Journal of Luminescence 194 (2018) 102–107

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Effective sensitization of Eu^{3+} and energy transfer in Sm^{3+}/Eu^{3+} co-doped ZPBT glasses for CuPc based solar cell and w-LED applications

Kaushal Jha, M. Jayasimhadri*

Luminescent Materials Research Lab (LMRL), Department of Applied Physics, Delhi Technological University, Delhi 110042, India

ARTICLE INFO

Keywords:
Optical glass
Photoluminescence
Energy transfer
Lifetime

ABSTRACT

Sm^{3+}/Eu^{3+} co-doped transparent Zinc Phosphate Barium Titanate (ZPBT) glasses have been successfully prepared via melt quenching technique. The photoluminescence properties and energy transfer mechanisms of these glasses were investigated in detail. The addition of Sm^{3+} as sensitizer expanded the excitation spectrum of Eu^{3+} in the Sm^{3+}/Eu^{3+} co-doped ZPBT glasses. The mechanism for energy transfer from Sm^{3+} to Eu^{3+} was dipole-dipole in nature, which was confirmed by Dexter energy transfer formula and Reisfeld's theory on emission spectra and Inokuti Hirayama (I-H) model on decay curves. The Sm^{3+}/Eu^{3+} co-doped ZPBT glasses reveal the capability to down-convert the n-UV and blue wavelength photons located in the weakest absorption of copper phthalocyanine (CuPc), to red-emitting photons in the optimal absorption of CuPc. The evaluated CIE chromaticity coordinates for the glasses move towards the red region with the increase in Eu^{3+} concentration under n-UV excitation wavelength. The above-mentioned results imply that the Sm^{3+}/Eu^{3+} co-doped ZPBT glasses are the potential candidate for applications in CuPc based solar cells and w-LEDs.

1. Introduction

In recent years, white light emitting diodes (w-LEDs) have received enormous attention as solid state light sources as they offer characteristics like high brightness, low power consumption and are environment-friendly. At present, w-LEDs are fabricated using single/multitude phosphor with n-UV/blue excitation sources. The approach for w-LEDs fabrication with the combination of RGB (red, green, and blue) phosphors and n-UV LED chips are seeking attention as they offer better CRI, CCT and free from halo effect in comparison to yellow phosphor with the blue LED chip. However, the red phosphor prepared from nitride and sulfide suffers from low chemical stability, low luminous efficiency, and the red phosphor $Y_2O_3:Eu^{3+}$ has intense excitation at 248 nm. Moreover, the quantum efficiency of InGaN LED chip has the maximum value at 400 nm, and "Droop" (where current density drops off) is also absent [1–4]. Hence, there is an urgent need for red photoluminescent component excitable by n-UV LED chips. Among various activators, the trivalent europium (Eu^{3+}) has gained significant attention due to its emission in the red region upon excitation with the n-UV/blue wavelengths [5,6]. The addition of sensitizer to an activator could extend the excitation region and enhance the emission intensity of activator. Many researchers have successfully expanded the Eu^{3+} excitation by use of suitable sensitizers. Among various sensitizers, Sm^{3+} was found to be the most appropriate sensitizer. The incorporation of Sm^{3+} as the sensitizer enhanced the Eu^{3+} emission in different host matrices. Kang et al. increased the emission intensity by 35% under 410 nm in the $Na_2Y_2Ti_3O_{10}$ host, while Fang et al. revealed the increment in Eu^{3+} emission under 403 nm in $CaLa_2(MoO_4)_4$ host lattice [4,7]. Biju et al. showed the enhancement in Eu^{3+} emission under 402 nm in zinc phosphate glasses [8]. Lin et al. revealed the emission improvement under 482 nm in borate glasses owing to energy transfer from Sm^{3+} to Eu^{3+} [9]. Moreover, the process of energy transfer can be used as a strategy to down convert unused photons of the solar spectrum to red emitting photons, which lie in the absorption region of the organic absorber material copper phthalocyanine (CuPC) [10,11]. The phosphor mentioned above is encapsulated in the organic resin made of polymer. The organic resin gets deteriorated at high temperatures, high power and/or high energy excitations light sources. Therefore, glasses doped with rare earth are preferred over phosphor as they have simpler manufacturing technique, lower production cost, highly durable, excellent thermal and mechanical stability [12–14]. Along with this, glasses serve the purpose of both the encapsulant and wavelength converter and is free from the organic resin.

