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Orange and reddish-orange light emitting phosphors: Sm^{3+} and Sm^{3+}/Eu^{3+} doped zinc phosphate glasses

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ABSTRACT

A spectroscopy study of Sm^{3+} and Sm^{3+}/Eu^{3+} doped zinc phosphate glasses is performed through photoluminescence spectra and decay time profile measurements. Under Sm^{3+} excitation at 344 nm, the Sm^{3+} singly doped glass shows an orange global emission with $x=0.579$ and $y=0.414$ CIE1931 chromaticity coordinates, whereas the Sm^{3+}/Eu^{3+} co-doped sample exhibits orange overall emissions ($x=0.581$ and $y=0.398$, and $x=0.595$ and $y=0.387$) and reddish-orange overall emission ($x=0.634$ and $y=0.355$) upon excitations at 344, 360 and 393 nm, respectively. Such luminescence from the co-doped sample is originated by the simultaneous emission of Sm^{3+} and Eu^{3+}. Under Sm^{3+} excitation at 344 and 360 nm, the Eu^{3+} emission is sensitized and enhanced by Sm^{3+} through a non-radiative energy transfer process. The non-radiative nature was inferred from the shortening of the Sm^{3+} lifetime observed in the Sm^{3+}/Eu^{3+} co-doped sample. An analysis of the Sm^{3+} emission decay time profiles using the Inokuti–Hirayama model suggests that an electric quadrupole–quadrupole interaction into Sm–Eu clusters might dominate the energy transfer process, with an efficiency of 0.17.

1. Introduction

Over years the incorporation of rare earths into metal oxide glasses has received considerable attention for diverse applications, such as waveguides, solid state laser hosts, and optical fibers, among others [1–3]. In particular, the zinc phosphate glass offers advantages associated with its low processing temperature, high transparency in the UV range, low phonon energy and high refractive index [4], which make the zinc phosphate glass a suitable host for most applications mentioned above. Due to its high transparency in the UV–vis range and its low phonon energy, the zinc phosphate glass has been studied as potential host for white light emitting diodes (W-LEDs) with UV-LEDs. For this purpose, UV absorbing ions, such as Ce^{3+}, allow to achieve white light emission when they transfer part of their energy to other activators ions, such as Tb^{3+}/Mn^{2+} [5] and Dy^{3+}/Mn^{2+} [6]. Among UV absorbing ions, it is well known that Sm^{3+} has many levels in the UV region, which turns it into an excellent activator for UV-based LEDs applications. In this direction, it has been reported that Sm^{3+} transfers energy efficiently to Eu^{3+} upon 401–405 nm excitation (which matches with the emission wavelength of GaN LEDs), allowing to obtain a global emission in the reddish-orange region that might be used as potential red emitting phosphor [7–10]. Moreover, this energy transfer process has been considered as strategy to down-convert the unused photons of solar spectrum to red emitting photons, which lie into the absorption region of copper phthalocyanine (CuPc) employed as absorber in organic solar cells [11,12]. Hence, considering the importance of studying luminescent materials that might be used potentially in ultraviolet W-LEDs and/or organic solar cells, in this work a spectroscopy study of zinc phosphate glasses doped with Sm^{3+} and Sm^{3+}/Eu^{3+} is performed. The study was focused on excitations at 344, 360 and 393 nm, which match well with the emissions of AlGaN, GaN and InGaN based LEDs, respectively [13–15]. The Eu^{3+} and Sm^{3+} overall emissions were in the orange and reddish-orange regions accordingly with their CIE1931 chromaticity coordinates. Non-radiative energy transfer from Sm^{3+} to Eu^{3+} was observed upon 344 and 360 nm excitations, and an analysis based on the decay time profile of Sm^{3+} using the Inokuti–Hirayama model was carried out as well.

