PHOTOLUMINESCENCE OF NANOCRYSTALS OF $LaPO_4:Eu^{3+}$

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The results of studying the luminescence spectra and its excitation, as well as the luminescence kinetics of the $LaPO_4:Eu^{3+}$ crystal are presented in this paper. Excitation spectra was measured under 337 nm nitrogen laser source and all observed peaks in the range of 230–460 nm were explained by electronic transition of Eu^{3+} ions as well as $LaPO_4$ matrix. Photoluminescence measurements were performed at 337 nm and 393 nm wavelengths for different Eu^{3+} concentrations. Obtained results are comparatively presented. All PL peaks observed in the visible range of the light are explained by electronic transition of Eu^{3+} ions and $LaPO_4$ matrix. Moreover, The emission decay kinetics for the maximum at 590 nm ($^5D_0 \rightarrow {}^7F_1$) were performed under 393 nm pulsed laser and the lifetime of electrons in the traps have been determined.

Keywords: Luminescence, nanocrystals, spectra, excitations, lifetime.
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INTRODUCTION

Rare-earth doped materials are widely investigated by world scientist due to very interesting physical properties, in particular optical properties. These ions create a local emission centers when introduced in host matrix and make a significant changes in physical properties. In particular, rare-earth doped sulfides and oxide[1-4] exhibit high PL emission in the visible region of light which promises great application prospects. Therefore, rare-earth doped materials are traditionally used as phosphors for white LEDs, lasers, displays etc. Depending on the application area, different materials can be a good candidate which used as active media for mentioned areas. Among them, rare-earth doped alkaline earth thiogallates should be especially noted due to very interesting optical properties. Wide bandgap, high emission intensity, high efficiency, extreme stability of photoluminescence spectra in wide range of excitation power density and high stability are characteristic properties these types of materials [5-7]. Although these materials are investigated since the 1970s, new combinations and new characteristics increase interest in these materials day by day. Until recent years, binary and ternary compounds of these types of materials were intensively investigated by world scientists [6-13]. However, it has become known in recent years that more interesting optical properties are observed when alkaline earth ions (or cations) are partially substituted with others. By this way, emission properties can be controlled in the certain wavelength interval.

EXPERIMENTAL

Nanocrystalline orthophosphates were obtained by precipitation with disubstituted ammonium orthophosphate at room temperature from aqueous solutions of nitrate salts of the corresponding metals at pH about 7 [14]. The precipitates were kept in the matrix solution for a day, after which they were washed by decantation, filtered, and dried in air at 110°C.

X-ray phase analysis was carried out using powder diffraction patterns obtained on a DRON-3 X-ray diffractometer (CuKα radiation). These compounds crystallize in the hexagonal crystal system and contain from 0.5 to 3 mol H_2O per formal unit. When heated, they lose water and transform into a monoclinic form of a monazite-type mineral [15].

The size of the nanoparticles was determined by the broadening of the diffraction peaks according to the Scherrer formula and by the method of an EM-125 transmission electron microscope (Usc=75kV).

Photon excitation λ=393 nm was obtained from two types of laser systems: with a pulsed nitrogen laser (Lazer Photonics LN1000, pulse energy - 0.14mJ, pulse frequency 0.6ns) and a dye laser (Lazer Photonics LN 102, RVVO). The reflected beam from the sample was collected using an optical fiber receiver located at a distance of 10 mm perpendicular to the sample surface and analyzed using a spectrometer (Jobin-Ivon Spektrometer HR 460) and a multichannel SDS charge detector for the visible and near-infrared regions of the spectrum. The attenuation spectra were analyzed using a PM Hamamatsu R928 spectrometer for the visible region. Photoluminescence curves were recorded using a PM Hamamatsu R5600 U and Tektronix TDC 784A with a time constant of about 1 ns.

RESULTS AND DISCUSSION

The excitation spectrum of the $La_{0.97}Eu_{0.03}PO_4$ nanocrystal for the band with a maximum at 613 nm is shown in Fig. 1. It is evident that the spectrum covers the wavelength range of 230–460 nm and has several maxima: at 320, 360, 375, 395, 410 nm, etc. The main maximum of the excitation spectrum is in the region of ~395 nm (3.13 eV).

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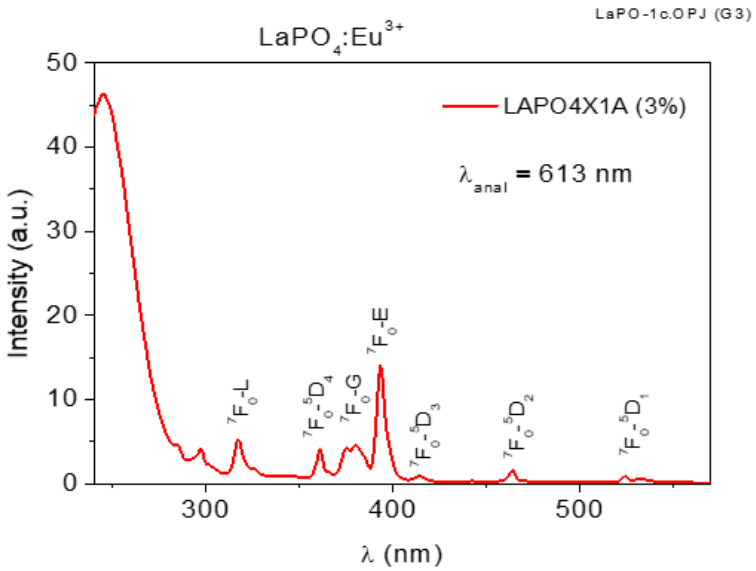

Fig. 1. Excitation spectrum of the $LaPO_4:Eu^{3+}$ nanocrystal.

