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White light generation through $Zn(PO_3)_2$ glass activated with Eu^{3+} and Dy^{3+}

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ABSTRACT

A spectroscopic investigation of $Zn(PO_3)_2$ glass activated with Eu^{3+} and Dy^{3+} ions is carried out from photoluminescence data. White light emission is obtained in the glass phosphor, and it is due mainly to europium $^5D_0 \rightarrow {}^7F_2$ and dysprosium $^4F_{9/2} \rightarrow {}^6H_{15/2,13/2}$ emissions, being Eu^{3+} sensitized by Dy^{3+} through a non-radiative energy transfer. Non-radiative energy transfer from Eu^{3+} to Dy^{3+} is also observed upon Eu^{3+} excitation at 414 nm. An electric quadrupole–quadrupole interaction might be the dominant mechanism in the energy transfer among Dy^{3+} and Eu^{3+} ions, as it was revealed from decay time data. The tonality of the white phosphor can be shifted from neutral white (0.364, 0.387) of 4522 K, upon 348 nm excitation, to warm white (0.393, 0.394) of 3811 K, upon 445 nm excitation. Excitations at 348–445 nm range can be attained with InGaN based LED chips, so that Eu^{3+} and Dy^{3+} codoped $Zn(PO_3)_2$ glasses excited by these LED chips could be appropriated for solid state lighting technology as neutral and warm white light sources.

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1. Introduction

Phosphate glasses are very suitable materials as hosts for luminescent trivalent lanthanide ions due to their wide transparency range, isotropic refractive index, low propagation losses and ease preparation, so that they can be used for a great variety of optical devices. In particular, ($Zn(PO_3)_2$) zinc phosphate glasses have been used in optical waveguides, optical amplifiers (as active media for lasers without an optical cavity), optical displays, solid state laser hosts, novel glass-polymer composite materials, long lasting phosphors and white-light-emitting devices. The latter ones are attracting a great interest for applications in both liquid crystal monitor screens and white light emitting diodes (W-LEDs). W-LEDs represent a next generation of lighting lamps [1], and they are of long lifetime, safety, reliability, saving energy and environmental-friendly, which make them very versatile for the replacement of conventional incandescent and fluorescent lamps. One of the most common methods to develop W-LEDs is to couple a near UV emitting LED, such as AlGaN-based LEDs [2], with the glass phosphor [3]. The advantages of the commercial diodes are their reduced size, longevity and mainly low energy consumption. UV-LEDs based on AlGaN are some of the most promising UV sources because the good excitation efficiency of phosphors as well as adequate spectral separation between the UV excitation and the visible emissions. An additional versatility of the zinc phosphate glass is its feasibility to incorporate near UV-blue light-absorbing activators for applications in W-LEDs with near UV-blue LED chips, since zinc phosphate glasses possess a high transparence in the near UV-blue region. Among such activators, Dy^{3+} ions can be activated by near UV-blue light. Moreover, Dy^{3+} ions can act as good sensitizers and transfer a part of their energy to other activator ions such as Tb^{3+} [4,5] or Eu^{3+} [6,7], so that part of the energy in the $^4F_{9/2}$ level of Dy^{3+} is transferred to the $^5D_4$ level of Tb^{3+} or $^5D_0$ level of Eu^{3+}. Additional advantages with Dy^{3+}-doped glass phosphors are the high quantum efficiency associated with negligible multiphonon relaxation because the wide energy gap between the $^4F_{9/2}$ emitting level and the next $^6F_{1/2}$ level lying lower ($\sim 7200\ cm^{-1}$), as well as the four-level laser scheme favorable for low-threshold laser operation. The Dy^{3+} ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) yellow emission is a hypersensitive (forced electric–dipole) transition, and its intensity exhibits a strong dependence on the ligand environment, whereas the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ blue emission is insensitive to the host. Thus, the yellow-to-blue (Y/B) emission intensity ratio can vary significantly in different hosts.

