

# Green-yellow-red tunable luminescence from $\text{Eu}^{3+}$ - $\text{Ho}^{3+}$ -doped $\text{TeO}_2$ - $\text{GeO}_2$ - $\text{Nb}_2\text{O}_5$ glass

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$\text{Eu}^{3+}$ - $\text{Ho}^{3+}$  doped  $\text{TeO}_2$ - $\text{GeO}_2$ - $\text{Nb}_2\text{O}_5$ - $\text{Li}_2\text{CO}_3$  (TGN) glasses was fabricated by melt-quenching and subsequent heating. Five emissions centered at 548 nm, 613 nm, 652 nm, 700 nm, and 755 nm are observed in the resulting TGN glass under 458 nm excitation, which corresponds to ( $^5\text{S}_2, ^5\text{F}_4$ ) $\rightarrow$  $^5\text{I}_8$ ,  $^5\text{D}_0\rightarrow$  $^7\text{F}_2$ ,  $^5\text{D}_0\rightarrow$  $^7\text{F}_3$ ,  $^5\text{D}_0\rightarrow$  $^7\text{F}_4$ , ( $^5\text{S}_2, ^5\text{F}_4$ ) $\rightarrow$  $^5\text{I}_7$  transitions. By adjusting concentration proportion of  $\text{Ho}^{3+}$  and  $\text{Eu}^{3+}$  ions, the color coordinate can be converted from green to yellow and eventually to red region. The luminescence decay curves evidenced that the energy transfer from  $\text{Eu}^{3+}$  to  $\text{Ho}^{3+}$  was responsible for color-tunable emissions. The  $\text{Eu}^{3+}$ - $\text{Ho}^{3+}$  co-doped TGN glasses could be potentially candidate for a white-light-emitting material under blue chip excitation.

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**Keywords:**  $\text{Eu}^{3+}$ ,  $\text{Ho}^{3+}$ , Energy transfer, White-LED

## 1. Introduction

In recent years, white light-emitting diodes (W-LED) has attracted much attention owing to its advantages such as long lifetime, lower energy-wasting, high luminous efficiency, environmental protection and so on [1-5]. Combining a GaN-based blue LED with a yellow-emitting (YAG:  $\text{Ce}^{3+}$ ) phosphor was regarded as an efficient and common way to realize W-LED [6-8]. However, the color rendering index (CRI) is low because of the lack of red emitting contribution. In order to improve this problem, many researches were focused on the novel materials which can emit red emission under the blue LED excitations, compensating for red component in yellow-emitting (YAG:  $\text{Ce}^{3+}$ ) phosphors. Nevertheless, chromatic aberrations caused by the different degradations of host phosphors suppress high CRI and re-absorption of emission colors resulting from using two or three different phases of phosphors decrease luminous efficiency [9, 10]. Thus it is necessary to explore a novel single-host material which emits yellow and red emissions simultaneously under blue chip LED excitation.

The trivalent europium  $\text{Eu}^{3+}$  and the holmium  $\text{Ho}^{3+}$  have a  $4f^6$  and  $4f^{10}$  electronic configurations, were reported as excellent emitting activators to realize homochromatic red and green emissions [11-15]. Site selective spectroscopy of  $\text{Eu}^{3+}$  and  $\text{Ho}^{3+}$  was observed in  $\text{Eu}^{3+}$  and  $\text{Ho}^{3+}$  doped oxyfluoride glass ceramics [16,17]. Red and green emissions were originated from the transitions of  $^5\text{D}_0\rightarrow$  $^7\text{F}_2$  ( $\text{Eu}^{3+}$ ) and ( $^5\text{S}_2, ^5\text{F}_4$ ) $\rightarrow$  $^5\text{I}_8$  ( $\text{Ho}^{3+}$ ) under UV excitation. According to tricolor principle, the yellow emissions will be achieved in  $\text{Eu}^{3+}$ - $\text{Ho}^{3+}$  co-doped phosphors. Further, the white emission will be obtained by exciting yellow phosphors with a blue chip LED. In this work,  $\text{Eu}^{3+}$ - $\text{Ho}^{3+}$  doped  $\text{TeO}_2$ - $\text{GeO}_2$ - $\text{Nb}_2\text{O}_5$ - $\text{Li}_2\text{CO}_3$  (TGN)