2. Experimental

The molar composition of the zinc phosphate glasses studied was 99.0 $Zn(PO_3)_2$ – 1.0 $Eu(PO_3)_3$, 99.5 $Zn(PO_3)_2$–0.5 $Sm(PO_3)_3$ and

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98.5 $Zn(PO_3)_2$–1 $Eu(PO_3)_3$–0.5 $Sm(PO_3)_3$, which will be referred hereafter as ZPOEu, ZPOSm and ZPOSmEu, respectively. These glasses were prepared by mixing appropriate quantities of ZnO (Aldrich 99+%), $NH_4H_2PO_4$ (Carlo Erba RPE), Sm_2O_3 (Aldrich 99.99+%) and Eu_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 time profiles were recorded in the phosphorescence mode using a delay time of 0.01 ms after the excitation pulse (3 μs half-width) and a 5 ms sample window. All measurements were carried out at room temperature.

3. Results and discussion

3.1. Sm^{3+} doped zinc phosphate glasses

Fig. 1 shows excitation (thin line) and (thick line) emission spectra of the ZPOSm glass. The excitation spectrum monitoring the Sm^{3+} emission at 598 nm ($^4G_{5/2}\rightarrow{}^6H_{7/2}$) exhibits several bands, which are associated with transitions from the $^6H_{5/2}$ ground state to $^4P_{5/2}$, $^4P_{3/2}$, $^4G(2)_{7/2}$, $^4D_{7/2}$, $^4D_{3/2}$, $^6P_{7/2}$, $^4L_{15/2}$, $^6P_{3/2}$, $^6P_{5/2}$, $^4M_{19/2}$, $^4M_{17/2}$, $^4F_{5/2}$, $^4I_{13/2}$, $^4M_{15/2}$, $^4I_{11/2}$, $^4I_{9/2}$, $^4G(4)_{7/2}$, $^4F_{3/2}$ and $^4G_{5/2}$ levels, indicated in Fig. 1. The emission spectrum upon 344 nm excitation ($^6H_{5/2}\rightarrow{}^4D_{7/2}$), which matches well with the emission of AlGaN LEDs [13], displays four emission bands centered at 561, 598, 644 and 704 nm, corresponding to radiative transitions from the $^4G_{5/2}$ level to the $^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$ and $^6H_{11/2}$ states of Sm^{3+}, respectively. These emission bands are originated from an initial population of the $^4D_{7/2}$ state, which relaxes non-radiatively to the $^4G_{5/2}$ emitting state through intermediate ones (Fig. 2). This process is induced through the small energy difference existing among the intermediate states [16,17]. The overall emission leads to an orange tonality with $x=0.579$ and $y=0.414$ CIE1931 chromaticity coordinates. Such luminescence is dominated by the samarium $^4G_{5/2}\rightarrow{}^6H_{7/2}$ emission. On the other hand, it is well known that emissions with $\Delta J=0,\ \pm1$ correspond to magnetic dipole (MD) transitions, whereas emissions with $\Delta J\leq 6$ when $\Delta J=2, 4, 6$, unless J and $J'=0$, correspond to electric dipole (ED) transitions. Whereby, the emissions centered at 561, 598 and 644 nm are MD, partially MD and partially ED, and ED transitions, respectively. Moreover, the emission intensity of the $^4G_{5/2}\rightarrow{}^6H_{5/2}$ MD allowed transition is insensitive to the host environment, whereas the $^4G_{5/2}\rightarrow{}^6H_{9/2}$ ED allowed transition is strongly influenced by the host environment. When Sm^{3+} is located into a non-inversion symmetry site, the intensity of the $^4G_{5/2}\rightarrow{}^6H_{9/2}$ emission is significantly higher than that of the $^4G_{5/2}\rightarrow{}^6H_{5/2}$ emission. Thus, the ($^4G_{5/2}\rightarrow{}^6H_{9/2}$)/($^4G_{5/2}\rightarrow{}^6H_{5/2}$) emission intensity ratio can be used to estimate the dominant symmetry around Sm^{3+} in the zinc phosphate host. In our case, the ($^4G_{5/2}\rightarrow{}^6H_{9/2}$)/($^4G_{5/2}\rightarrow{}^6H_{5/2}$) emission intensity ratio resulted to be 1.44, which suggests that Sm^{3+} ions tend to be distributed into non-inversion symmetry sites. This behavior is similar with that reported for Sm^{3+} in transparent glass ceramics [17].

