for efficient dipole-dipole energy transfer. However, this concentration is not reachable in NaI:(Tl, Eu) due to the solubility limit of  $\text{Eu}^{2+}$  in NaI crystal.

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