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Green to white tunable light emitting phosphors: Dy^{3+}/Tb^{3+} in zinc phosphate glasses

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ABSTRACT

Dy^{3+}/Tb^{3+}-doped zinc phosphate glasses of composition in mol.%: 98.0Zn$(PO_3)_2$–2.0Dy_2O_3, (100.0−x)Zn$(PO_3)_2$–$x$$Tb_2O_3$ and (98.0−x)Zn$(PO_3)_2$–2.0Dy_2O_3–$x$$Tb_2O_3$, $x = 0.6$, 1.0, 2.0 and 5.0, were prepared by conventional melt quenching technique, and characterized by photoluminescence and decay time spectroscopy. The emission color can be adjusted from neutral white of 4279 K (98.0 Zn$(PO_3)_2$-2.0 Dy_2O_3 glass) toward the green region by codoping with Tb^{3+} from 0.6 to 5.0 mol% of Tb_2O_3 upon Dy^{3+} excitation at 392 nm. The Tb^{3+} emissions ($^5D_4 \rightarrow {}^7F_{6,5,4,3}$) being sensitized by Dy^{3+} through a non-radiative energy transfer. Dysprosium $^4F_{9/2}$ level emissions can also be sensitized through excitation of Tb^{3+} at 284 nm with an efficiency up to of 80%. Additionally, upon 284 nm excitation dominant $^5D_4 \rightarrow {}^7F_5$ green emission in detriment of the $^5D_3 \rightarrow {}^7F_J$ blue one is promoted by a cross relaxation process between Tb^{3+} and Dy^{3+} in addition to that among Tb^{3+} ions. In consequence, the most intense green emission observed in the ZP2Dy5Tb phosphor gives rise to a color purity of 67.8% and chromaticity coordinates (0.29, 0.59) very close to those (0.29, 0.60) of European Broadcasting Union illuminant green. Such cross relaxation processes enhancing the green emission of Tb^{3+} with ultraviolet excitation might contribute to increment the spectral response of solar photovoltaic cells by down-shifting of the incident solar spectrum.

1. Introduction

Nowdays, the finding of phosphor materials pumped by ultraviolet (UV) light emitting diodes (LEDs) has been the subject of intense research due to the necessity of increasing the efficiency in white light emitting solid state devices for application in next generation lighting lamps [1]. Phosphate glasses are very appropriate materials as hosts for luminescent trivalent rare earth ions because of their wide transparency range, isotropic refractive index, low propagation losses and above all ease to prepare. Such features of phosphate glasses make them suitable for a great variety of optical devices. In addition, trivalent rare-earth ions exhibit a characteristic intra-4f shell luminescence making them nearly independent of host material. In particular, zinc phosphate glasses have been used as solid state laser hosts, solders and welds between metallic parts and glassy in electronic circuits and television tubes because their thermal expansion coefficients are similar to those of many metals. Zinc phosphate glasses have also been used in optical amplifiers (as active media for lasers without an optical cavity), optical waveguides, optical displays, novel glass–polymer composite materials, long lasting phosphors and white-light-emitting devices. The latter ones are of great interest for applications in both liquid crystal monitor screens and white light emitting diodes (W-LEDs). All these applications of the zinc phosphate glass are possible to the zinc, because of its good chemical durability, wide glass-forming compositional range, low glass transition temperature, and particular property of acting as a network modifier/former. W-LEDs are considered to be fourth-generation lighting sources because of their long lifetime, reliability, safety, saving energy, high luminous efficiency, good stability, fast response and environmental-friendly by absence of toxic mercury, which make them very versatile for the replacement of conventional fluorescent and incandescent lamps [2]. One of the methods to develop W-LEDs that is gaining great acceptance, due to its high potential of tuning the emitted color, has been to couple near-ultraviolet (NUV) emitting LEDs with a glass phosphor, which converts the LED light to white light [3]. NUV-LEDs based on AlGaN [4], GaN [5], InGaN [6] and InGaN/AlGaN [7] are some of the most suitable NUV sources because of their high excitation efficiency of phosphors as well as

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appropriate spectral separation between the NUV excitation and visible emission. NUV light-absorbing ions can be doped in zinc phosphate glasses for applications in W-LEDs with NUV-LED chip considering that these glasses possess a high transparence in the NUV region [8]. Among the dopant ions, Dy^{3+} ions can act as good sensitizers of the NUV radiation to activator ions such as Tb^{3+} [9–11], Eu^{3+} [11–14] and Sm^{3+} [15]. Considering the importance of finding efficient white phosphors based on zinc phosphate, here it is reported a spectroscopic investigation of $Zn(PO_3)_2$ glass activated with Dy^{3+}/Tb^{3+} ions as function of the Tb^{3+} concentration to generate light emissions white and green upon UV excitation, which are useful for producing white LEDs and as luminescent concentrator for solar cell applications, respectively.

