Scintillation properties deterioration due to hydroxyl and oxygen presence in Eu doped alkali halides

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Introduction

It is known that oxygen traces can significantly change radiation stability, emission spectra, light yield and afterglow level in conventional scintillators [1]. The last trend to development of hygroscopic Eu-doped alkali- and alkali-earth halides claims for an extra pure raw material and dry or vacuum atmosphere during crystal growth and processing [2].

In general the study of oxygen-containing impurity influence on luminescence is an actual problem for conventional and new halide scintillator.

Luminescence study of Eu^{2+} doped CsI crystals deals mainly with the afterglow suppression in CsI(Tl) scintillators [3-6]. Afterglow is usually associated with oxygen-containing impurities. At the same time it was proved that Eu^{2+} ions react with oxygen ions and act as a scavenger in growing process. Along with that, a part of europium ions penetrates into CsI crystal which leads to the formation of emission centers [5].

The entering of Eu^{2+} ions into the CsI lattice requires charge compensation. It may be performed by cation vacancy and/or anion impurity. This was the reason for choosing CsI:Eu crystals as suitable object for Eu^{2+} emission details study.

Materials and methods

CsI:Eu crystals were grown by Czochralski method.

Spectral characteristics of photoemission were studied using FLS920 fluorescence spectrometer. IR-absorption spectra were recorded by Spectrum One FT-IR spectrometer.

X-ray luminescence spectra were measured by X-ray tube (W anode, 30 mA, 30 kV). Irradiation of the samples was realized by X-ray tube (W anode, 10 mA, 150 kV).

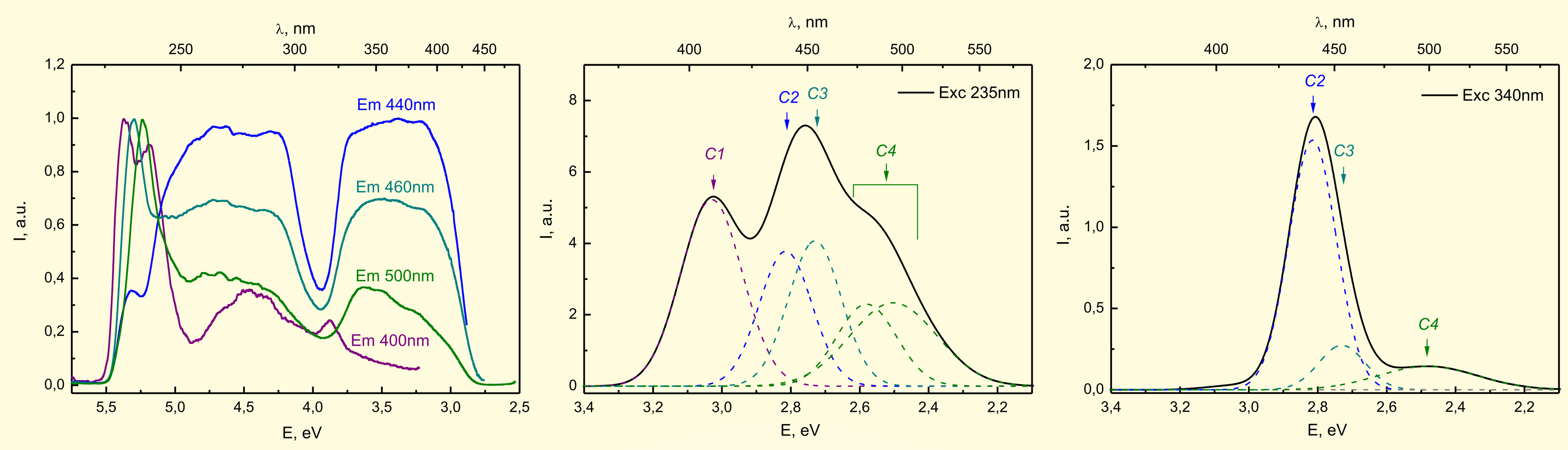
Measurement of thermostimulation luminescent curves was carried out at heating rate of 0.08 K/sec and 0.2 K/sec in the range of 20-350 K and 290-550 K correspondingly.

The aim of the work is to study the luminescence properties deterioration due to hydroxyl / oxygen presence in Eu doped CsI crystals.