glasses were fabricated by melt-quenching and subsequent heating, and its photoluminescence excitation, emissions and decay spectra were studied under the 458 nm excitations. As a result, the bright green, red and yellow emissions were observed in  $\text{Eu}^{3+}$ - $\text{Ho}^{3+}$  doped TGN glasses under the 458 nm excitations. Moreover, by adjusting concentration of  $\text{Ho}^{3+}$  ions, color coordinate converted from green to yellow and eventually to red region, due to the energy transfer from  $\text{Eu}^{3+}$  to  $\text{Ho}^{3+}$  and the cross relaxation between  $\text{Ho}^{3+}$  ions.

## 2. Experimental

All the chemicals used as received in the synthesis process were not further purified. The raw materials are  $\text{TeO}_2$  (99.99%),  $\text{GeO}_2$  (99.95%),  $\text{Nb}_2\text{O}_5$  (99.95%),  $\text{Li}_2\text{CO}_3$  (AR),  $\text{EuF}_3$  (99.99%) and  $\text{HoF}_3$  (99.99%). The samples were prepared with the following composition (in mol. %):  $70\text{TeO}_2$ - $15\text{GeO}_2$ - $10\text{Nb}_2\text{O}_5$ - $5\text{Li}_2\text{CO}_3$ . The single  $\text{Eu}^{3+}$ -doped and  $\text{Ho}^{3+}$ -doped TGN systems were realized by adding the appropriate amount of  $\text{EuF}_3$  (0.25, 0.50, 0.75 and 1.0 mol%) and  $\text{HoF}_3$  (0.25, 0.50, 0.75, 1.0 and 1.5 mol %), respectively. The  $\text{Eu}^{3+}$ / $\text{Ho}^{3+}$  co-doped TGN systems were prepared by changing the  $\text{HoF}_3$  concentrations from 0.25 to 1.0 mol% with  $\text{EuF}_3$  concentration fixed at 0.75 mol%. The well-mixed stoichiometric chemicals were put into an alumina crucible and melted at 950°C for 0.45 h. The glasses were fabricated by pouring the melt into a brass mold and then annealed at 300°C for 2 h to relinquish the inner stress. The excitation spectra, emission spectra and decay curves were measured on an Edinburgh Instruments FLS920 spectrofluorometer. All the measurements were carried out at room temperature.

### 3. Results and discussion

The excitation spectra of the TGN:  $\text{Eu}^{3+}$  monitored at 613 nm and TGN:  $\text{Ho}^{3+}$  monitored at 548 nm are shown in Fig. 1(a). The excitation spectra of TGN:  $\text{Eu}^{3+}$  sample consists of two excitation bands centered at 393 nm and 463 nm, which are assigned to the characteristic excitation lines of  $\text{Eu}^{3+}$ , while the excitation spectra of TGN:  $\text{Ho}^{3+}$  sample shows a very broad excitation band from ultraviolet to blue regions. Obviously, the excitation spectra bands for two trivalent ions in TGN glass exhibit a broad overlap at the blue region (450–470 nm), which is consistent with the strongest emission of GaN-based blue LED chip. Fig. 1(b) presents the emission spectra of the  $\text{Eu}^{3+}$ -doped,  $\text{Ho}^{3+}$ -doped and:  $\text{Ho}^{3+}/\text{Eu}^{3+}$  co-doped TGN glasses under 458 nm excitations, respectively. The  $\text{Eu}^{3+}$ -doped TGN glass shows a series of red emission bands, which attribute to  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$  (579 nm),  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  (590 nm),  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  (613 nm),  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$  (652 nm) and  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$  (700 nm) transitions of  $\text{Eu}^{3+}$  ions [18]. There are three emission bands are observed in  $\text{Ho}^{3+}$ -doped TGN glass, which origin from  $({}^3\text{S}_2, {}^5\text{F}_4) \rightarrow {}^5\text{I}_8$  (548 nm),  ${}^5\text{F}_5 \rightarrow {}^5\text{I}_8$  (662 nm) and  $({}^3\text{S}_2, {}^5\text{F}_4) \rightarrow {}^5\text{I}_7$  (755 nm) transitions of  $\text{Ho}^{3+}$  ions, presenting a bright green emission [19]. Moreover, when  $\text{Eu}^{3+}$  and  $\text{Ho}^{3+}$  ions are simultaneously doped into TGN glass, the sample exhibits all the above emission bands of the two doped ions, showing a bright yellow emission.

