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Three primary colors emitting from Er^{3+}–Eu^{3+} co-doped oxygen-deficient glasses

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ABSTRACT

Three individual primary colors were generated from only one piece of Er^{3+}–Eu^{3+} co-doped oxygen-deficient germanate glass under UV light irradiation. Blue, green, and red emissions were originated from Ge-related oxygen-deficient defect centers (GODCs), Er^{3+} ions, and Eu^{3+} ions, respectively. Detailed photoluminescence spectra, decay curve analyses, and electron paramagnetic resonance measurements were carried and the results indicate the existence of energy transfer between Er^{3+} and Eu^{3+} ions, GODCs and Eu^{3+} ions.

1. Introduction

Realization of new, red-green-blue (RGB) full-color displays have attracted considerable interests in flat-panel display systems and lighting technology [1–4]. Traditional methods of a variety of colors generation typically rely on mixing various primary colors from different emitting materials [5,6]. An alternative approach is generation of three primary color lights from a single material, which have advantages such as superior stability, easy fabrication, and low cost [2,3]. A large amount of researchers focused on organic materials due to their variety of attainable emission colors and high quantum efficiency [7,8]. On the other hand, many attentions have been paid to inorganic transparent solid materials due to their outstanding stabilities in contrast with organic materials [1,9]. Compared with other materials like organic films and power phosphors, glass has some advantages such as homogeneous light emitting and excellent thermal and chemical stabilities [10,11]. In addition, glasses and glass-ceramics represent ideal materials for the initiation of multi-mode emission because emission centers can be present in many different forms (redox states, ligand environment) [12]. Therefore, rare earth doped glasses and glass-ceramics used for lighting and display devices have been extensively investigated in recent years [10–19]. In our previous work, we have reported high efficiency blue light emission originates from Ge-related oxygen deficient centers (GODCs) in calcium aluminum germanate glass [20]. Moreover these luminescent centers can co-doped with other transition-metal or rare earth ions in glasses and exhibits multi-color emissions [21,22]. Considering the ideal green and red emission from Er and Eu ions, we envisaged that three primary colors emission can be achieved by co-doped Er and Eu ions with GODCs in glasses. Just like what we envisaged, here we present three individual primary colors (blue, green, and red) emitting from only one piece of Er^{3+}–Eu^{3+} co-doped oxygen-deficient glass under ultraviolet (UV) irradiation. The luminescence properties and the energy transfer processes between Er^{3+}, Eu^{3+} ions and GODCs in these glasses have also been studied.

2. Experimental details

A series of glass samples with the nominal composition of $38.8CaO–26.2Al_2O_3–5.8Al–29.2GeO_2–Er_2O_3–xEu_2O_3$ ($x = 0$, 0.25, 0.5, 1, 1.5, 3) (mol %) were obtained by conventional melt-quenching technique using high-purity $CaCO_3$, Al_2O_3, Al (all of 99. 9%), GeO_2, Er_2O_3, Eu_2O_3 (all of 99.99%) as raw materials. $CaO–Al_2O_3–GeO_2$ glasses show good mechanical strength and chemical durability [23]. It is worth emphasizing that if the glass sample was obtained by single step, the Eu^{3+} in the glass would react with Al and be reduced to Eu^{2+}, resulting in yellow emission instead of red emission. Therefore, we used two melting steps to obtain the final glass samples. Firstly, the mixtures of $CaCO_3$, Al_2O_3, Al, GeO_2, and Er_2O_3 were melted in alumina crucibles with alumina caps at 1500 °C for 1 h under the ambient atmosphere. The melts were poured onto

