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Blue and white light emission in Tm^{3+} and Tm^{3+}/Dy^{3+} doped zinc phosphate glasses upon UV light excitation

A.N. Meza-Rocha [a, *], A. Speghini [b, c], R. Lozada-Morales [d], U. Caldiño [e]

[a] CONACYT-Benemérita Universidad Autónoma de Puebla, Postgrado en Física Aplicada, Facultad de Ciencias Físico-Matemáticas, Av. San Claudio y Av. 18 sur, Col. San Manuel Ciudad Universitaria, Puebla, Pue, C. P. 72570, Mexico
[b] Dipartimento di Biotecnologie, Università di Verona, and INSTM, UdR Verona, Strada Le Grazie 15, I-37314 Verona, Italy
[c] IFAC CNR, Nello Carrara Institute of Applied Physics, MDF Lab, I-50019 Sesto Fiorentino, FI, Italy
[d] Benemérita Universidad Autónoma de Puebla, Postgrado en Física Aplicada, Facultad de Ciencias Físico-Matemáticas, Av. San Claudio y Av. 18 sur, Col. San Manuel Ciudad Universitaria, Puebla, Pue, C. P. 72570, Mexico
[e] Departamento de Física, Universidad Autónoma Metropolitana-Iztapalapa, P.O. Box 55-534, México, D.F. 09340, Mexico

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ABSTRACT

A spectroscopic study based on photoluminescence spectra and decay time profiles in Tm^{3+} and Tm^{3+}/Dy^{3+} doped $Zn(PO_3)_2$ glasses is reported. The Tm^{3+} doped $Zn(PO_3)_2$ glass, upon 357 nm excitation, exhibits blue emission with CIE1931 chromaticity coordinates, $x = 0.157$ and $y = 0.030$, and color purity of about 96%. Under excitations at 348, 352 and 363 nm, which match with the emissions of AlGaN and GaN based LEDs, the Tm^{3+}/Dy^{3+} co-doped $Zn(PO_3)_2$ glass displays natural white, bluish white and cool white overall emissions, with correlated color temperature values of 4523, 10700 and 7788 K, respectively, depending strongly on the excitation wavelength. The shortening of the Dy^{3+} emission decay time in presence of Tm^{3+} suggests that $Dy^{3+} \rightarrow Tm^{3+}$ non-radiative energy transfer occurs. By using the Inokuti-Hirayama model, it is inferred that an electric quadrupole-quadrupole interaction might be the dominant mechanism involved in the energy transfer. The efficiency and probability of this energy transfer are 0.12 and 126.70 s^{-1}, respectively.

1. Introduction

The incorporation of Tm^{3+} into a great variety of glasses has been considered for potential applications in fiber optic amplifiers, medical lasers, chemical sensings among others [1–3]. Because of its $^1D_2 \rightarrow {}^3F_4$ blue emission centered at 455 nm, Tm^{3+} doped inorganic hosts have attracted the attention as blue phosphors with promissory applications in white light emitting diodes (W-LEDs), plasma display panels, field emission displays, and so on [4,5]. On the other hand, Dy^{3+} doped materials have found recently promissory features in W-LEDs, optical temperature sensors, solid state laser applications, among others [6–8]. Due to the emissions blue of Tm^{3+} and white and/or yellowish-green of Dy^{3+}, Tm^{3+}/Dy^{3+} co-doped materials exhibit white tunable overall emission upon near ultraviolet (NUV) excitation [9,10], which fulfill the requirements for W-LED devices operating with NUV LEDs. Such emissions are frequently achieved by co-excitations of Tm^{3+} and Dy^{3+} and non-radiative energy transfer processes between Tm^{3+} and Dy^{3+} [10], which allow to modulate the tonality of the white light emission, being suitable for W-LEDs applications [9]. In this direction, Tm^{3+} and Tm^{3+}/Dy^{3+} ions have been successfully incorporated into several kinds of transparent glasses such as phosphate, oxyfluoride germanate, alumino-boro-silicate, sodium-boro-silicate among others [9–12]. Among the glass hosts tested for the incorporation of Tm^{3+} and Tm^{3+}/Dy^{3+} ions, zinc phosphate glasses possess low phonon energy, high transparency in the UV–Vis range and excellent photoluminescence performance when they are doped with lanthanides ions [8,13–15]. Owing to the importance of searching suitable systems with potential applications as blue and white light emitting phosphors, in this work a spectroscopic study based on excitation and emission spectra and decay times of Tm^{3+} and Tm^{3+}/Dy^{3+} doped zinc phosphate glasses is performed. Analysis of the CIE1931 chromaticity coordinates, color purity, and non-radiative energy transfer by using the Inokuti-Hirayama model, is carried out as well.