2. Experimental

The molar compositions of the zinc phosphate glasses activated with Dy^{3+}, Tb^{3+} and Dy^{3+}/Tb^{3+} ions were 98.0 $Zn(PO_3)_2$-2.0 Dy_2O_3, 99.4 $Zn(PO_3)_2$-0.6 Tb_2O_3, 99.0 $Zn(PO_3)_2$-1.0 Tb_2O_3, 98.0 $Zn(PO_3)_2$-2.0 Tb_2O_3, 95.0 $Zn(PO_3)_2$-5.0 Tb_2O_3, 97.4 $Zn(PO_3)_2$-2.0 Dy_2O_3-0.6 Tb_2O_3, 97.0 $Zn(PO_3)_2$-2.0 Dy_2O_3-1.0 Tb_2O_3, 96.0 $Zn(PO_3)_2$-2.0 Dy_2O_3-2.0 Tb_2O_3 and 93.0 $Zn(PO_3)_2$-2.0 Dy_2O_3-5.0 Tb_2O_3, which will be referred as ZP2Dy, ZP06Tb, ZP1Tb, ZP2Tb, ZP5Tb, ZP2Dy06Tb, ZP2Dy1Tb, ZP2Dy2Tb and ZP2Dy5Tb, respectively. The glasses were prepared by mixing appropriate quantities of ZnO (Aldrich 99+%), $NH_4H_2PO_4$ (Aldrich 99+%), Tb_2O_3 (Aldrich 99.99%) and Dy_2O_3 (Aldrich 99.99+%) in a sintered alumina crucible and melting the composition for 2 h at 1100 °C. The melts were quenched onto a copper plate. The glasses resulted to be fully amorphous and transparent in bubble-shape of 5–6 mm in diameter with a maximum thickness of 3 mm, so that cutting and polishing were not required for photoluminescence measurements. The glasses were annealed for 12 h at 350 °C to attain structural and thermal stability.

The photoluminescence spectra of the glass phosphors were recorded by using a Horiba Jobin-Yvon Fluorolog 3-22 spectrofluorometer equipped with double excitation monochromators, a 450 W ozone-free Xe lamp for the steady state mode and a pulsed Xe lamp for the phosphorescence mode. 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 5–10 ms sample windows.

3. Results and discussion

3.1. Photoluminescence upon 392 nm excitation

The emission spectra of zinc phosphate glasses codoped with 2.0 mol% of Dy_2O_3 and different contents of Tb_2O_3 (0.6–5.0 mol%) upon excitation into the Dy^{3+} ($^6H_{15/2} \rightarrow {}^4K_{17/2}, {}^4M_{19/2,21/2}, {}^4I_{13/2}, {}^4F_{7/2}$) band at 392 nm are shown in Fig. 1. Excitation at 392 nm matches well with the emission of InGaN LEDs [6]. At this wavelength (25,510 cm^{-1}) Tb^{3+} ions cannot be excited as it can be seen in the Tb^{3+} energy level diagram portrayed in Fig. 2. Even so, $^5D_4 \rightarrow {}^7F_{6,5,4,3}$ emissions of Tb^{3+} are observed in addition to $^4I_{15/2} \rightarrow {}^6H_{15/2}$, $^4F_{9/2} \rightarrow {}^6H_{15/2}$, $^4F_{9/2} \rightarrow {}^6H_{13/2}$, $^4F_{9/2} \rightarrow {}^6H_{11/2}$ and $^4F_{9/2} \rightarrow {}^6H_{9/2}, {}^6F_{11/2}$ emissions of Dy^{3+}. Additionally, it can be observed that the intensity of the dysprosium $^4F_{9/2} \rightarrow {}^6H_{13/2}$ yellow emission decreases at the expense of an enhancement of the terbium $^5D_4 \rightarrow {}^7F_5$ green emission when the Tb^{3+} content increases from 0.6 up to 5.0 mol% of Tb_2O_3. These facts reveal that Tb^{3+} emissions can be sensitized by Dy^{3+} excited at 392 nm.