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Besides such *Y*/*B* ratio plays an important role in tuning the chromaticity coordinates in CIE1931 diagram, if the *Y*/*B* ratio is larger or less than the unity, then the glass phosphor can be suitable for laser light generation in the spectral region yellow [8,9] or blue [10,11], respectively. According to all these perspectives and considering the importance of finding efficient luminescent materials for the design of optical devices as white light sources based on zinc phosphate, here we report a spectroscopic investigation of Eu^{3+} and Dy^{3+} codoped $Zn(PO_3)_2$ glass focused on the generation of white light. A non-radiative energy transfer takes place among Dy^{3+} and Eu^{3+} ions.

2. Experimental

The molar composition of the zinc phosphate glasses studied was $99.0Zn(PO_3)_2$–$1.0Eu_2O_3$, $99.5Zn(PO_3)_2$–$0.5Dy_2O_3$ and $98.5Zn(PO_3)_2$–$1.0Eu_2O_3$–$0.5Dy_2O_3$, which will be referred hereafter as ZPEu, ZPDy and ZPEuDy, respectively. These glasses were prepared by mixing appropriate quantities of ZnO (Aldrich 99+%), $NH_4H_2PO_4$ (Carlo Erba RPE), Eu_2O_3 (Aldrich 99.999%) and Dy_2O_3 (Aldrich 99.99+%) in a sintered alumina crucible, and melting the composition for 2 h at 1250 °C. The melts were quenched onto a copper plate. The glasses are fully amorphous and transparent in bubble-shape of 6–7 mm in diameter with a maximum thickness of 4 mm. Thus, cut and polish were not necessary for photoluminescence measurements; however, they were annealed for 12 h at 350 °C to obtain thermal and structural stability.

Photoluminescence spectra were recorded by means of a Horiba Jobin-Yvon Fluorolog 3–22 spectrofluorometer equipped with a 150W ozone-free Xe lamp for the steady state mode and with a pulsed Xe lamp for decay time measurements. Decay time profiles were recorded in the phosphorescence mode with a delay time of 0.01 ms after the excitation pulse (3 μs half-width) and a 5 ms sample window. All the measurements were recorded at room temperature.

3. Results and discussion

The emission spectra of the (ZPEuDy) Dy^{3+} and Eu^{3+} codoped $Zn(PO_3)_2$ glass excited at 348 and 445 nm into the dysprosium $^6H_{15/2}\rightarrow{}^4M_{15/2}$, $^6P_{7/2}$ and $^6H_{15/2}\rightarrow{}^4I_{15/2}$ (excitation) absorption bands, respectively, are shown in Fig. 1. Excitations at 348 and 445 nm perfectly match the output wavelengths of InGaN based LED chips [12]. Thus, the ZPEuDy phosphor could be suitable for use in white lighting devices based on InGaN LED chips. Although Eu^{3+} cannot be excited at 348 and 445 nm, as it can be appreciated from the

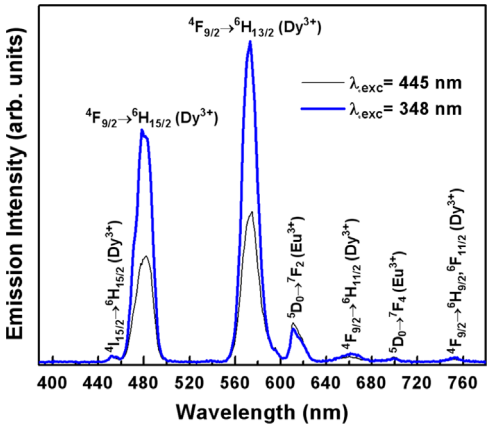

Fig. 1. Emission spectra of the ZPEuDy glass excited at 348 and 445 nm.