Results

The nature of emission centers in CsI:Eu

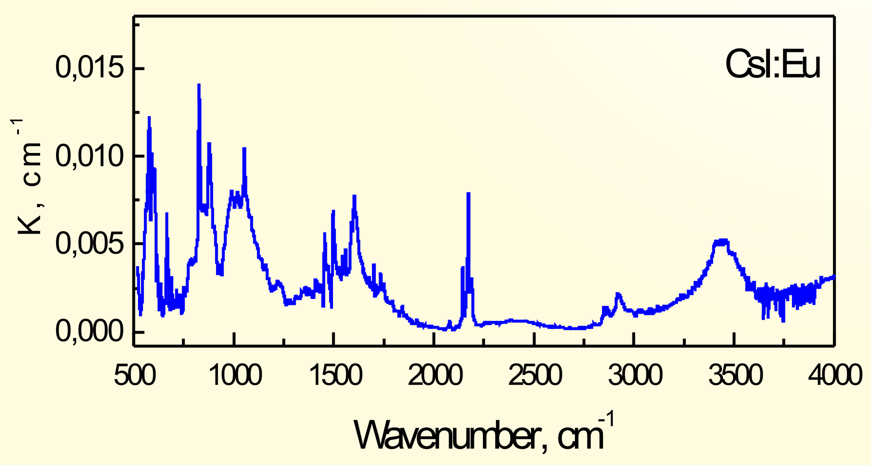
Photo luminescence CsI:Eu (10^{-3} mass%)



Different types of emission centers in Eu doped CsI crystals were observed:
C1 (410 nm), C2 (442 nm), C3 (455 nm), C4 (480-530 nm).

- Luminescence spectra depend on Eu concentration and excitation region.
- *C1 center* is caused by the radiative relaxation at the vacancy type defect, localized near the Eu ion.
- *C2 center* is typical for *d-f* transitions in Eu^{2+}.
- *C3 center* dominates at high concentration (up to 10^{-1} mass%).

IR absorption as an evidance of oxygen containing anions presence



IR bands of H_2O, OH^- were revealed. The total content of oxygen radicals is comparable with the Eu^{2+} concentration in the crystal (10^{-3} mass%).

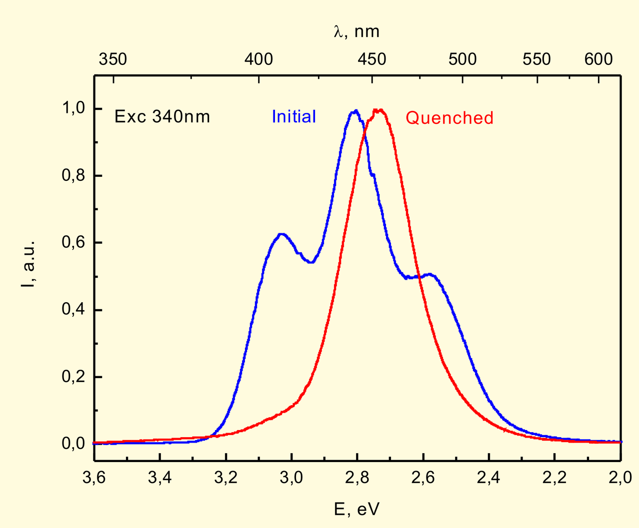
Therefore, it can be assumed that the hydroxyl / oxygen ions may be a part of luminescence centers.

Luminescence centers in CsI:Eu

Center	Photo emission, nm	Supposed nature
C1	410	Eu^{2+} near defect
C2	442	Eu^{2+} (symmetric)
C3	455	Eu^{2+} (H_2O^-) υ_c^-
C4	480-530	O^{2-} / Eu^{2+}-O^{2-}

