White emission from $Tm^{3+}/Tb^{3+}/Eu^{3+}$ co-doped fluoride zirconate under ultraviolet excitation*

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We synthesize $Tm^{3+}/Tb^{3+}/Eu^{3+}$ triply-doped ZrF_4–BaF_2–LaF_3–AlF_3–NaF (ZBLAN) transparent glass by using a melt-quenching method. Under excitation of 365 nm, the white emission with Commission internationale deL'Eclairage (CIE) coordinates of (0.33, 0.33) is achieved at the Eu^{3+} concentration of 1.1 mol%. The mechanisms for white emission and the energy transfer process of $Tb^{3+} \rightarrow Eu^{3+}$ are discussed in terms of the photoluminescence, photoluminescence excitation spectra, and the light emission decay curves. The nature for the $Tb^{3+} \rightarrow Eu^{3+}$ energy transfer is described with the aid of an energy level diagram.

Keywords: white light emitting glass, photoluminescence, energy transfer process

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1. Introduction

In recent years, material with white emission has attracted significant attention for solid-state lighting (SSL), microscopic imaging, etc.[1–4] White emitting glass, which has been given serious attention of light, has a simple manufacture procedure, lower production cost, and better thermal stability, and is more likely to show improvement in performance than current phosphors[5] and implies the potential value in white light-emitting diodes (WLEDs).

The rare earth (RE) or transition metal ions, known as activators, are suitable candidates for multicolor light emission and even white emission when they are added to glass. The white emission from Dy^{3+}-doped borosilicate glass and oxyfluoride glass ceramics were early observed under the blue chip excitation by Jayasimhadri[6] and Babu.[7] In the second report, the emission intensity ratio from yellow to blue from Dy^{3+} was modulated by varying the annealing temperature. However, the standard Commission Internationale deL'Eclairage (CIE) coordinates ($x = 0.33$, $y = 0.33$) in the white light zone was found to be difficult to achieve.

Compared with single doping, multi-doped glass is a dominant candidate for realization of white emission and the improvement of the color rendering index. In 2007, the white emission was observed from the combination of green and orange-red emission by Tb^{3+} and Sm^{3+} co-doped silicate and borosilicate glass.[8] The effect of the Tb^{3+}-to-Sm^{3+} concentration ratio on the luminescence properties in a different glass matrix was discussed and related to the two mechanisms including the self-quenching effects of Sm^{3+} ions and the energy transfer from Tb^{3+} $^5D_4$ to Sm^{3+} $^4G_{5/2}$. The white emission was also achieved in Tm^{3+} and Dy^{3+} co-doped oxyfluoride germinate glass by the energy transfer process from Dy^{3+} ($^4F_{9/2}$) to Tm^{3+} ($^1G_4$).[9] Later, a white emission with the CIE coordinate ($x = 0.31$, $y = 0.33$), in which the fluorescence emissions of blue, green, and red were simultaneously obtained, from $Ce^{3+}/Tb^{3+}/Mn^{2+}$ triple-doped borosilicate glass under ultraviolet excitation.[10] The comparison for the photoluminescence (PL) and photoluminescence excitation (PLE) spectra were conducted by the assembly of ion doping and supported to the energy transfer from Ce^{3+} to Tb^{3+}. In 2013, the white emission was observed from the combination of blue, green, and orange-red emission by Tm^{3+}, Tb^{3+}, and Eu^{3+} co-doped oxyfluoride[11] and phosphate glass.[12] However, different electron transition mechanisms were presented. Up to now, it is generally considered that multi-doped glass is desirable for realization of white emission and the improvement of the color rendering index.

To be considered as low phonon energy (560 cm^{-1})[13] and high dopant solubility, fluorozirconate glass or glass ceramic has been represented as a promising new direction for fluorescent materials.[14,15] In this study, a triply-doped transparent ZrF_4–BaF_2–LaF_3–AlF_3–NaF (ZBLAN) glass with Tm^{3+}, Tb^{3+}, and Eu^{3+} ions was synthesized by the melt-quenching method. The fluorescent emission spectra were measured under excitation of 365 nm and the luminescence mechanism was discussed base on the PLE and decay time

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spectra.