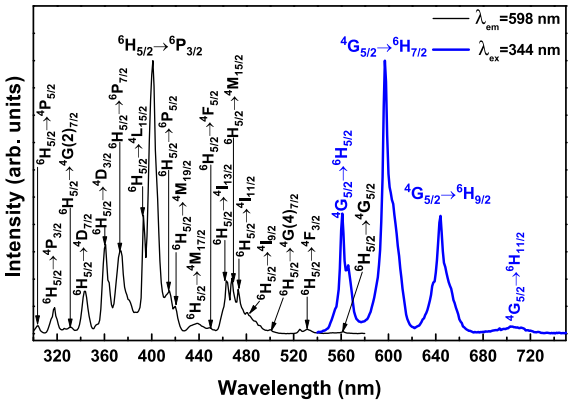

Fig. 1. Excitation (thin line) and emission (thick line) spectra of the ZPOSm glass. The excitation spectrum was recorded by monitoring the Sm^{3+} emission at 598 nm. The emission spectrum was recorded upon 344 nm excitation.

3.2. Sm^{3+} and Eu^{3+} co-doped zinc phosphate glasses

Fig. 3 shows excitation spectra of the Eu^{3+} singly doped (ZPOEu) and Eu^{3+}/Sm^{3+} co-doped (ZPOSmEu) zinc phosphate glasses monitoring the europium $^5D_0\rightarrow{}^7F_2$ emission at 622 nm, wherein Sm^{3+} does not emit. The spectrum of the ZPOEu glass displays several excitation bands associated with transitions from the $^7F_0$ ground and $^7F_1$ states to $^5F_4$, $^5I_5$, $^5H_6$, $^5H_{3,7}$, $^5D_4$, $^5L_{10}$, $^5G_{2,3,4,5}$, $^5L_8$, $^5L_7$, $^5L_7$, $^5D_3$, $^5L_6$, $^5D_2$, $^5D_2$, $^5D_1$ and $^5D_1$ levels reported previously [3]. The spectrum of the ZPOSmEu glass shows in

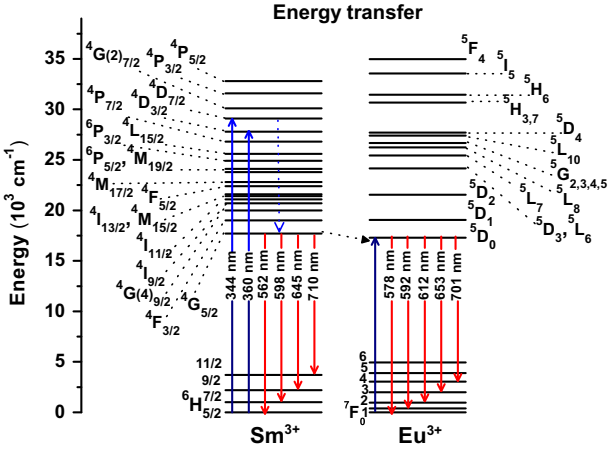

Fig. 2. Energy level scheme of Sm^{3+} and Eu^{3+} illustrating the Sm^{3+} excitation and emission processes as well the $Sm^{3+}\rightarrow Eu^{3+}$ energy transfer mechanism.

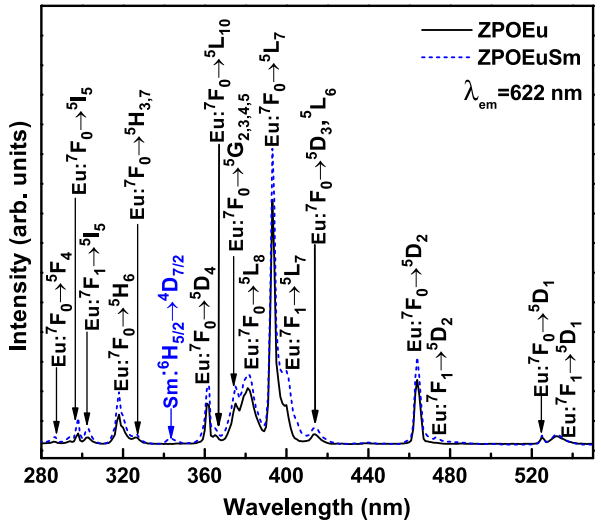

Fig. 3. Excitation spectra of the ZPOEu (solid line) and ZPOSmEu (dot line) glasses monitoring the Eu^{3+} emission at 622 nm.