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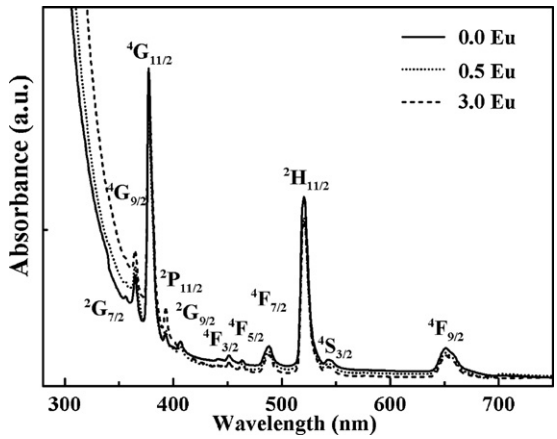

Fig. 1. Absorption spectra of Er^{3+}–Eu^{3+} co-doped glass with different concentration of Eu^{3+} ions.

a stainless plate and pressed with another stainless plate to obtain the original glasses. Then the original glass was grinded into powder and mixed with Eu_2O_3 thoroughly. Secondly, the mixtures of original glass powder and Eu_2O_3 were melted for 20 min under the same condition as above-mentioned to obtain the final glass samples. In the first-step, the Al melt has been reacted completely. Then, in the second-step there was no Al to react with Eu^{3+}. Finally, the reduction of Eu^{3+} to Eu^{2+} can be suppressed. The final glass samples were cut and optically polished to a size of 10mm × 10mm × 2 mm. The composition of the glasses were determined by Thermo ESCALAB 250 X-ray photoelectron spectrometer (XPS), using monochromatic Al Kα (1468.6 eV) as the excitation source. Electron paramagnetic resonance (EPR) spectra were obtained using a JEOL JES-FA200 ESR spectrometer (300 K, 9.063 GHz, X-band). Absorption spectra were recorded with a JASCO V-570 UV/VIS/NIR spectrophotometer. Photoluminescence excitation (PLE) and photoluminescence (PL) spectra of the samples in UV and visible wavelength ranges were recorded on a JASCO FP-6500 spectrophotometer equipped with a Xenon lamp source, and the luminescence photographs of glasses were also obtained with an excitation of a Xenon lamp in the spectrophotometer. Decay curves were measured with a FLS920 fluorescence spectrophotometer. The refractive indices of samples at 632.8, 1310 and 1550 nm were measured by SPA 4000 prism coupler. All of the measurements were carried out at room temperature.

3. Results and discussion

The composition of the prepared glass samples was measured by XPS and the result is shown in Table 1. A little Ge was evaporated during the melting process. The optical absorption spectra of the Er^{3+}–Eu^{3+} co-doped glasses recorded in the spectral range of 200–750 nm are shown in Fig. 1. In accordance with energy level diagram and literature data [24,25], the observed absorption bands

Table 1
Glass composition of 38.8CaO–26.2Al_2O_3–5.8Al–29.2GeO_2–Er_2O_3–xEu_2O_3 recorded by XPS analysis (at.%).

Sample	Ca	Al	Ge	O	Er	Eu
x = 0	11.49	17.24	7.47	63.23	0.57	0
x = 0.25	11.48	17.22	7.46	63.13	0.57	0.14
x = 0.5	11.46	17.19	7.45	63.04	0.57	0.29
x = 1.0	11.43	17.14	7.43	62.86	0.57	0.57
x = 1.5	11.40	17.09	7.41	62.68	0.57	0.85
x = 3.0	11.30	16.95	7.34	62.16	0.56	1.69

were assigned to appropriate electronic *f–f* transitions of the Er^{3+} from the $^4I_{15/2}$ ground state to different excited states. From Fig. 1, it also observed that the optical absorption edge of the glass shifted to the longer wavelength region with the increase in Eu_2O_3 concentration. It was attributed to the increasing of non-bridging oxygen (NBO) with the increasing of Eu_2O_3 concentration. Generally, rare-earth ions entering the aluminosilicate or germanate glass usually act as network modifiers, causing the formation of a wide distribution of NBO [26]. It has been reported that [20], the shift of the absorption edge to longer wavelength (red-shift) is related to the formation of NBO, which binds electrons less tightly than bridging oxygen (BO). When the Eu_2O_3 was doped to the glass, the oxygen in Eu_2O_3 would exist as the form of NBO in the glass. Hence, the absorbance edge shows a red-shift with the increase in Eu_2O_3 concentration.