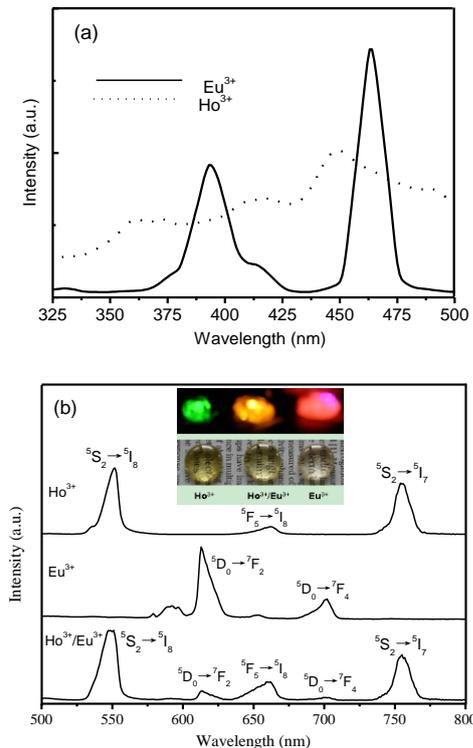


Fig. 1. (a) Excitation spectra of the TGN: 0.75mol% $\text{Eu}^{3+}$  ( $\lambda_{em}=613\text{nm}$ ) and TGN: 0.7 mol% $\text{Ho}^{3+}$  ( $\lambda_{em}=548\text{nm}$ ) glasses; (b) Emissions spectra of the TGN: 0.75mol% $\text{Eu}^{3+}$ , TGN: 0.75mol%  $\text{Ho}^{3+}$  and TGN: 0.75mol% $\text{Ho}^{3+}/0.75\text{mol}\%\text{Eu}^{3+}$  glasses under 458 nm excitations. The inset shows the three prepared samples and their photoluminescence photographs under 458 nm excitations.

Furthermore, the effects of  $\text{Ho}^{3+}$  concentration on emission intensity of  $\text{Eu}^{3+}/\text{Ho}^{3+}$  co-doped TGN samples are explored. As shown in Fig. 2, when the  $\text{Eu}^{3+}$  concentration is fixed at 0.75 mol%, with increasing  $\text{Ho}^{3+}$  concentration from 0 to 0.75 mol%, the intensities of 613 nm, 652 nm, and 700 nm red emissions of  $\text{Eu}^{3+}$  ions decrease gradually, which suggests that the energy transfer (ET) between  $\text{Eu}^{3+}$  and  $\text{Ho}^{3+}$  ions becomes active with increase of  $\text{Ho}^{3+}$  concentration. In addition, the intensities of green and red emissions of  $\text{Ho}^{3+}$  ions firstly increase and then decrease, with a maximum existing at about 0.5 mol%, which suggests that the cross relaxation (CR) process between  $\text{Ho}^{3+}$  ions becomes active at high  $\text{Ho}^{3+}$  concentration. The emission spectra for  $\text{Eu}^{3+}$ - $\text{Ho}^{3+}$  doped TGN glass were converted to the Commission International de l'Eclairage (CIE) 1931 chromaticity diagram [11], as plotted in Fig. 3. The CIE chromaticity diagram of  $\text{Eu}^{3+}$ - $\text{Ho}^{3+}$  doped TGN glass shows that the color coordinate can be converted from green to yellow and eventually to red region by adjusting concentration proportion of  $\text{Eu}^{3+}$  and  $\text{Ho}^{3+}$  ions. Thus, it is possible to realize the white emission by exciting yellow phosphors with a 458 nm blue chip LED.