* Corresponding author.
E-mail address: anehemiasme@conacyt.mx (A.N. Meza-Rocha).

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2. Experimental

The molar compositions of the $Zn(PO_3)_2$ glasses studied were 99 $Zn(PO_3)_2$-1 $Tm(PO_3)_3$, 99 $Zn(PO_3)_2$-1 $Dy(PO_3)_3$ and 98 $Zn(PO_3)_2$-1 $Tm(PO_3)_3$-1 $Dy(PO_3)_3$, which will be referred hereafter as ZPTm, ZPDy and ZPTmDy, respectively. These glasses were prepared by mixing appropriate quantities of ZnO (Aldrich 99+%), $NH_4H_2PO_4$ (Carlo Erba RPE), Tm_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 1250 °C. The melts were quenched onto a copper plate. The glasses were annealed for 12 h at 350 °C to obtain thermal and structural stability. Photoluminescence spectra were recorded by a Horiba Jobin-Yvon Fluorolog 3–22 spectrofluorometer operating with a 150 W ozone-free Xe lamp in the steady mode or with a pulsed Xe lamp for decay time profile measurements. The decay times were recorded in the phosphorescence mode using a delay time of 0.01 m after the excitation pulse (3 μs half-width) and a 5 m sample window. All measurements were carried out at room temperature.

3. Results and discussion

3.1. ZPTm glass as blue phosphor

Fig. 1 shows the typical excitation and emission spectra of the ZPTm glass. The excitation spectrum monitoring the Tm^{3+} emission at 455 nm, displays a peak centered at 357 nm, which is assigned to the $^3H_6 \rightarrow {}^1D_2$ excitation transition. The emission spectrum under 357 nm excitation exhibits two bands located at 455 and 478 nm, associated with the $^1D_2 \rightarrow {}^3F_4$ and $^1G_4 \rightarrow {}^3H_6$ transitions, respectively. These emissions, illustrated in Fig. 2, are originated by an initial population in the $^1D_2$ level, which relaxes radiatively and non-radiatively to the $^3F_4$ and $^1G_4$ ones, respectively. This latter level decays to the $^3H_6$ state, giving rise to the small emission band at 478 nm. The emission tonality of the glass excited at 357 nm was characterized by its CIE1931 chromaticity coordinate, which resulted to be $x = 0.157$ and $y = 0.030$ (Fig. 3). These coordinates are close to those of the European Broadcasting Union (EBU) ($x = 0.15$ and $y = 0.06$) and National Television System Committee (NTSC) ($x = 0.14$ and $y = 0.08$) blue illuminant [4]. The color purity was evaluated from the following equation [16]:

$$color\ purity = \frac{\sqrt{(x_s - x_i)^2 + (y_s - y_i)^2}}{\sqrt{(x_d - x_i)^2 + (y_d - y_i)^2}} \times 100, \quad (1)$$

where (x_s,y_s) and (x_i,y_i) are respectively the CIE1931 coordinates of the sample and illuminating point (standard source C with $x_i = 0.310$ and $y_i = 0.316$ coordinates), (x_d,y_d) represents the CIE1931 coordinates of the dominant wavelength, in this case 455 nm ($x_d = 0.154$ and $y_d = 0.018$). Therefore, the calculated color purity is around 96%, which is close to those values reported previously [4,17]. Such high color purity is strongly influenced by the dominant thulium $^1D_2 \rightarrow {}^3F_4$ blue emission. The high color purity, obtained upon an excitation (357 nm) that matches well with the emission of commercial GaN diodes [18], might be attractive for W-LEDs applications.