Just like what we envisaged, the GODCs, Er and Eu co-doped glass shows multi-color emissions when excited by different UV light. Fig. 2 shows the PLE and PL spectra of $2Er^{3+}$–$0.5Eu^{3+}$ co-doped glass sample. The inset reveals three primary colors (blue, green, red) emission when the glass excited by 340, 379, and 395 nm UV lights, respectively. When this glass excited by 379 nm UV light, green emission bands were detected at 526 and 550 nm which can be ascribed to typical $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions of Er^{3+} ions [24,25]. And when excited by 395 nm UV light, red emission bands were detected at 580, 590 and 615 nm which were due to typical $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$ transitions of Eu^{3+} ions [24,25]. In order to exclude the presence of Eu^{2+} ions, EPR analysis was taken. Only an apparent ESR signal appeared at $g = 1.994$, which can be ascribed to GODCs (Fig. 3a) [20,27]. As reported in our previous work, the GODCs were produced by following reaction:

$$\equiv Ge\text{–}O\text{–}Ge\equiv + Al \rightarrow \equiv Ge\text{–}Ge\equiv (GODC) + Al\text{–}O \quad (1)$$

For comparison, we therefore have prepared a Eu^{2+} doped glass sample with a composition of 40CaO–27Al_2O_3–

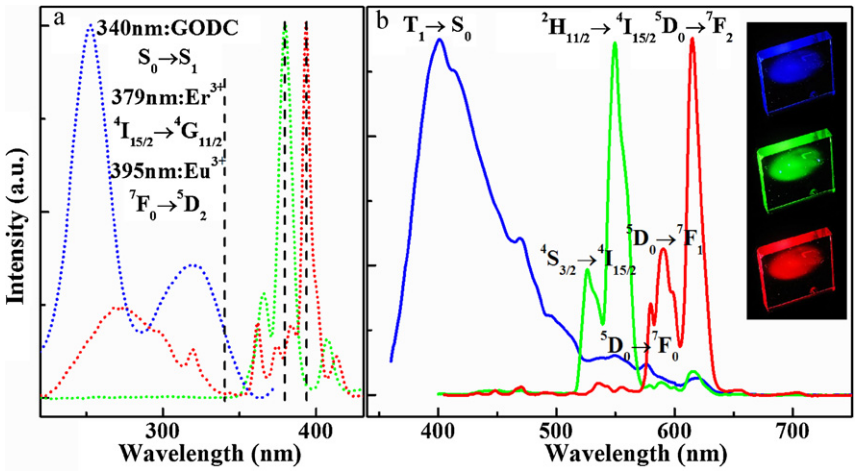

Fig. 2. (a) PLE (monitored at 402, 550, and 615 nm) and (b) PL (excited by 340, 379, and 395 nm) spectra of $2Er^{3+}$–$0.5Eu^{3+}$ co-doped glass sample, the inset shows the three primary colors emission excited by 340, 379, and 395 nm UV lights, respectively.

