Quantum efficiency of europium doped $LaPO_4$ phosphors for UV sensing applications

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Abstract—The radiation conversion phenomenon is used for UV sensing applications with rare earth doped phosphors. This paper presents the results of structural and optical measurements of undoped and europium doped $LaPO_4$ phosphors. $LaPO_4$ phosphors with 1% mol, 2% mol, and 5% mol of europium were fabricated by the co-precipitation method. The effect of Eu^{3+} concentrations on the luminescence characteristics under UV LED excitation was investigated. The maximum quantum efficiency of luminescence (c.a. 82%) was obtained in sampled doped with 5% of europium.

Phosphors are chemical compounds that exhibit strong luminescence when exposed to external optical radiation. Usually doped with trivalent lanthanides, they have relatively narrow emission bands. The phosphors may be inorganic chemical compounds including, inter alia: oxides, fluorides or phosphates, doped or composed of rare earth elements. They are resistant to photodegradation, high temperature, oxidation processes, chemical agents, and ultraviolet radiation (UV) [1]. Phosphors doped with lanthanide ions have been investigated as potential materials in the field of high-resolution optical devices. They have found applications in cathode ray tubes, mercury lamps, and electroluminescent displays. Currently, there is a strong increase in research work on the use of nanophosphors in medicine as next generation tools for fluorescence imaging, drug delivery, and image-guided therapy [2–4]. This is especially important in applications where fluorescent nanoparticles can effectively cross physiological barriers to reach target sites and safely enhance the treatment of disease areas (e.g., cancer). The doped phosphors exhibit high energy conversion efficiency, spectral color purity, and high thermal stability.

An important property of nanophosphor is the ability to shape their luminescent properties while maintaining high thermal stability and minimizing optical degradation (UV). Due to limitations associated with low thermal conductivity (0.1–0.2 W/mK) and low thermal stability of phosphors used in commercial light-emitting diode (LED) [5–7], alternative materials and innovative methods of their fabrication are being sought [8]. For this reason, phosphors doped with rare earth ions are used.

One of the rare earths used for doping phosphors is europium. The triple-positive europium ions (Eu^{3+}) are characterized by strong absorption of radiation in the spectral range 300–400 nm, which facilitates their excitation from the ground state using relatively low optical power. This fact effectively enhances the luminescence at a wavelength in the 620 nm band for phosphors doped with Eu^{3+} ions [9]. The characteristic properties of orthophosphate compound $LaPO_4$, such as low toxicity, good physical and chemical stability, very low solubility in water, and high refractive index, make this compound a suitable material for phosphor construction. Orthophosphates are promising materials that can be used as master matrices [10]. Based on studies over the past few years, $LaPO_4$ doped with rare earth ions is useful for producing phosphors that emit radiation in a wide range. Emission of radiation in the visible range is relatively easy to achieve, since introducing Eu^{3+} ions into the parent matrices yields materials with easy excitation by UV radiation [11].

The co-precipitation method is presented as a fabrication technology of $LaPO_4$ nanophosphors undoped and doped with 1% mol, 2% mol, and 5% mol of Eu_2O_3. To synthesize the phosphors there were used: La_2O_3, Eu_2O_3 (Sigma-Aldrich, 99.99%), nitric acid (V), $NH_4H_2PO_4$ (Chempur), and glycerol (Sigma-Aldrich, 99.5%). First, lanthanum oxide and europium oxide were dissolved in nitric acid. The prepared solution was mixed with 75 ml of deionized water and 25 ml of glycerin. Then the mixture was stirred using a magnetic stirrer until the temperature reached 50°C. 50 ml of aqueous ammonium phosphate solution was dropped in the next step. The suspension was stirred for another 30 min while maintaining a constant temperature of 50°C. The next step was to centrifuge the suspension and then the precipitate was washed three times with deionized water and once with ethanol. The precipitate was placed for 48 hours in

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an oven, set at 80°C. Then the finished product was annealed in an oven at 1000°C for 2 hours.