3.2. ZPTmDy glass: as white phosphor

Fig. 4 displays the excitation spectra of the ZPTmDy glass, inspecting the dysprosium $^4F_{9/2} \rightarrow {}^6H_{13/2}$ and thulium $^1D_2 \rightarrow {}^3F_4$ emissions at 572 and 455 nm, respectively. The excitation spectrum of the 572 nm emission (wherein Tm^{3+} does not emit) exhibits the

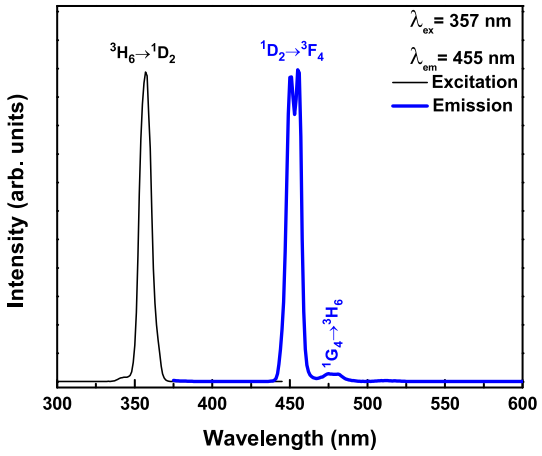

Fig. 1. Excitation and emission spectra of the ZPTm glass.

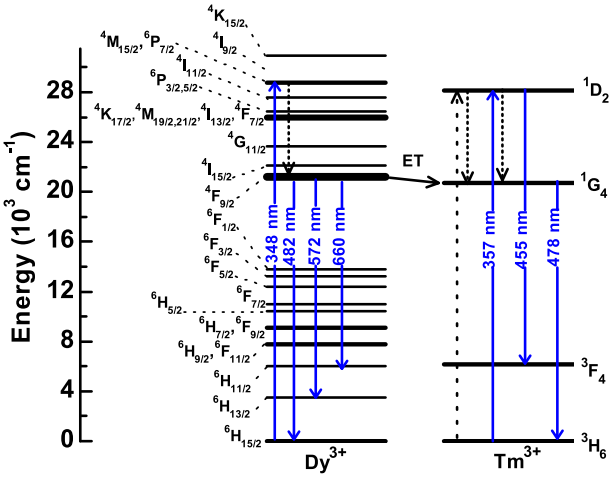

Fig. 2. Dy^{3+} and Tm^{3+} energy level scheme illustrating the emissions and the Dy^{3+} to Tm^{3+} energy transfer process.

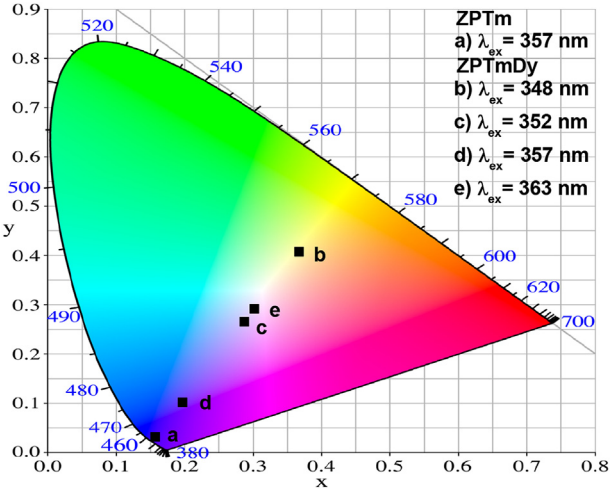

Fig. 3. CIE1931 chromaticity diagram illustrating the color tonalities of the ZPTm and ZPTmDy glasses.

well-known Dy^{3+} bands at 322, 336, 348, 363, 376, 384, 424, 452 and 470 nm, related with transitions from the $^6H_{15/2}$ ground level to