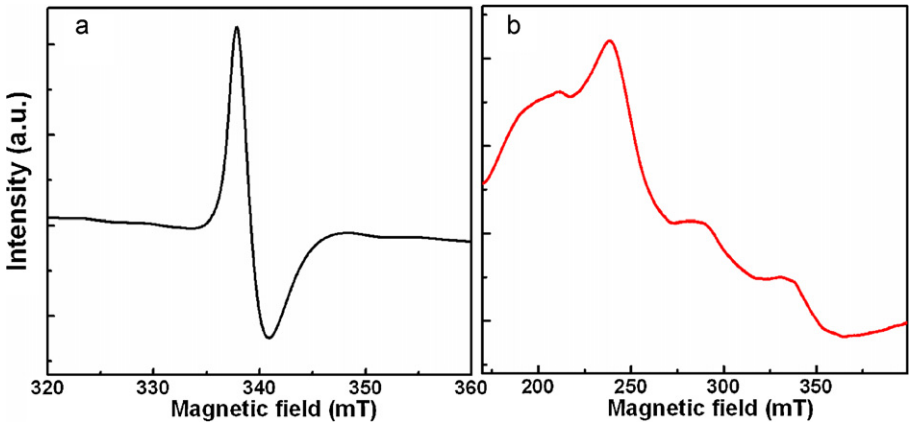

Fig. 3. EPR spectrum of the (a) $2Er^{3+}$–$0.5Eu^{3+}$ co-doped glass sample and (b) Eu^{2+} doped glass sample.

$6Al–30GeO_2–1Eu_2O_3$. In this glass the Eu^{3+} ions was almost reduced to Eu^{2+} ions. And we detect some Eu^{2+} EPR signals in this glass (Fig. 3b) [28]. In addition, the Eu^{2+} doped glass shows a yellow emission with a broad emission band from 400 to 600 nm, while the Eu^{3+} doped glass reveals a typical red emission. So we can confirm that the Eu ions in the glass are mainly Eu^{3+} ions. It has been reported that the GODCs has two PL bands at 300 and 395 nm with the corresponding excitation bands at 250 and 330 nm [27]. Then, the blue emission band centered at 402 nm might attribute to $T_1 \rightarrow S_0$ transition of GODCs [21,29].

To elucidate the luminescence properties of the glass, we recorded the emission yield (EY) of the glasses from the measurements using a standard substance and the following equation, which was adopted from Ref. [30]:

$$\frac{\Phi_X}{\Phi_S} = \frac{F_X}{F_S} \cdot \frac{A_S}{A_X} \cdot \frac{n_X^2}{n_S^2} \quad (2)$$

where F was the emission intensity, A was the absorption coefficient, n was the refractive index, and subscripts S and X represented the standard and sample, respectively. In this experiment, 1 mol/L Rhodamine B in ethanol was used as the standard (Φs = 0.65) and the refractive index n_0 of glass samples were measured by SPA 4000 prism coupler. We keep the geometry of glass sample and standard nearly the same. The standard Rhodamine B in ethanol was put in a 2 mm thick cuvette. The volume of the Rhodamine B solution was kept approximately 10mm × 10mm × 2 mm which was nearly the

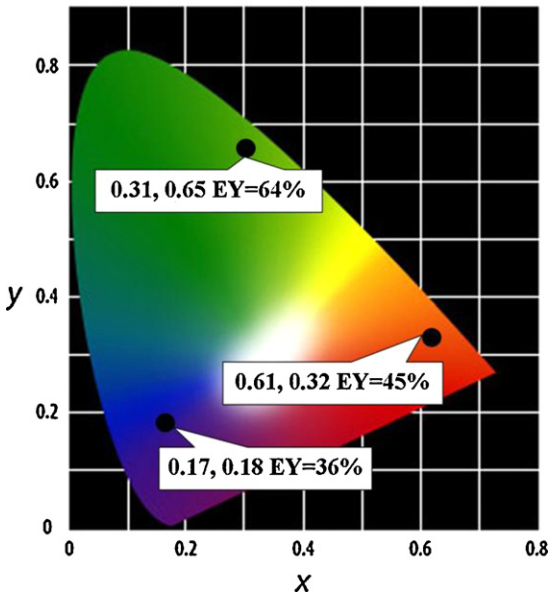

Fig. 4. CIE diagram and emission yield of three primary colors emission of $2Er^{3+}$–$0.5Eu^{3+}$ co-doped glass.

