

Carriers trapping and radiative recombination in Ce, Eu and Pr-doped LiLuF₄ crystals

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Received 19 December 2006; accepted 1 February 2007

Abstract

The optical properties of as-grown and X-ray irradiated Ce, Eu and Pr-doped LiLuF₄ crystals, prospective for lasers, display panels, fluorescent lamps and scintillation application, are presented. The luminescence of Ce³⁺-doped crystal exhibits the fast radiative spin-allowed *df* transitions in the UV region, whereas Pr³⁺ containing sample shows the UV *df* and visible *ff* emissions. LiLuF₄:Eu reveals the line emission spectrum of Eu³⁺ ions and the band peculiar to Eu²⁺ ion as well. It was found that the X-ray induced absorption bands and the TSL peak positions are independent of the type of RE³⁺ impurity due to intrinsic nature of radiation defects. The total radiation damage and TSL spectra are specific for each dopant. The distinctive features of the energy storage in RE-doped LiLuF₄ crystals are discussed with respect to redox reaction and level positions of RE ion within the gap.

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Keywords: Ce, Eu and Pr-doped LiLuF₄; Luminescence; Radiation damage; Redox reaction; Colourability

1. Introduction

RE-doped LiLuF₄ crystals were chosen for the present study since they exhibit strong capability in applications such as a substrate for solid state lasers, plasma display panels, mercury-free discharge fluorescent lamps and scintillators. The radiative transitions of Ce³⁺, Pr³⁺, Eu³⁺ ions in the wide gap fluorides were studied (Dorenbos, 2003). It was determined that under irradiation the valence of RE³⁺ ion can be changed. Ce³⁺ ions are known as an electron trapping impurity, Pr³⁺ ions oxidize, transforming into Pr⁴⁺, whereas Eu³⁺ ions capture electrons reducing to Eu²⁺ (Pawlik and Spaeth, 1997; Maslankiewicz et al., 2005; Shiran and Gektin, 2005). The investigations devoted to the energy transfer and particularly to the radiation induced afterglow and colour centre generation in these crystals are restricted. Some data on LiLuF₄:Ce luminescence were announced in Voronova et al. (2005). It is important to compare the carrier trapping and radiative recombination in the same

matrix activated by different RE ions. The aim of this work was to reveal the distinctive features of the energy transformation in Ce³⁺, Pr³⁺ and Eu³⁺-doped LiLuF₄ crystals.

2. Experimental

The high-quality Ce, Pr and Eu-doped LiLuF₄ crystals were grown by the Czochralski technique in CF₄ atmosphere prohibiting the contamination by oxygen (for details see Shimamura et al., 2001). The concentration of RE dopant in the starting material was equal to 1 mol% CeF₃, PrF₃ and 2 mol% EuF₃.

Luminescence measurements were performed using a fluorescence spectrometer FLS 920. Excitation and emission spectra were corrected for experimental distortions. A Specord 40 spectrophotometer was used for optical absorption measurements. The glow curves were detected in a range of 20–400 °C at a constant heating rate of 0.2 °C/s. The thermoluminescence spectra were recorded using a Cary Eclipse spectrofluorimeter. The irradiation was performed by an X-ray tube (160 kV, 10 Gy/min).

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3. Results and discussion

Typical RE³⁺ ions transitions are manifested in the absorption and X-ray excited luminescence spectra of as-grown Ce, Pr and Eu-doped LiLuF₄ crystals (Fig. 1). The emission of Ce³⁺ doped crystal exhibits UV doublet band concerned with the spin-allowed $5d-4f$ transitions. The Pr³⁺ containing sample shows the several UV bands peculiar to $4f5d-4f^2$ transitions as well as narrow lines in the VIS and near IR ranges connected with the spin-forbidden $4f^2-4f^2$ emission. The same spectra were registered in the process of the direct photoexcitation in the main absorption bands.

Luminescence of Eu doped LiLuF₄ crystal reveals the lines in the red range corresponding to the $4f^6-4f^6$ Eu³⁺ transitions and the emission at ~ 412 nm typical for Eu²⁺ ion $4f5d-4f^7$ transitions. The excitation spectrum of blue luminescence shown in the insert of Fig. 1 has the distinctive feature of Eu²⁺ ion. Thus, the europium dopant in as-grown LiLuF₄ crystal is partially in divalent and partially in trivalent state. The same situation was found in LiYF₄:Eu crystal previously (Maslankiewicz et al., 2005).