The substrate phosphate glass with nominal molar composition [mol%] $63P_2O_5 - 10Al_2O_3 - 8BaO - 7ZnO - 5Na_2O - 7MgO$ was synthesized by the standard melt-quenching technique. All reagents were characterized by high purity (Sigma-Aldrich, 99.99%). A homogenous set of glass was placed in a quartz crucible and melted in an electric furnace at 1350°C. Next, melts were poured on a stainless brass plate at room temperature (RT), then annealed at 450°C to reduce thermal stresses.

The next step was to cut the produced rod into thick tiles. The tiles prepared in this way were placed on a ceramic stand. Layers of $LaPO_4$ phosphors (undoped and doped Eu_2O_3) homogeneously suspended in ethanol were applied to the top surface of the glass. Upon annealing, the powders fused with the glass surface (Fig. 1). The sintering process was carried out at 830°C for 5 minutes.

The application of nanophosphors on the glass made it possible to carry out luminescence and quantum efficiency measurements. In addition, this provides the opportunity to use an uncomplicated, low-cost method to apply fabricated phosphors in future sensor systems. Three samples doped with different concentrations of europium ions and a reference sample without rare earth dopants were made.

Fig. 1. Picture of fabricated glass samples covered by LaPO4 phosphor.

Measurements of optical properties in the range 350 nm – 750 nm were realized by using a BROADCOM Qmini optical spectrometer and a high-power laser diode emitting optical radiation in the ultraviolet UV range (Fig. 2). The surfaces of manufactured powder on the glass were shown using electron scanning microscopy (SEM). Also, X-ray diffraction (XRD) of samples was measured. XRD measurements at room temperature were performed using an Empyrean Panalytical powder diffractometer equipped with Cu X-ray tube (K_α radiation, $\lambda = 1.540598$ Å).

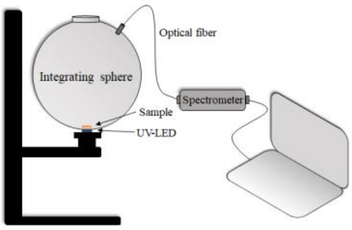

Fig. 2. Quantum efficiency measurement system.

Figure 3 shows a cross-sectional view of the sample with applied phosphor. It was observed that the thickness of the applied phosphor varies from 235 µm to 357 µm. The scatter in the thickness of the phosphor layer is due to the non-uniform particle size of the $LaPO_4$ crystal.

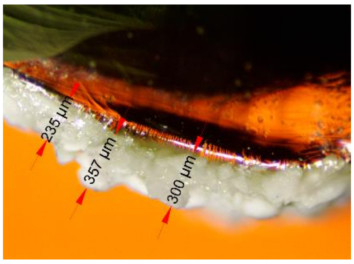

Fig. 3. Microscopy photo of a cross-section of a sample with applied $LaPO_4$ phosphor.

In the SEM image of $LaPO_4$: $5\%Eu^{3+}$ on the glass (Fig. 4.) single crystals of nanometer size and large agglomerates of a few to several micrometers in size can be seen. Also, black spots are visible, probably they are holes in the structure of the material formed by evaporation of one of the compounds in the process of annealing under high temperature.

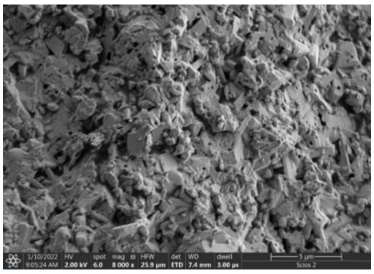

Fig. 4. SEM image of $LaPO_4$: $5\%Eu^{3+}$ on glass.

According to X-ray diffraction (Fig. 5.) measurements, all the fabricated phosphors disclose reflections corresponding to the crystalline phase of the $LaPO_4$ with a monoclinic crystal structure of monazite type ($P12_1/c1$ no. 14). The red line shows the XRD distribution for the substrate glass. The observed broad halo effect confirms the amorphous nature of the fabricated phosphate glass. At the same time, the absence of the halo effect for the deposited phosphors, allows us to conclude that the substrate glass does not change the structural properties of the fabricated $LaPO_4$ phosphors.