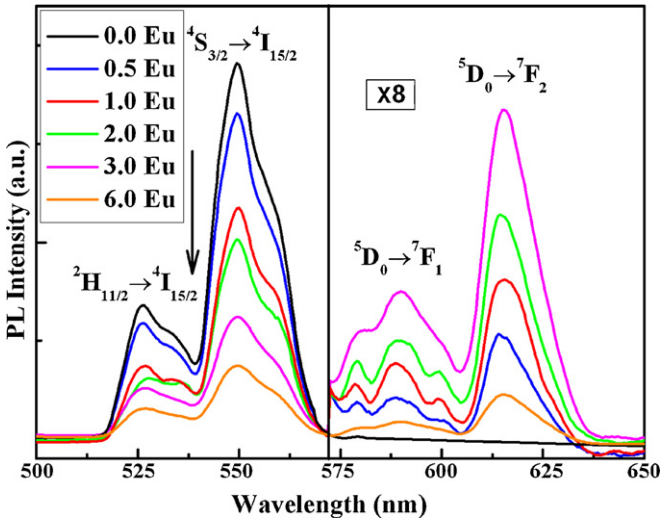

Fig. 5. PL spectra of Er^{3+}–Eu^{3+} co-doped glass with different concentration of Eu^{3+} ions excited by 379 nm UV light.

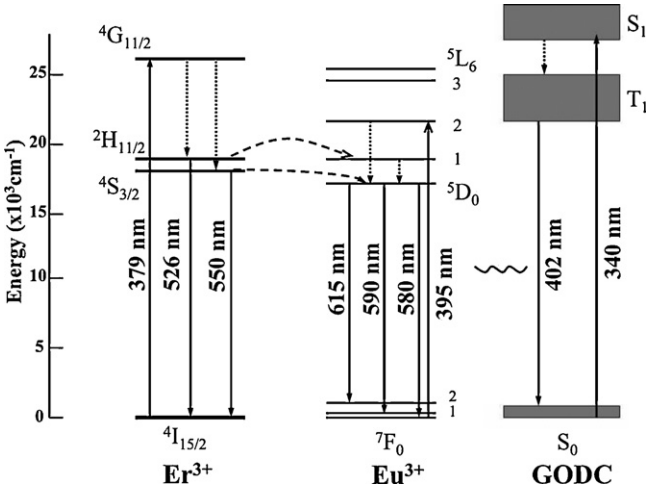

Fig. 6. Simplified energy level diagram and observed transitions in Er^{3+}–Eu^{3+} co-doped glass.