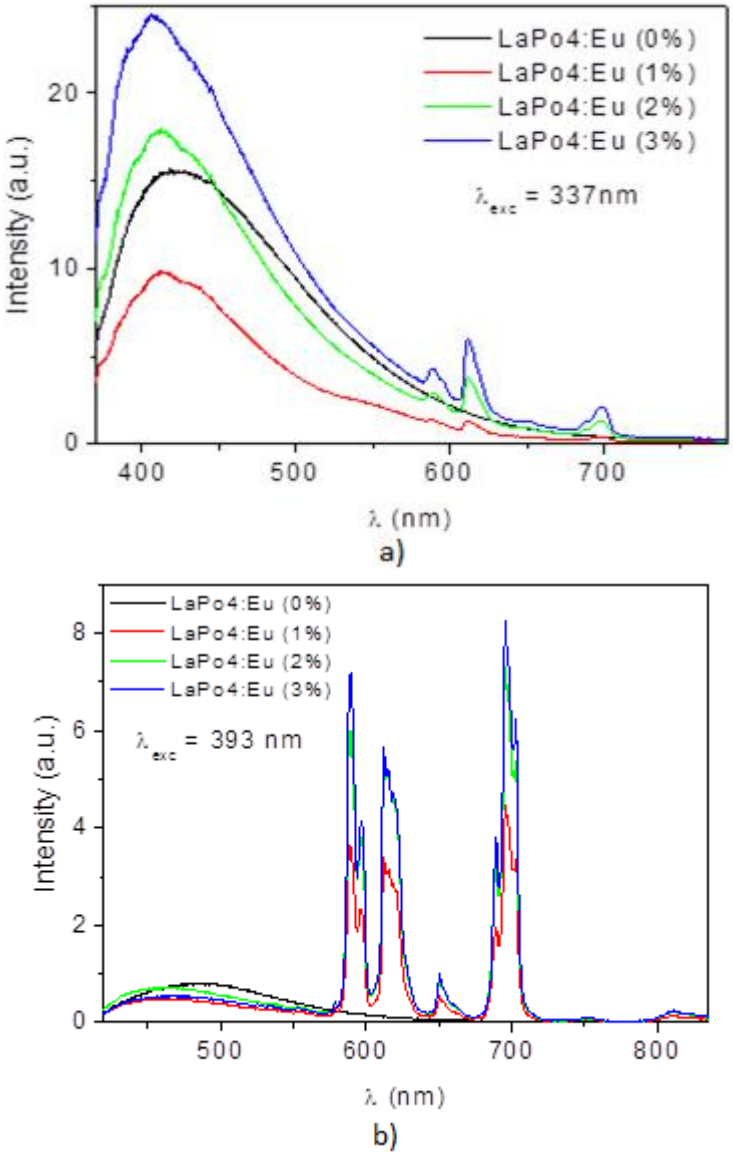

Fig. 2. Luminescence spectrum of the $LaPO_4:Eu^{3+}$ nanocrystal at λ_{ex}=337 nm: a - matrix radiation, b - luminescence spectrum of the Eu^{3+} ion in the $LaPO_4:Eu^{3+}$ crystal.

Figure 1. shows the luminescence spectra of the $LaPO_4$ nanocrystal for various Eu^{3+} concentrations (0, 1, 2, 3%) under conditions of nitrogen laser excitation (λ_{ex}=337 nm) (Fig. 2a) and at a wavelength of 393 nm (Fig. 2b). It evident that the spectrum consists of one intense broad band with emission maxima at 410 nm and a narrow line in the wavelength range of 580–710 nm. This broad band is associated with matrices, and narrow lines are associated with Eu^{3+} ions (Fig. 2b).

These narrow-band emissions, which are observed in the spectra in the wavelength range 580-600nm, 610-630nm, 650-660nm and 680-710nm, are associated, respectively, with the transitions $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ of the Eu^{3+} ion (Fig. 3). The emission intensity increases with the concentration of Eu^{3+} ions and it is maximum at 3 at. %.

The emission decay kinetics for the maximum at 590nm ($^5D_0 \rightarrow {}^7F_1$) at room temperature is shown in Fig.4. Analysis of the obtained results shows that at short times ($t<5x10^{-8}$s) the intensity of photoluminescence (PL) rapidly decreases with time. In this case, the time dependence of the PL intensity for $LaPO_4:Eu^{3+}$ is exponential ($I=I_0e^{-t/\tau}$). We determine the lifetime of electrons in the trap with two values -3ns and 14ns. In [10], a value of 42 ms was found for this decay.

