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Luminescence properties of CsI:Eu crystals

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ABSTRACT

The work is aimed to research of CsI:Eu single crystals' luminescence at different excitations in the wide temperature range (from 8 to 300 K) and admixture concentration from 10^{-4}% up to 10^{-1}% of Eu^{2+} ions. This study was directed to separation of different luminescence mechanisms and luminescence quenching explore. It is found that due to the temperature quenching the room temperature yield is decreased in order of magnitude even for heavy Eu doped CsI crystals. Intense low temperature luminescence band at 441–448 nm connected with Eu^{2+} $4f^6\,5d \rightarrow 4f^7$ radiative transition is observed. The results obtained show that the excitonic mechanism plays the main role in energy transfer process to Eu^{2+} ions and this is the reason for relatively low light yield of this emission at RT. The nature of the additional emission bands (410, 450, 480 and 500 nm) are apparently caused by the significant non-isomorphism of cations and/or by the presence of oxygen-containing admixtures.

1. Introduction

Search of new luminescence transformers in general, and scintillator compounds in particular, claim to the new combination of RE doped crystal studies. High efficiency of $4f^6\,5d \rightarrow 4f^7$ Eu^{2+} radiative transition in alkali earth halide crystals leads to appearance of new candidates for radiation detectors [1]. It is significant that thermal and optical stimulated luminescence' parameters of Eu-doped alkali halide crystals (KBr:Eu, RbBr:Eu, CsBr:Eu, etc. [2–4]) correspond well for UV dosimetric and X-ray imaging applications.

At the same time Eu-doped classical scintillation alkali iodide crystals have not been practically studied. If in case of Eu doped NaI crystals luminescence the first publications have appeared recently [5,6], whereas the origin of emission centers in Eu doped CsI, to our knowledge, minimal data have been published [7,8].

It has to be noted a factor influencing on the CsI:Eu crystal properties is the non-isomorphism of the system. The large radii difference between Cs^+ and Eu^{2+} ions with the requirement of charge compensation, limits the formation of CsI–EuI_2 solid solution.

The current work is aimed to research CsI:Eu single crystals' luminescence properties at different excitations in the wide temperature range and admixture concentration.

2. Experimental

Transparent Eu doped CsI crystals with various europium concentrations have been grown from pure anhydrous CsI and EuI_2 salts in evacuated sealed quartz ampoules by Bridgman method as well as in platinum crucible by Czochralski technique in controlled atmosphere. The polished plates of 2 mm thickness were used in spectral measurements. Due to the hygroscopic nature of EuI_2, all processing was performed under dry conditions. Content of Eu^{2+} ions in samples was varied from 10^{-4} up to 10^{-1} mass% of Eu^{2+} and determined by chemical and absorption methods.

The absorption spectra were measured at the room temperature by means of SPECORD 40 spectrophotometer. Spectral and kinetic characteristics of photoemission were obtained using FLS 920 combined steady state and fluorescence lifetime spectrometer. X-ray excited luminescence spectra were measured under cooling condition from 350 K to of 15 K in helium cryostat (X-tube, W-anode, V = 30 keV, A = 30 mA). The spectroscopic investigation of crystals emission was performed at the SUPERLUMI setup of HASYLAB at DESY (Hamburg, Germany) under synchrotron radiation excitation.

3. Results

3.1. Absorption and photoluminescence

Absorption spectrum of CsI:Eu crystal with europium concentration 10^{-3}% consists of two wide bands in the range 250–310 and 330–450 nm (Fig. 1), typical for $^8S_{7/2} \rightarrow 4f^6\,5d$ transitions in Eu^{2+} ions [6,7].

As a result of excitation in this range the luminescence band consisting of intense narrow band with maximum of 441 nm ($H_{1/2}$ = 0.15 eV) and additional one in the range of 500 nm (Fig. 2) is observed. Excitation in short-wavelength region (230–240 nm), corresponding to the fundamental absorption edge, stimulates

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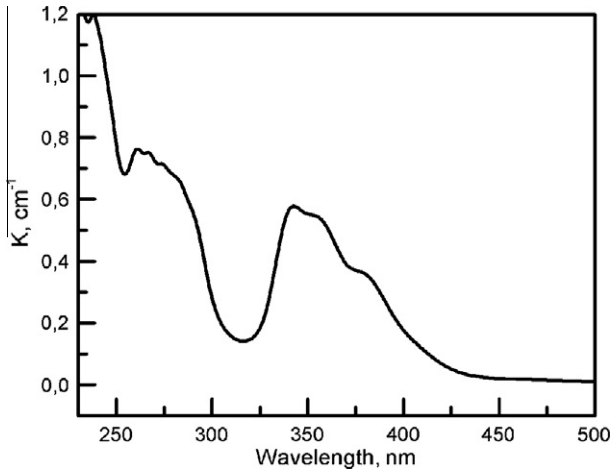

Fig. 1. Absorption spectrum of CsI:Eu crystal (10^{-3}% Eu).