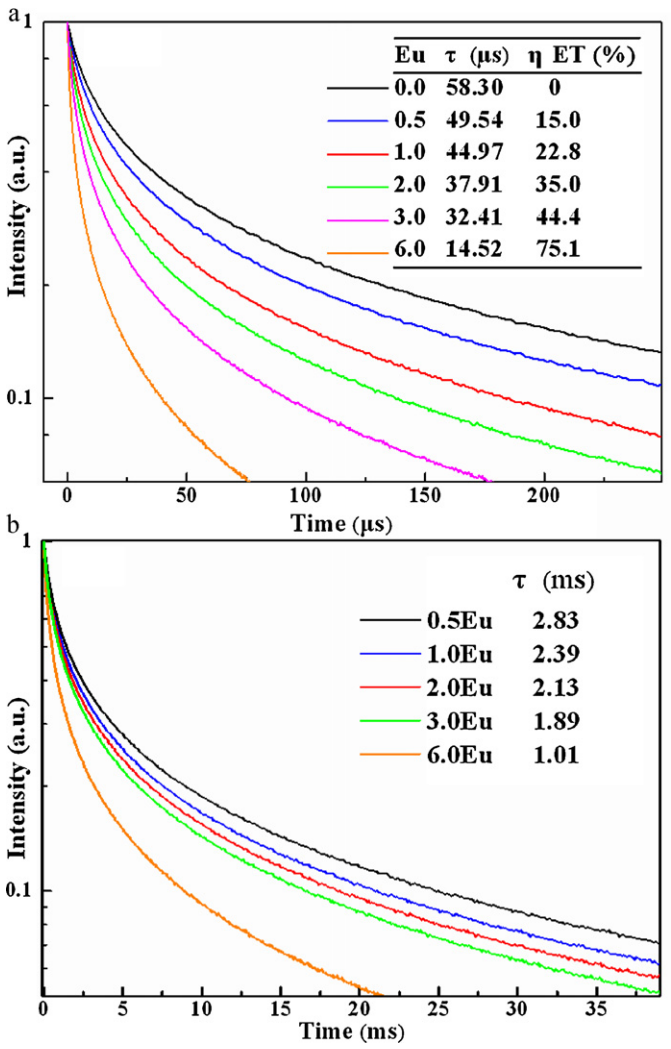

Fig. 7. Decay curves for (a) Er^{3+} emission (550 nm) and (b) Eu^{3+} emission (615 nm) with different concentration of Eu^{3+} ions. Inset is the calculated average lifetime and ET efficiency.

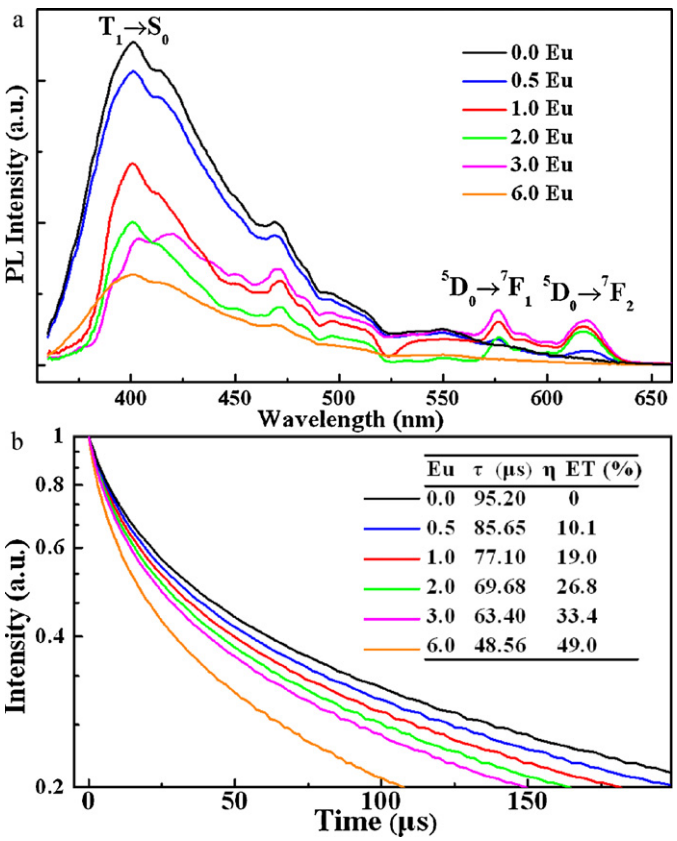

Fig. 8. (a) PL spectra of Er^{3+}–Eu^{3+} co-doped glass with different concentration of Eu^{3+} ions excited by 340 nm UV light and (b) decay curves for GODC emission (402 nm) with different concentration of Eu^{3+} ions. Inset is the calculated average lifetime and ET efficiency.

same to the glass samples. So the parameters for absorption and emission experimental were nearly the same. As shown in Fig. 4, the EY of the three primary colors were as follows: 36% (blue), 64% (green), and 45% (red). We also calculated the Commission Internationale de l'Eclairage (CIE) chromaticity coordinates of the three primary colors emission [31]. The obtained CIE (x, y) were (0.17, 0.18), (0.31, 0.65), and (0.61, 0.32), respectively. These would fall well within the blue, green, and red region as the 1931 CIE diagram (Fig. 4). Considering the ideal CIE (x, y) for blue, green, and red were (0.15,0.06), (0.30, 0.60), and (0.64, 0.33), respectively [28], the green and red emission from our glass were desired, while the blue emission was not so ideal.