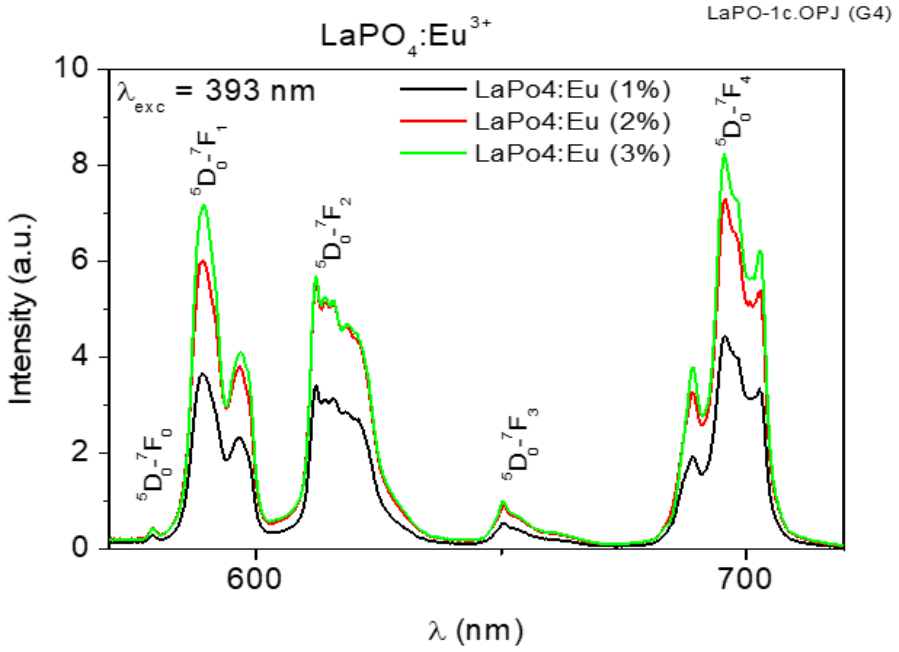

Fig. 3. Luminescence spectrum of the $LaPO_4:Eu^{3+}$ nanocrystal at λ_{ex}=393nm.

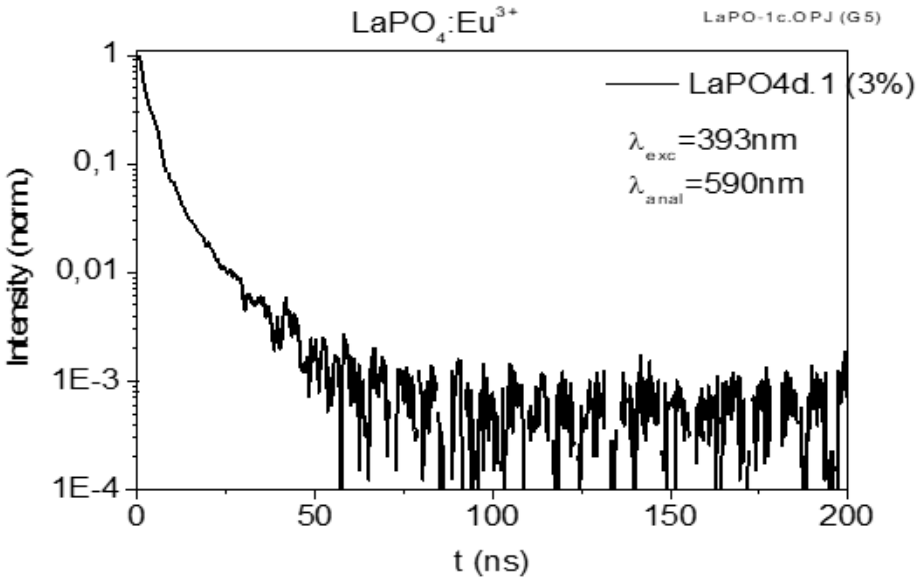

Fig. 4. Time dependence of the emission line of Eu^{3+} ions at 590 nm in a $LaPO_4:Eu^{3+}$ nanocrystal exposed to the 393nm line.

4. CONCLUSION

PL measurements for Eu^{3+} doped $LaPO_4$ were performed at room temperature. It was determined the PL excitation spectra under 337 nm wavelength consist of several narrow peaks due to electronic transition of Eu^{3+} ions and one intense wide band is due to $LaPO_4$ matrix. The main maximum of the excitation spectrum is in the region of ~395 nm (3.13 eV) which corresponds to F-D transition of Eu^{3+} ions. PL emission peaks at 337 nm and 393 nm are observed in the visible range of spectrum. The PL spectra consist of one intense broad band with emission maxima at 410 nm and a narrow line in the wavelength range of 580–710 nm. The broad band is associated with matrices, and narrow PL peaks, in the range 580-600nm, 610-630nm, 650-660nm and 680-710nm, are associated, respectively, with the transitions $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ of the Eu^{3+} ion. The maximum emission intensity is observed at 3 at% doped Eu^{3+} ions. It was determined that the lifetime of electrons in the trap with two values - 3 ns and 14 ns.

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