The shapes of X-ray induced absorption curves for Ce³⁺ and Pr³⁺-doped LiLuF₄ crystals do not practically differ and consist of a number of the overlapped bands (Fig. 2). In the UV region the induced bands strongly recover the activator absorption in LiLuF₄:Ce crystal. In order to clear up their position, the excitation spectrum of colour centre luminescence with the maximum at 540 nm was measured. This emission was found out in irradiated pure LiLuF₄ and assigned to F₂ colour centre (Nikanovich et al., 1988). For irradiated Ce and Pr-doped LiLuF₄, crystal excitation peaks at ~ 200 , 245, 305, 355 and 518 nm become distinctively apparent in spectra presented in Fig. 3. The bands localized in a range of 250–315 nm were presumably connected with F-centres, whereas peaks revealed in 350–550 nm region might be corresponded to aggregates (F_n-centres). Radiation damage was estimated according to the

integral squares under the induced absorption spectra (Fig. 2, insert). The Pr-doped crystal possesses the higher colouration in comparison with Ce-doped one. It allows to assume that in LiLuF₄:Pr the reducing reaction $\text{Pr}^{3+} \rightarrow \text{Pr}^{4+}$ takes place under the irradiation. The similar process was discovered in the Pr-doped fluorides by EPR method (Pawlik and Spaeth, 1997). The hole capture by Pr³⁺ ion leads to electron stabilization and F-centre colouration rises. The electron trapping by cerium (or by defect situated nearby) preferably is realized, whereas the

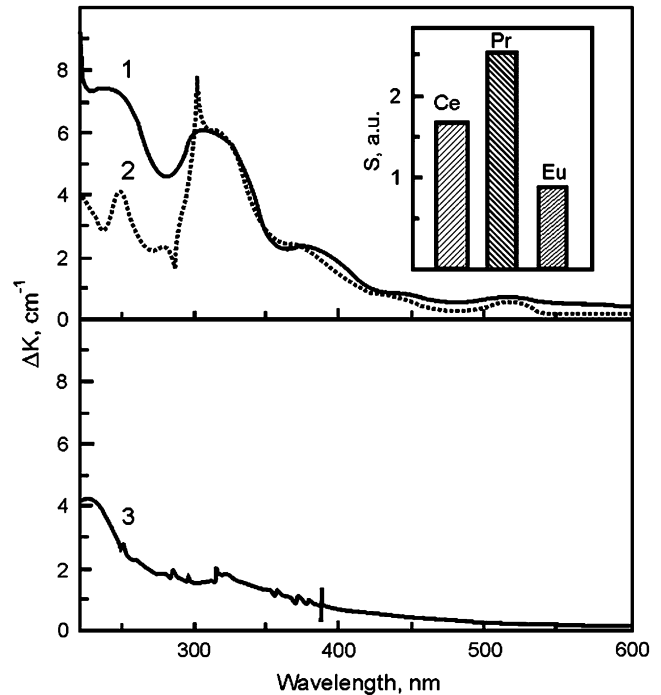


Fig. 2. Induced absorption spectra of Pr (1), Ce (2) and Eu (3)-doped LiLuF₄. Insert: integral squares under the induced absorption spectra. Dose 10 Gy, $T = 300$ K.