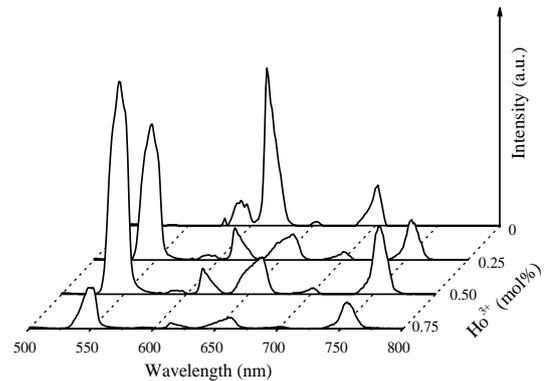


Fig. 2. The dependence of luminescence intensity of  $\text{Eu}^{3+}$ - $\text{Ho}^{3+}$  doped TGN glasses on  $\text{Ho}^{3+}$  concentration under 458 nm excitation.

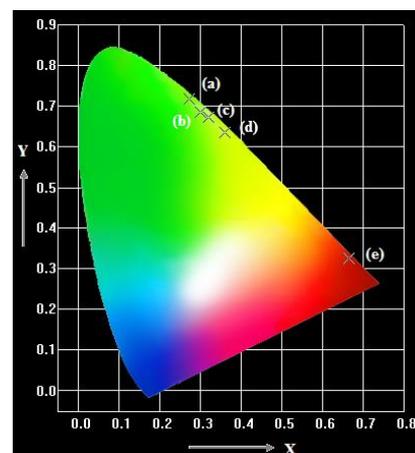


Fig. 3. 1931-CIE(X,Y) coordinate diagram showing chromaticity points of luminescence for TGN glasses doped with (a) 0.75mol% $\text{Eu}^{3+}/0.25\text{mol}\%\text{Ho}^{3+}$ , (b) 0.75mol% $\text{Ho}^{3+}$ , (c) 0.75mol%  $\text{Eu}^{3+}/0.50\text{mol}\%\text{Ho}^{3+}$ , (d) 0.75mol% $\text{Eu}^{3+}/0.75\text{mol}\%\text{Ho}^{3+}$ , (e) 0.75mol% $\text{Eu}^{3+}$ .

Room-temperature luminescence decay curves of  $\text{Eu}^{3+}$ :  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  (613 nm) and  $({}^5\text{S}_2, {}^5\text{F}_4) \rightarrow {}^5\text{I}_8$  (548 nm) transitions in  $\text{Eu}^{3+}$ - $\text{Ho}^{3+}$  doped TGN glasses are shown in Fig. 4. Because of the nonexponential nature of these curves, the decay time value  $\tau$  can be obtained by fitting the exponential data by the following equation

