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 Eu2+-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 Eu2+ 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 Eu2+ 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 Eu2+ emission details study.

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 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 Eu2+ ion.
- C2 center is typical for f–f transitions in Eu2+.
- C3 center dominates at high concentration (up to 10−5 mass%).

IR absorption as an evidence of oxygen containing anions presence

Infrared spectra were recorded by Spectrum One FT-IR spectrometer. IR-absorption bands of H2O, OH− were revealed. The total content of oxygen radicals is comparable with the Eu2+ concentration in the crystal (10−5 mass%). Therefore, it can be assumed that the hydroxyl/oxygen ions may be a part of luminescence centers.

Luminescence centers in CsI:Eu

<table>
<thead>
<tr>
<th>Center</th>
<th>Photo emission, nm</th>
<th>Supposed nature</th>
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</thead>
<tbody>
<tr>
<td>C1</td>
<td>410</td>
<td>Eu2+―OH defect</td>
</tr>
<tr>
<td>C2</td>
<td>442</td>
<td>Eu2+ (symmetric)</td>
</tr>
<tr>
<td>C3</td>
<td>455</td>
<td>Eu2+(H2O)2χ2</td>
</tr>
<tr>
<td>C4</td>
<td>480-530</td>
<td>G2 / Eu2+/O2−</td>
</tr>
</tbody>
</table>

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 Eu2+/O2− 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

Dose dependences of the luminescence yield of CsI:Eu crystals were grown by Czochralski method.

- X-ray luminescence spectra were measured by X-ray tube (W anode, 30 mA, 30 kV).
- Irradiation of the sample was realized by X-ray tube (W anode, 15 mA, 150 kV).
- Radiation induced effects were measured at heating rate of 0.08 K/sec and 2 K/sec in the range of 250–3000 K and 250–5000 K correspondingly.

Dose dependences of the luminescence yield of CsI:Eu

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 Eu2+ ions.

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

Reference:


Acknowledgments

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Materials and methods

CsI : Eu crystals were grown by Czochralski method. Spectral characteristics of photoemission were studied using FLUO3000 fluorescence spectrometer. IR-absorption spectra were recorded by Spectrum One FT-IR spectrometer.

Measurement of thermoluminescence curves was carried out at heating rate of 0.08 K/sec and 2 K/sec in the range of 250–3000 K and 250–5000 K correspondingly.

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