Among various inorganic glasses, phosphate glasses have been extensively studied as they offer unique characteristics like transparency in the wide spectral region, low melting and softening temperature, and high mechanical and thermal stability. Phosphate glasses provide 1000 times greater rare earth ion solubility than borate and silicate glasses

* Corresponding author.
E-mail address: jayaphysics@yahoo.com (M. Jayasimhadri).

http://dx.doi.org/10.1016/j.jlumin.2017.09.049
Received 25 July 2017; Received in revised form 19 September 2017; Accepted 19 September 2017
Available online 21 September 2017

which make them an appropriate candidate as the host material for luminescence applications. However, the poor chemical durability and the hygroscopic nature of these glasses are a major limitation for practical applicability in devices. Zinc oxide (ZnO) offers unique properties like low toxicity, non-hygroscopic, direct band gap, low cost, intrinsic emitting property and large exciton binding and makes phosphate glasses moisture resistant due to the formation of P–O–Zn bonds. The addition of BaO to phosphate structure lowers the melting temperature as well as leads to disruption of the glass network. The heavy metal oxide like TiO_2 incorporation to the phosphate glasses significantly improves chemical durability and stabilization of the glass structure [12,14].

Therefore, in the present investigation Sm^{3+}/Eu^{3+} co-doped ZPBT glasses were synthesized for the first time via melt quenching technique and the energy transfer mechanisms were discussed in detail. Furthermore, the efficiency and probability of energy transfer and CIE Chromaticity coordinates were calculated. The aim is to investigate these glasses for applications in the field of optoelectronics.

2. Experimental

The glasses were prepared with conventional melt-quenching technique with molar composition as mentioned below:

(1) $39ZnO\text{-}35P_2O_5\text{-}20BaO\text{-}5TiO_2\text{-}XSm_2O_3$ (X = 0.1, 0.5, 1.0, 1.5, and 2.0) (Sample name with X = 1.0 was named as SM01)
(2) $39ZnO\text{-}35P_2O_5\text{-}20BaO\text{-}5TiO_2\text{-}1Eu_2O_3$ (Sample name = EU01)
Along with these two glass samples, a series of glasses doped with Sm_2O_3 and Eu_2O_3 were prepared in the molar composition as follows:
(3) $(39\text{-}X)ZnO\text{-}35P_2O_5\text{-}20BaO\text{-}5TiO_2\text{-}1Sm_2O_3\text{-}XEu_2O_3$

The values for X were 0.50, 1.0, 1.5 and 2.0 and the glasses were named as SE01, SE02, SE03, and SE04, respectively. The starting materials were Analytical Reagent (A.R) grade ZnO, TiO_2, $BaCO_3$, $NH_4H_2PO_4$, high purity Sm_2O_3, and Eu_2O_3. The chemicals were ground in an agate mortar for 1 h using acetone as the wetting medium. The mixture was then placed in the muffle furnace at 1150 °C for 1 h, and the melt was then poured on the preheated brass plate and annealed at 400 °C for 3 h to remove mechanical and thermal stress. Finally, colorless and transparent glasses were obtained. The photoluminescence (PL) properties were measured using Shimadzu RF-5301PC spectrofluorophotometer fitted with xenon flash lamp. The decay analysis was performed using an Edinburgh FLS920, where xenon lamp was excitation source.

3. Results and discussion

3.1. Photoluminescence properties of Sm^{3+} doped ZPBT glasses

Fig. 1 represents the excitation and emission spectra of Sm^{3+} doped ZPBT glasses. The excitation spectrum was recorded by monitoring emission at 599 nm. The excitation spectrum revealed several peaks originating from the $^6H_{5/2}$ ground level to different excited levels at 343, 359, 372, 399, 418, 437 and 467 nm corresponding to the $^4H_{9/2}$, $^4D_{3/2}$, $^6P_{7/2}$, $^4F_{7/2}$, $^6P_{5/2}$, $^4G_{9/2}$, and $^4I_{11/2} + {}^4I_{13/2} + {}^4M_{15/2}$ transitions of Sm^{3+} ions, respectively. The emission spectrum under 399 nm excitation revealed three emission bands centered at 563, 599 and 645 nm corresponding to $^4G_{5/2}\rightarrow{}^6H_{5/2}$, $^4G_{5/2}\rightarrow{}^6H_{7/2}$, and $^4G_{5/2}\rightarrow{}^6H_{9/2}$ transitions, respectively. The $^4G_{5/2}\rightarrow{}^6H_{5/2}$ is magnetic dipole (MD) transition in nature following the selection rules ($\Delta J = 0, \pm 1$; J is angular momentum), whereas $^4G_{5/2}\rightarrow{}^6H_{9/2}$ is attributed to forced electric dipole (ED) transition following the selection rule ($\Delta J \leq 6$; $\Delta J = 2, 4$, and 6 if J or $J' = 0$). The MD transition is insensitive to the crystal environment whereas forced ED transition is hypersensitive in nature, and the emission intensity of this transition gets strongly affected by the crystal field of the ligand atoms. The $^4G_{5/2}\rightarrow{}^6H_{7/2}$ emission band arose due to both MD and forced ED transitions [15,16]. The intensity ratio of forced ED to MD transition indicate about the symmetry of environment around the rare earth. In the present case, the MD transition is more intense than ED transition which suggests that there is no deviation from the inversion symmetry. The emission intensity of the Sm^{3+} doped ZPBT glasses increased up to 1 mol% and decreased after that as shown in the inset of Fig. 1. The decrease in the emission intensity arises due to the concentration quenching phenomenon [17].