$$F = A + B_1 \exp(-t/T_1) + B_2 \exp(-t/T_2), \quad (1)$$

$$\tau = \Sigma(\text{Ti} * \text{Rel}\%), \quad (2)$$

where  $F$  is the instantaneous intensity of sample,  $A$  is the dark current of the detectors,  $B_1$  and  $B_2$  is weight factors for a certain system,  $t$  is the time,  $\text{Rel}\%$  is contribution percentage of the different luminescence,  $\tau$  is decay time value. The decay time values of 613 nm red emission are 878.71  $\mu\text{s}$  and 644.18  $\mu\text{s}$  for the TGN: 0.75 mol%  $\text{Eu}^{3+}$  and the TGN: 0.75 mol%  $\text{Eu}^{3+}$ /0.75 mol%  $\text{Ho}^{3+}$  samples. The decay time values of 548 nm green emission are 5.98  $\mu\text{s}$  and 6.56  $\mu\text{s}$  for the TGN: 0.75 mol%  $\text{Ho}^{3+}$  and the TGN: 0.75 mol%  $\text{Eu}^{3+}$ /0.75 mol%  $\text{Ho}^{3+}$  samples. It is obviously that, after  $\text{Ho}^{3+}$  is doped, the decay time values of 613 nm red emissions decrease, while the decay time values of 548 nm red emissions increase. These results suggest that the energy transfer from  $\text{Eu}^{3+}$  to  $\text{Ho}^{3+}$  ions occurs, and the red emission levels  ${}^5\text{D}_2$  and  ${}^5\text{D}_1$  of  $\text{Eu}^{3+}$  acts as energy donors, while the green emission level  $({}^5\text{S}_2, {}^5\text{F}_4)$  of  $\text{Ho}^{3+}$  acts as energy acceptor.

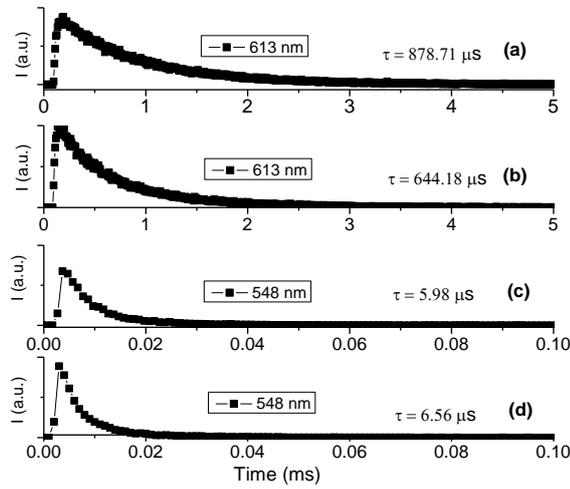


Fig. 4. Room-temperature luminescence decay curves under 458 nm excitation in TGN glasses doped with (a) 0.75 mol%  $\text{Eu}^{3+}$ , (b) 0.75 mol%  $\text{Eu}^{3+}$ /0.75 mol%  $\text{Ho}^{3+}$ , (c) 0.75 mol%  $\text{Ho}^{3+}$ , (d) 0.75 mol%  $\text{Eu}^{3+}$ /0.75 mol%  $\text{Ho}^{3+}$ .

The energy transfer between  $\text{Ho}^{3+}$  and  $\text{Eu}^{3+}$  was discussed in calibo glass under UV excitation [20]. Energy transfer between  $\text{Eu}^{2+}$  and  $\text{Ho}^{3+}$  ions was observed in  $\text{CaF}_2$  crystals under 5512  $\text{\AA}$  excitation [21]. Basing on the energy levels of  $\text{Ho}^{3+}$  and  $\text{Eu}^{3+}$  ion, the energy transfer and cross relaxation process are schematically illustrated in Fig.

5. Under 458 nm excitation,  $\text{Ho}^{3+}$  and  $\text{Eu}^{3+}$  ions are excited directly to the higher excited states  ${}^5\text{F}_2$  and  ${}^5\text{D}_2$  respectively, then relax to next energy level through nonradiative relaxations. The green, yellow, and red emissions are produced by the radiative transitions from  ${}^5\text{D}_0$  to  ${}^7\text{F}_n$  ( $n = 0, 1, 2, 3, 4$ ) transitions of  $\text{Eu}^{3+}$  and from  $({}^5\text{S}_2, {}^5\text{F}_4) \rightarrow {}^5\text{I}_8$ ,  ${}^5\text{F}_5 \rightarrow {}^5\text{I}_8$  and  $({}^5\text{S}_2, {}^5\text{F}_4) \rightarrow {}^5\text{I}_7$  (755 nm) transitions of  $\text{Ho}^{3+}$ . According to the Miyakawa–Dexter theory [22, 23], the probability of phonon-assisted energy transfer is expressed as