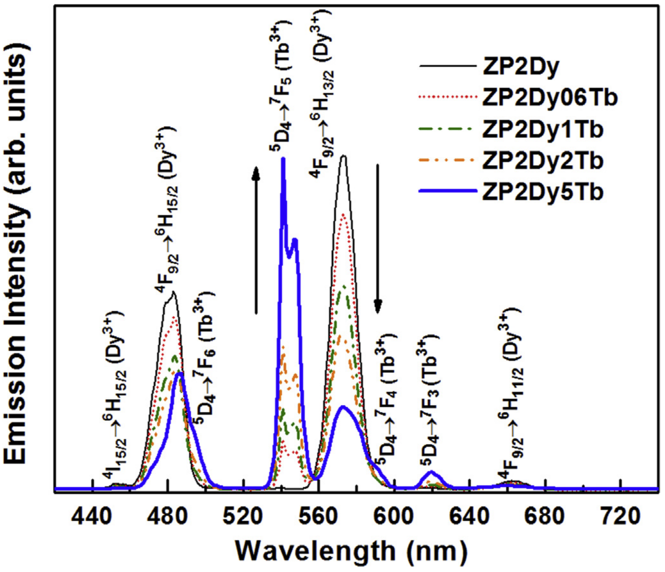

Fig. 1. Emission spectra of the ZP2Dy, ZP2Dy06Tb, ZP2Dy1Tb, ZP2Dy2Tb and ZP2Dy5Tb glasses excited at 392 nm.

Excitation spectrum of the ZP2Dy2Tb glass monitored at 541 nm, within the terbium $^5D_4 \rightarrow {}^7F_5$ emission and wherein Dy^{3+} does not emit, is shown in Fig. 3. The codoped glass excitation spectrum exhibits in addition to terbium $4f^8 \rightarrow 4f^8$ transitions, also dysprosium $4f^9 \rightarrow 4f^9$ transitions. The presence of Dy^{3+} excitation bands in the excitation spectrum of Tb^{3+} shows clear evidence of a Dy^{3+} to Tb^{3+} energy transfer. Such energy transfer is feavoured because the energy level of Dy^{3+} ($^4F_{9/2}$) is a little higher (~570 cm^{-1}) than that of Tb^{3+} ($^5D_4$), so that the $Dy^{3+} \rightarrow Tb^{3+}$ energy transfer could be (Fig. 2) [10]:

$$^4F_{9/2}\ [Dy^{3+}] + {}^7F_6\ [Tb^{3+}] \rightarrow {}^6H_{15/2}\ [Dy^{3+}] + {}^5D_4\ [Tb^{3+}]. \qquad \text{(i)}$$

According to the Dexter's energy transfer expression for multipolar interaction and Reisfeld's approximation, the following relation can be obtained [16,17]:

$$\frac{\eta_{Dy}}{\eta_{Dy+Tb}} \propto C^{n/3}, \qquad (1)$$

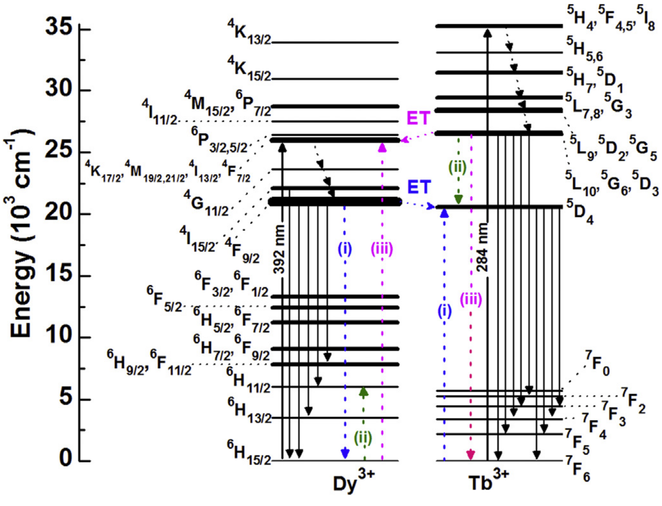

Fig. 2. Energy level scheme showing the transitions involved in processes non-radiative of (i) $Dy^{3+} \rightarrow Tb^{3+}$ energy transfer, (ii) $Tb^{3+} \rightarrow Dy^{3+}$ cross-relaxation, and (iii) $Tb^{3+} \rightarrow Dy^{3+}$ energy transfer.