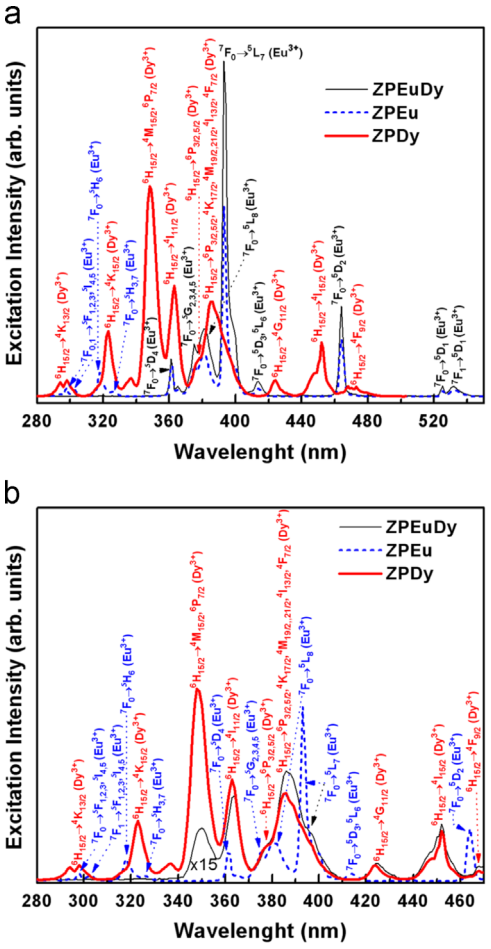

Fig. 2. (a) Excitation spectra of the glasses ZPEuDy (λ_{em}=615 nm), ZPEu (λ_{em}=615 nm) and ZPDy (λ_{em}=573 nm). (b) Excitation spectra of the glasses ZPEuDy (λ_{em}=480 nm), ZPEu (λ_{em}=615 nm) and ZPDy (λ_{em}=573 nm).

excitation spectrum monitored at 615 nm for the ZPEu glass (Fig. 2), emissions from its $^5D_0$ level to $^7F_2$ and $^7F_4$ manifolds are observed in addition to dysprosium $^4I_{15/2}\rightarrow{}^6H_{15/2}$, $^4F_{9/2}\rightarrow{}^6H_{15/2,13/2,11/2,9/2}$ and $^4F_{9/2}\rightarrow{}^6F_{11/2}$ emissions. This fact evidences that Dy^{3+} sensitizes the Eu^{3+} emission. The most intense emissions are observed for the yellow ($^4F_{9/2}\rightarrow{}^6H_{13/2}$) and blue ($^4F_{9/2}\rightarrow{}^6H_{15/2}$) transitions of $Dy^{3+}$and red ($^5D_0\rightarrow{}^7F_2$) transition of Eu^{3+}. The yellow-to-blue (*Y*/*B*) emission intensity ratio increases from 1.32 up to 1.45, and the yellow-to-red (*Y*/*R*) emission intensity ratio decreases from 12.7 up to 5.8, upon excitations at 348 and 445 nm, respectively. These variations in the *Y*/*B* and *Y*/*R* ratios with the excitation wavelength affect strongly the chromaticity coordinates of the phosphor global emission as being discussed below.

Fig. 2 shows excitation spectra of the ZPEuDy glass monitored into the Eu^{3+} ($^5D_0\rightarrow{}^7F_2$) 615 nm (Fig. 2(a)) and Dy^{3+} ($^4F_{9/2}\rightarrow{}^6H_{15/2}$) 480 nm (Fig. 2(b)) emissions. In both spectra, the excitation ones of the ZPDy and ZPEu singly-doped glasses monitored into the Dy^{3+} ($^4F_{9/2}\rightarrow{}^6H_{13/2}$) 573 nm and Eu^{3+} 615 nm emissions, respectively, are also shown for comparison. In the Eu^{3+} excitation spectrum of the codoped glass (Fig. 2(a)) the europium $^7F_0\rightarrow{}^5H_6$, $^5H_{3,7}$ and $^7F_{0,1}\rightarrow{}^5F_{1,2,3}$, $^5I_{4,5}$ excitation bands, overlapping with the dysprosium $^6H_{15/2}\rightarrow{}^4K_{15/2}$ and $^6H_{15/2}\rightarrow{}^4K_{13/2}$ excitation transitions, respectively, are completely quenched. In the Dy^{3+} excitation spectrum of the codoped glass (Fig. 2(b)) the dysprosium $^6H_{15/2}\rightarrow{}^4K_{15/2}$ and $^6H_{15/2}\rightarrow{}^4K_{13/2}$ excitation bands, overlapping with the europium $^7F_0\rightarrow{}^5H_6$, $^5H_{3,7}$ and $^7F_{0,1}\rightarrow{}^5F_{1,2,3}$, $^5I_{4,5}$ excitation transitions, respectively, are also completely quenched. The quenching of Eu^{3+} and Dy^{3+} excitation bands can be attributed to cross relaxation processes among

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