$$W_{\text{ET}} = W_{\text{ET}}(0) \exp(-\beta\Delta E), \quad (3)$$

where  $\Delta E$  is an energy gap between the energy levels of the donor and acceptor,  $W_{\text{ET}}(0)$  is the transfer rate when  $\Delta E = 0$ , and  $\beta$  is a function of effective phonon energy and electron-phonon coupling strength. The equation implies that the smaller the energy gap is, the faster the energy transfer occurs; the larger energy mismatch is, the smaller the energy transfer probability will be. When the  $\text{Ho}^{3+}$  ions was doped into TGN:  $\text{Eu}^{3+}$  samples, according to small energy gap between  ${}^5\text{D}_1$  ( $\text{Eu}^{3+}$ ) and  $({}^5\text{S}_2, {}^5\text{F}_4)$  ( $\text{Ho}^{3+}$ ) levels, the ET process:  ${}^5\text{D}_1$  ( $\text{Eu}^{3+}$ )  $\rightarrow$   $({}^5\text{S}_2, {}^5\text{F}_4)$  ( $\text{Ho}^{3+}$ ) is easy to carry out, resulting in the decrease of red emission and the increase of green emission, as shown in Fig.2. However, with the increase of  $\text{Ho}^{3+}$  concentration, the cross-relaxation process:  $({}^5\text{S}_2, {}^5\text{F}_4) + {}^5\text{I}_8 \rightarrow {}^5\text{I}_6 + {}^5\text{I}_6$  between  $\text{Ho}^{3+}$  ions become active, leading to the quenching of green and red emissions of  $\text{Ho}^{3+}$  ions [19].

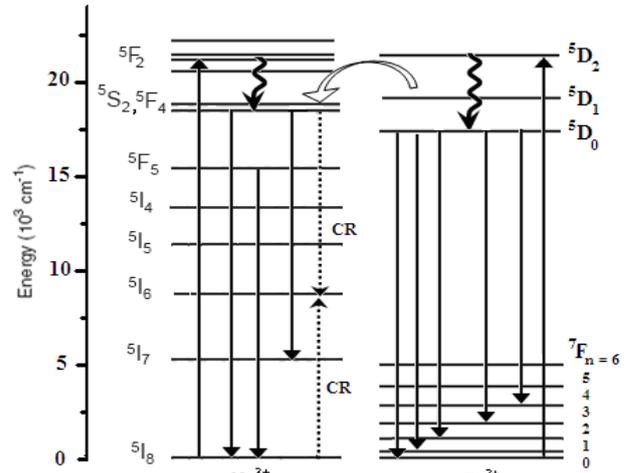


Fig. 5. Energy transfer between  $\text{Eu}^{3+}$  and  $\text{Ho}^{3+}$  ions under 458 nm excitation.

#### 4. Conclusions

$\text{Eu}^{3+}$  and  $\text{Ho}^{3+}$  doped TGN glasses were fabricated by melt-quenching and subsequent heating. The green and red emissions were observed in the  $\text{Eu}^{3+}$  and  $\text{Ho}^{3+}$  doped TGN glasses under 458 nm excitation, and the color-tunable

green, yellow and red emissions were achieved by controlling concentration proportion of  $\text{Eu}^{3+}$  and  $\text{Ho}^{3+}$  ions. The energy transfer from  $\text{Eu}^{3+}$  to  $\text{Ho}^{3+}$  ions was responsible for color-tunable emissions. The  $\text{Eu}^{3+}/\text{Ho}^{3+}$  co-doped TGN glass could be used as a white-light-emitting material under blue chip excitation.

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