Heat treatment and radiation influence

Quenching and Annealing

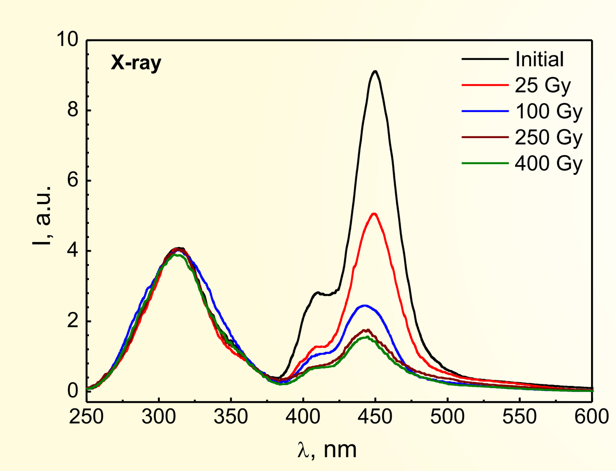


Emission centers in CsI:Eu are stable up to T≈ 300°C. Restructuring or aggregation of centers was not found in treatment process. This fact contradicts the previous concepts on the decisive role of Eu^{2+}-υ_c^- dipoles aggregation in process of storage and low temperature annealing of crystals CsI:Eu [7, 8].

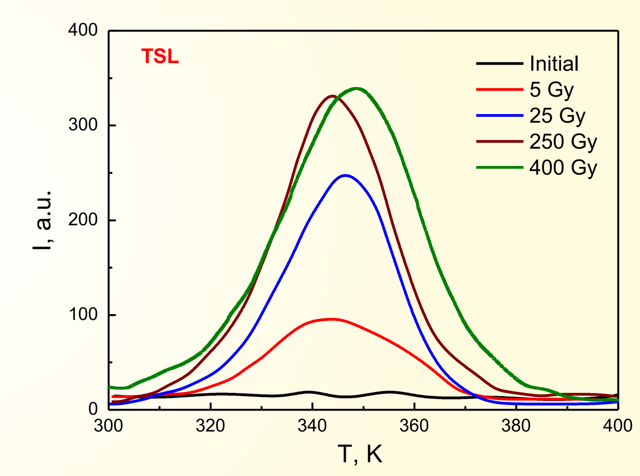
The rise of annealing temperature up to 450°C followed by quenching leads to increase of the *C3 (460 nm)* centers and reduce of *C1 (410 nm)*, *C2 (440 nm)* and *C4 (480-530 nm)* bands.

Irradiation induced effects

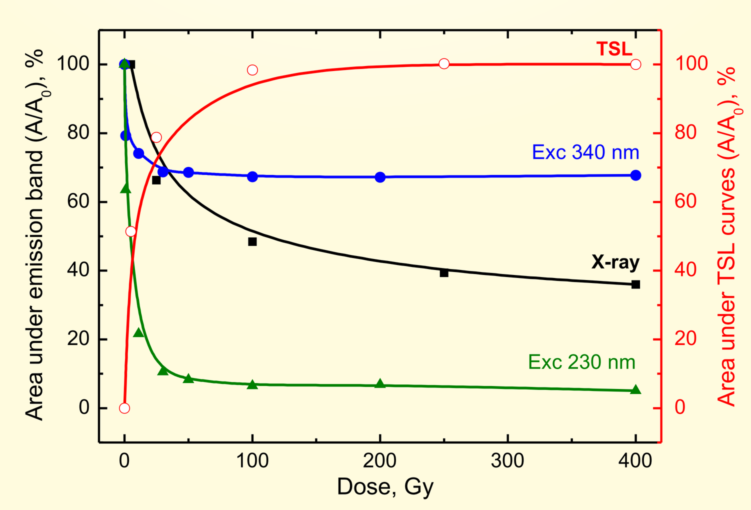
X-ray luminescence



TSL curves



Dose dependences of the luminescence yield of CsI:Eu



- Irradiation leads to the decrease of the integral light output and change of luminescence spectra.
- At the initial stages of irradiation (D < 50 Gy) the most notable is the suppression of C1, C3, C4 centers.
- The higher doses cause the decrease of C1 center.
- Process is accompanied by the TSL peaks emergence and growth, which indicates the formation of intrinsic and activator color centers.

Conclusions

Several types of activator centers were revealed in CsI:Eu crystals. Emission centers are stable at room temperature but their structure and concentration change under heat treatment and irradiation.

The irradiation leads to decrease of emission efficiency related with the charge carriers capturing and restructuring of activator centers. The nature of some emission centers is determined by the presence of intrinsic and extrinsic defects near Eu^{2+} ions.

The dominant luminescent centers include not only vacancies, but also oxygen and/or hydroxyl ions.

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Acknowledgments

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