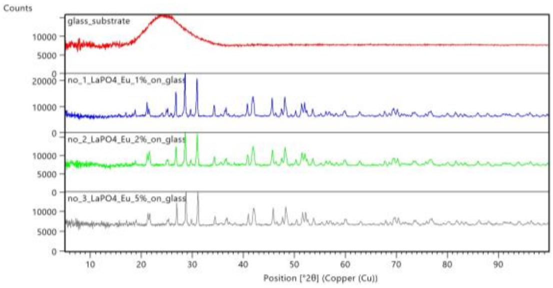

Fig. 5. X-ray diffraction diagrams of glass and $LaPO_4$ phosphors with different % mol content of Eu^{3+} ions.

The luminescence spectra of fabricated phosphors doped with Eu^{3+} ions are shown in Fig. 6. After excitation with radiation in the spectral range 395–405 nm, Eu^{3+} ions have characteristic emission spectra at wavelengths of 585 nm, 595 nm, 612 nm, 651 nm, and 695 nm, which are related to the radiative transition $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$, $^5D_0 \rightarrow {}^7F_4$, respectively. The luminescence intensity increases with an increasing content of Eu^{3+} ions, and the highest luminescence level is observed for the phosphor doped with 5% mol Eu^{3+}. The strongest luminescence for $LaPO_4$ doped europium occurs at 585 nm.

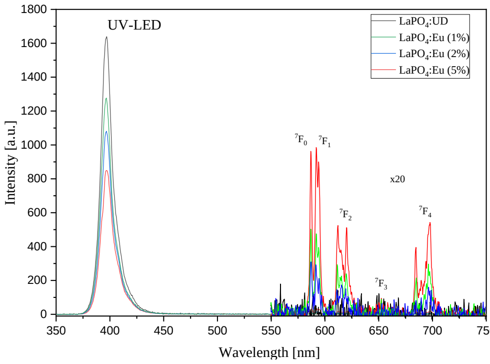

Fig. 6. Emission spectrum for $LaPO_4$ phosphors doped with Eu^{3+} ions recorded at the QE measurement setup.

Equation (1) was used to calculate the quantum yield:

$$QE = \frac{N_{em}}{N_{abs}} = \frac{\int \frac{\lambda}{hc}\left[I_{em}^{pb}(\lambda) - I_{em}^{ref}(\lambda)\right]d\lambda}{\int \frac{\lambda}{hc}\left[I_{ex}^{ref}(\lambda) - I_{ex}^{pb}(\lambda)\right]d\lambda} = \frac{S_2 - 0}{S_0 - S_1} \quad (1)$$

where: N_{em} and N_{abs} are the numbers of photons emitted and absorbed respectively, λ - wavelength, *h* - Planck's constant, *c* - speed of light, *pb* - test sample, *ref* - reference sample, *em* - emission, *ex* - excitation, also S_0 - excitation spectrum, S_1 - scattered photons, S_2 - photons emitted.

Table 1 shows the obtained results of QE calculations for Eu-doped phosphors. The quantum efficiency increases with an increasing active dopant content, for the sample with a 5% mol concentration of Eu^{3+} it is about 82%. In produced samples, luminescence quenching was not observed. However, in our case, the quantum efficiency of fabricated phosphors is similar to the results presented in the literature, where the obtained QE value reaches 90% [12]. The lower value of fabricated samples is related to the inhomogeneity of the powder deposition on the glass. Our technology will be evaluated in future research.

Table 1. Quantum efficiency of fabricated phosphors

No.	**Phosphor**	**Rare earth**	**%mol**	**QE[%]**
1	$LaPO_4$	Eu	1	8.06
2	$LaPO_4$	Eu	2	24.69
3	$LaPO_4$	Eu	5	82.03

Typically, when a phosphor is doped with a large content of another element > 10–12 %, luminescence quenching will occur.

In summary, we have shown the results of structural and optical investigations of $LaPO_4$ samples doped with different contents of europium. It has been presented that luminescence intensity (at excitation in the spectral range 395–405 nm) and quantum efficiency rise with an increasing europium dopant amount. A novel method of thermal deposition of phosphor on glass substrate has been also presented as a possible way to obtain volume samples that can be useful in lighting applications.

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