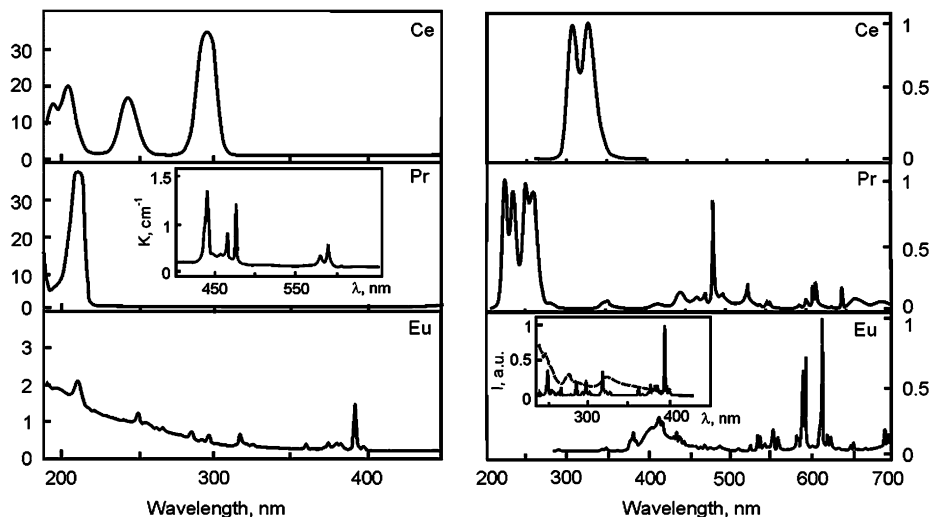


Fig. 1. Absorption (left) and X-ray excited luminescence (right) of Ce, Pr, and Eu-doped LiLuF₄ crystals. Insert: excitation spectra of luminescence $\lambda_{\text{em}} = 613$ nm (solid), $\lambda_{\text{em}} = 413$ nm (dash) for Eu doped LiLuF₄.

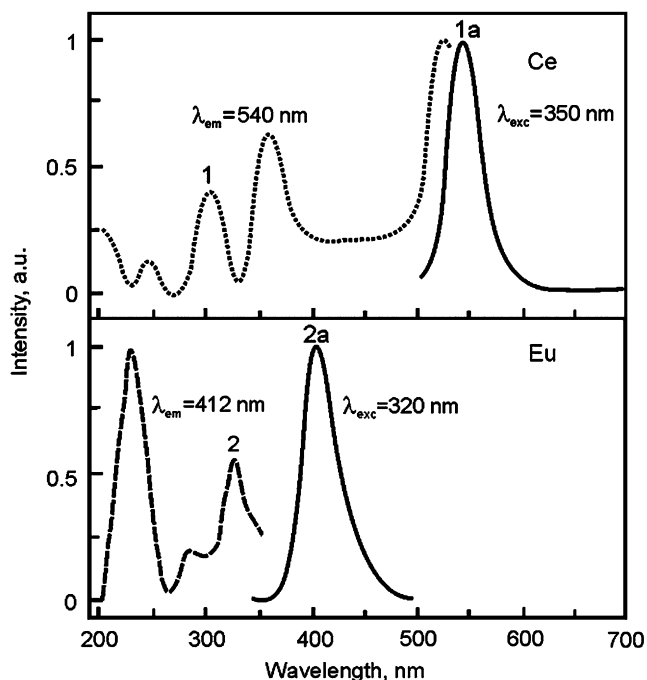


Fig. 3. Excitation spectra and luminescence spectra of Ce (1,1a) and Eu doped LiLuF₄ (2,2a) after X-ray irradiation 50 Gy.

hole capture is less effective in Ce-doped fluorides as a rule (Shiran and Gektin, 2005). The results obtained demonstrate probability of both these processes in LiLuF₄: Ce crystal.

Contrary to Pr and Ce activated crystals, the transparency of irradiated LiLuF₄: Eu changes slightly (Fig. 2). The excitation in the induced weak bands at 230, 285 and 320 nm stimulates the appearance of only blue luminescence specific for the Eu²⁺ ions (Fig. 3).

The relation between Eu²⁺ and Eu³⁺ emission intensities changes with the X-ray dose rise simultaneously: blue band connected with Eu²⁺ ions increases, while the discrete red luminescence of Eu³⁺ decreases. It points to the radiation stimulated reaction of reduction Eu³⁺ → Eu²⁺.

Europium-doped LiLuF₄ crystal sample is less susceptible to colouration than Pr and Ce-doped ones. This feature is related to the electron capture competition between the intrinsic and activator defects. It should be noted that Eu³⁺ substitutes the Lu³⁺ ion without any compensation, while charge of Eu²⁺ ion has to be compensated by the fluorine vacancy. However, these positive defects appearance has to be accompanied by F-centre colouration rise, which was not observed actually. It may be explained assuming the formation of neutral {Eu²⁺v_F⁺} dipole in LiLuF₄: Eu.

It should be noted that the intense phosphorescence was observed in Pr-doped (and to a lesser extent in Ce-doped) samples immediately after the irradiation procedure. Its occurrence indicates the presence of filled traps, being emptied at RT. The subsequent heating leads to the radiative relaxation of irradiated samples followed by the characteristic RE-ion luminescence. The glow curve shapes of Ce, Pr and Eu-doped LiLuF₄ crystals are similar: the main peak is at 100 °C and the weak one is at