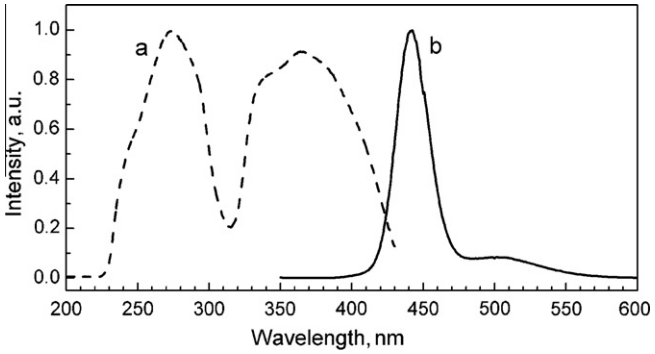

Fig. 2. Excitation of 441 nm emission (a) and luminescence excited by 340 nm (b) of CsI:Eu crystal (10^{-3}% Eu).

the appearance of several emission bands with maxima at 410, 450 and 480 nm, clearly distinguishable by Gaussian components spectral decomposition (Fig. 3). Luminescence spectral content depends on the activator concentration. Increasing the concentration up to $\sim 10^{-1}$% leads to intensity redistribution, and broader band at 465 nm becomes dominating ($H_{1/2}$ = 0.24 eV).

3.2. Photoluminescence kinetics

Under intracenter excitation (340 nm) of CsI:Eu crystal with activator content $\sim 10^{-3}$% the main emission band of 441 nm is characterized by exponential decay with the time constant close to 550 ns (Fig. 4). At high europium concentration ($\sim 10^{-1}$%) the rise stage of 480–500 nm emission is observed, if excitation is performed at the fundamental absorption edge (Fig. 5). At this, the decay time is delayed to 770 ns and the additional component 1.5–3 μs is revealed.

3.3. Temperature peculiarities of radioluminescence

Typical spectra of CsI:Eu radioluminescence measured under samples cooling from 350 to 19 K are demonstrated in Fig. 6. At the ambient temperatures several overlapped peaks at 410, 448 and 484 nm are observed as well as weak UV band (~305 nm). The latter one is the well known intrinsic emission of pure CsI crystal [9–15]. In order to determine temperature dependence, all emission spectra were decomposed on Gaussians and areas under the relative curves were determined. Temperature evolutions of main

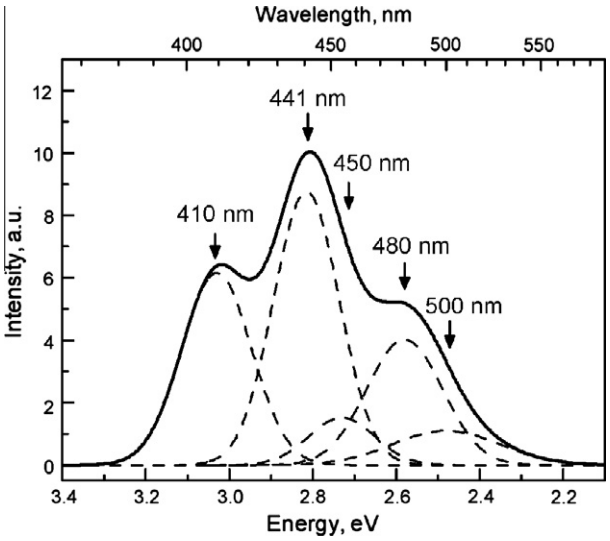

Fig. 3. Luminescence spectra excited by 240 nm of CsI:Eu crystal (10^{-3}% Eu).

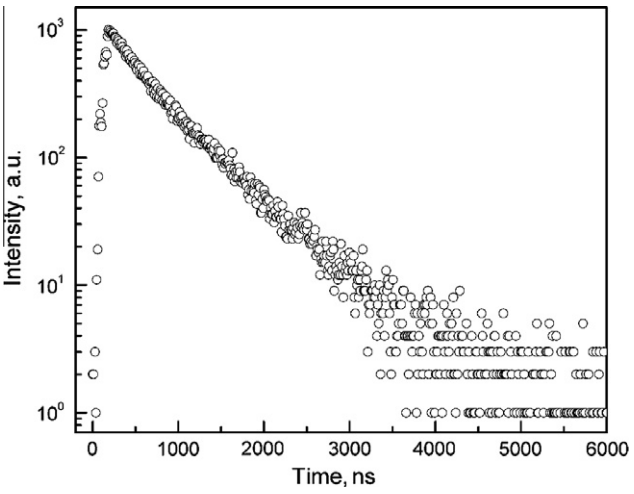

Fig. 4. Decay of 441 nm luminescence band excited by 340 nm in CsI:Eu crystal (10^{-3}% Eu).

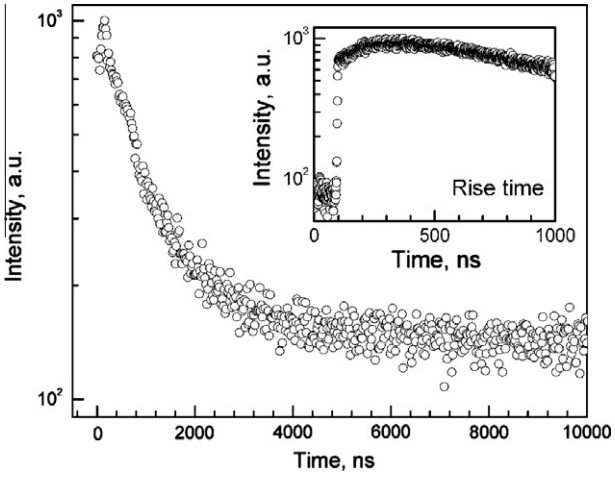

Fig. 5. Kinetics of 550 nm luminescence band excited by 240 nm in CsI:Eu crystal (10^{-1}% Eu).