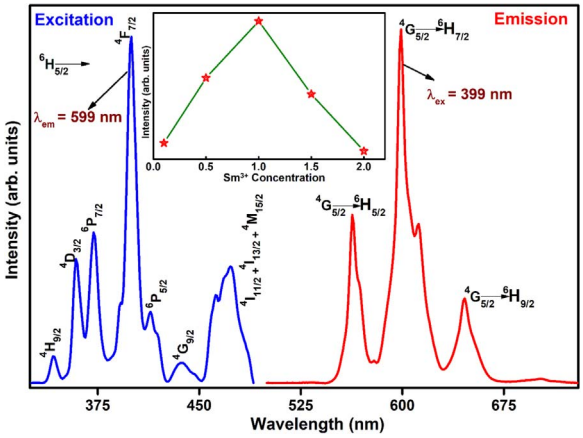

Fig. 1. Excitation spectrum of SM01 glass by monitoring emission at 599 nm and emission spectrum under 399 excitation. (Inset: Represents variation in emission intensity of 599 nm peak with different Sm^{3+} concentrations in ZPBT glasses).

3.2. Photoluminescence properties of Sm^{3+}/Eu^{3+} co-doped ZPBT glasses

Fig. 2 compares the excitation spectrum of EU01 and SE03 (1 mol% of Eu^{3+} and 1.5 mol% Sm^{3+} co-doped ZPBT glasses) by monitoring emission at 613 nm. The emission at 613 nm is due to Eu^{3+}, but the excitation spectrum for the Sm^{3+}/Eu^{3+} co-doped ZPBT glass revealed peaks of Sm^{3+} also in addition to that of Eu^{3+}. The peaks at 343, 399, 437 and 473 nm are associated with Sm^{3+} as discussed previously, and the peaks at 360, 381, 392, 412, and 462 nm are attributed to $^7F_0\rightarrow{}^5D_4$, $^7F_0\rightarrow{}^5L_7$, $^7F_0\rightarrow{}^5L_6$, $^7F_0\rightarrow{}^5D_3$, and $^7F_0\rightarrow{}^5D_2$ transitions, respectively of Eu^{3+} [18]. A few reports on the Sm^{3+} doped and Eu^{3+} doped glasses have been examined and revealed the excitation peaks of either Sm^{3+} or Eu^{3+} ions [19–24]. However, in the present case, the excitation spectrum of Eu^{3+} is extended and also enhanced the intensity of peaks by co-doping Sm^{3+}. Therefore, the introduction of Sm^{3+} has revealed the sensitization effect on Eu^{3+} in the Sm^{3+}/Eu^{3+} co-doped ZPBT glasses. The emission spectra of the co-doped ZPBT glasses i.e. Sm^{3+}

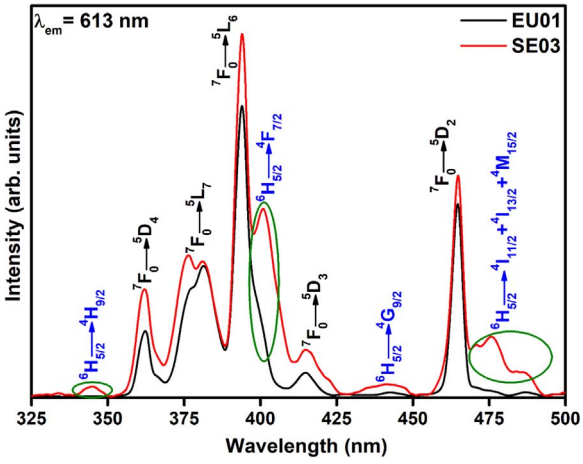

Fig. 2. Excitation spectra of EU01 and SE03 glasses by monitoring emission at 613 nm.