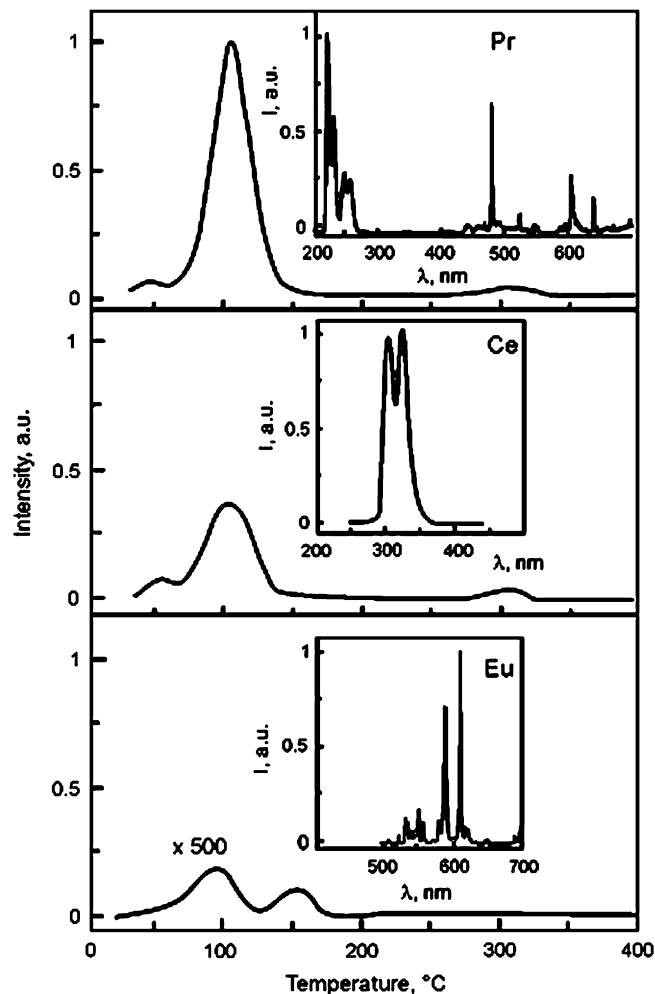


Fig. 4. Glow curves of Ce, Pr and Eu-doped LiLuF₄. 0.5 Gy. Insert: thermoluminescence spectra.

~ 300 °C, whereas the TSL yields significantly differ (Fig. 4). The integral under the TSL curve of LiLuF₄: Pr is two times higher than that of LiLuF₄: Ce and 1000 times higher than that of LiLuF₄: Eu. The spectra of thermoluminescence coincide with the photo- and X-ray excited emission for LiLuF₄: Ce and LiLuF₄: Pr (see Fig. 1). The TL intensity of Eu-doped crystal is too low and so only the most intense *ff* lines of Eu³⁺ ion were detected. Thus, TSL spectral distribution corresponds to the emission of the activator ions, which present the radiative recombination centres in all the considered crystals.

4. Conclusions

The optical properties of as-grown and irradiated Ce, Eu and Pr-doped LiLuF₄ crystals are presented. The luminescence spectrum of Ce³⁺-doped crystal exhibits only the fast radiative spin-allowed *d–f* transitions in the UV region. The Pr³⁺ containing sample shows the *df* and visible *ff* emissions. The Eu doped samples reveal both the typical *df* emission band of an Eu²⁺ ion and the line spectrum of the spin-forbidden *f–f* transitions attributable to Eu³⁺ ion.

It was found that the spectral location of the X-ray induced absorption bands and the TSL peak positions are similar and independent of the type of RE³⁺ impurity due to intrinsic nature of the radiation defects. The total radiation damage and the TL spectra are revealed to be specific for each of the dopants. Thus, Pr-doped LiLuF₄ possesses the essential colourization and afterglow at RT stipulated mainly by oxidation reaction Pr³⁺ → Pr⁴⁺. The electron capture process prevails in a Ce-containing crystal. The colourability and the TSL yield of Eu doped samples are low whereas the reduction reaction Eu³⁺ → Eu²⁺ takes place.

As a whole, the energy storage in Ce³⁺, Pr³⁺ and Eu³⁺ doped LiLuF₄ crystals is determined by the oxidation–reduction reactions and the level positions within a gap peculiar to these ions. The results obtained show the presence of deep traps in the case of LiLuF₄-doped with Ce and Pr, so these crystals have no prospective for scintillation usage. At the same time, the bright visible and near IR luminescence of Pr³⁺ and Eu³⁺ ions observed under the UV and X-ray excitation matches well the sensitivity of the photodiode detectors and CCD cameras. Therefore, LiLuF₄:Pr and LiLuF₄:Eu have future trends to be applied as phosphors for fluorescent lamps and display panels.

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