Fig. 5 demonstrates typical PL spectra of Er^{3+}–Eu^{3+} co-doped glasses excited by 379 nm. It was observed a decrease in Er^{3+} PL bands (green) with the increase in concentration of Eu^{3+} ions, which might indicate the energy transfer (ET) from Er^{3+} to Eu^{3+} ions. In addition, since the energy gap between the Er^{3+}: $^4S_{3/2}$ level and Eu^{3+}: $^5D_0$ level was within 1000 cm^{-1}, whereas Er^{3+}: $^2H_{11/2}$ and Eu^{3+}: $^5D_1$ levels almost overlap on each other, hence the energy transfer process from Er^{3+} to Eu^{3+} was possible, as given in the following equation:

$$^4S_{3/2}, ^2H_{11/2}(Er^{3+}) \rightarrow {}^5D_0, {}^5D_1(Eu^{3+}) + \text{phonons} \quad (3)$$

Moreover, a decrease of red emission has been observed when the Eu concentration exceeds 6% mol, which was due to concentration quenching.

Fig. 6 shows a simplified energy level diagram of Er^{3+} and Eu^{3+} ions and supposed energy transitions. To gain a deeper insight onto the transitions, we have recorded the decay curves of the Er^{3+} emissions at 550 nm excited by 379 nm UV light (shown in Fig. 7a). The idea of energy transfer was strengthened by the decay curve analysis, which was fitted in second order exponential in Er^{3+}–Eu^{3+} co-doped glass, in place of single exponential used in singly doped Er^{3+} glass. We have also calculated the energy transfer efficiencies (μ_{ET}) using the equation given by Joshi [32].

$$\mu_{ET} = \frac{1-\tau}{\tau}. \quad (4)$$

where τ and τ_0 denoted the average lifetimes of donor ion (Er^{3+}) in the presence and absence of acceptors (Eu^{3+}), respectively. Similar energy transfer process was reported by Dwivedi et al. [25]. The detailed mechanism could refer to Ref [25]. The decay curves for the emission transition of $^5D_0 \rightarrow {}^7F_2$ of Eu^{3+} ions are also shown in Fig. 7b. It can be seen that the lifetime was decreased when the doped concentration was increased, which can be attributed to the non-radiative relaxation caused by the surface defects that act as a quenching center [33]. When the doped concentration was increased, the sample had more quenching centers and the non-radiative rate increased, which caused the lifetime to be shortened.

We also studied the emission properties of GODCs excited by 340 nm light. It was also observed a decrease in intensity of GODCs PL bands with the increase in concentration of Eu^{3+} (as shown in Fig. 8), which might demonstrated the energy transfer from GODC to Eu^{3+} ions. As the $T_1 \rightarrow S_0$ transitions of GODCs centered at

402 nm, ranging from 350 to 500 nm, this energy could be absorbed by $^7F_0 \rightarrow {}^5D_2$ transitions of Eu^{3+} ions, hence the energy transfer might be possible. Decay curves for GODC emission (402 nm) with different concentration of Eu^{3+} ions are also shown in Fig. 8b. The μ_{ET} was also being calculated.

4. Conclusions

Three primary colors were achieved by only one piece of Er^{3+}–Eu^{3+} co-doped oxygen-deficient glass under UV irradiation. Blue, green, and red emissions originated from GODCs, Er^{3+}, and Eu^{3+} ions were confirmed by analyzing of photoluminescence properties of the prepared samples. The emission yield and CIE chromaticity coordinate of the blue, green, and red are 36% (0.17, 0.18), 64% (0.31, 0.65), and 45% (0.61, 0.32), respectively. Energy transfers from Er^{3+} ions to Eu^{3+} ions and from GODCs to Eu^{3+} ions were confirmed by PL spectra and decay curve analysis.

Acknowledgments

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