2. Experimental

The melt-quenching method was employed for preparation of glass samples in this paper. A mixture containing purity grade of ZrF_4, BaF_2, LaF_3, AlF_3, and NaF, was weighted with chemical composition of $53ZrF_4$, $20BaF_2$, $4LaF_3$, $3AlF_3$, and 20NaF in mole percent. The selected RE ion doping amount was 1 mol% Tm_2O_3, 0.1 mol% Tb_4O_7, and different Eu_2O_3 concentration of 0.5, 0.7, 0.9, 1.1, and 1.2 mol%, which was labeled as $Tm^{3+}{}_1$–$Tb^{3+}{}_{0.1}$–$Eu^{3+}{}_x$. After being mixed and grinded thoroughly, the mixture was melted at about 800 °C for 0.5 h and then was annealed at 300 °C for 2 h to release its inner stress. To confirm the luminescence mechanism, the reference samples including single-doped Tm^{3+}, Tb^{3+}, and Eu^{3+} at 1 mol% (denoted as $Tm^{3+}{}_1$, Tb^{3+}_1, $Eu^{3+}{}_1$) and double-doped 0.1 mol% Tb^{3+}/1.1 mol% Eu^{3+} (denoted as $Tb^{3+}{}_{0.1}$–$Eu^{3+}{}_{1.1}$) were obtained under the same conditions.

The X-ray diffraction (XRD) pattern of the triply-doped glass sample was examined with a Rigaku-Dmax 2500 diffractometer employing Cu Kα radiation ($\lambda = 0.15405$ nm) with a 2θ range from 10° to 60°. The transmission spectrum was monitored in the wavelength range between 300 and 800 nm by a U-4100 spectrophotometer. The fluorescence spectra between 400 and 650 nm, the fluorescence emission decay spectra, and the luminescence quantum efficiency were measured by a Jobin Yvon FL3 spectrofluorometer. All measurements were carried out at room temperature.

3. Results and discussion

The XRD pattern of triply-doped $Tm^{3+}{}_1$–$Tb^{3+}{}_{0.1}$–$Eu^{3+}{}_{1.1}$ sample is shown in Fig. 1(a), while two broad diffraction peaks are at about 26° and 47°, respectively, representing the typical diffraction pattern for glass.[16] The sharp peaks in the curve might arise from a noisy signal. The absorption spectrum in the UV–Vis range is shown in Fig. 1(b). The observed main absorption peaks at 356 nm, 360 nm, 374 nm, 379 nm, 392 nm, 414 nm, and 464 nm can be attributed to the transition of Tm^{3+}, Tb^{3+}, and Eu^{3+}, respectively. From the optical transmission spectrum in the inset, the light transmittance can be estimated to be 30% in the visible range.

The PL spectra for triply-doped ZBLAN samples with a doping concentration of $Tm^{3+}{}_1$–$Tb^{3+}{}_{0.1}$–Eu^{3+}_x were collected under excitation at 365 nm and are shown in Fig. 2(a). The typical emission peaks in red, green, and blue bands were acquired, corresponding to the transition from $^5D_0 \rightarrow {}^7F_1$ (589 nm) and $^5D_0 \rightarrow {}^7F_2$ (611 nm) of Eu^{3+}, $^5D_4 \rightarrow {}^7F_6$ (487 nm) and $^5D_4 \rightarrow {}^7F_5$ (541 nm) of Tb^{3+} and $^1D_2 \rightarrow {}^3F_4$ (449 nm) of Tm^{3+}, respectively. The emission intensity for Eu^{3+} exhibits modulation with various Eu^{3+} doped concentrations. The luminescence quantum efficiency of the triply-doped $Tm^{3+}{}_1$–$Tb^{3+}{}_{0.1}$–$Eu^{3+}{}_{1.1}$ sample is measured to be 36.2%. The calculated CIE values with different Eu^{3+} concentrations are also shown in Fig. 2(b). The value for the sample at the concentration of 1.1 mol% is ($x = 0.332$, $y = 0.3303$) in accordance with the standard white emission ($x = 0.33$, $y = 0.33$), and its correlated color temperature is 5506 K. The color rendering index is estimated to be 98.5 from the Walter method.

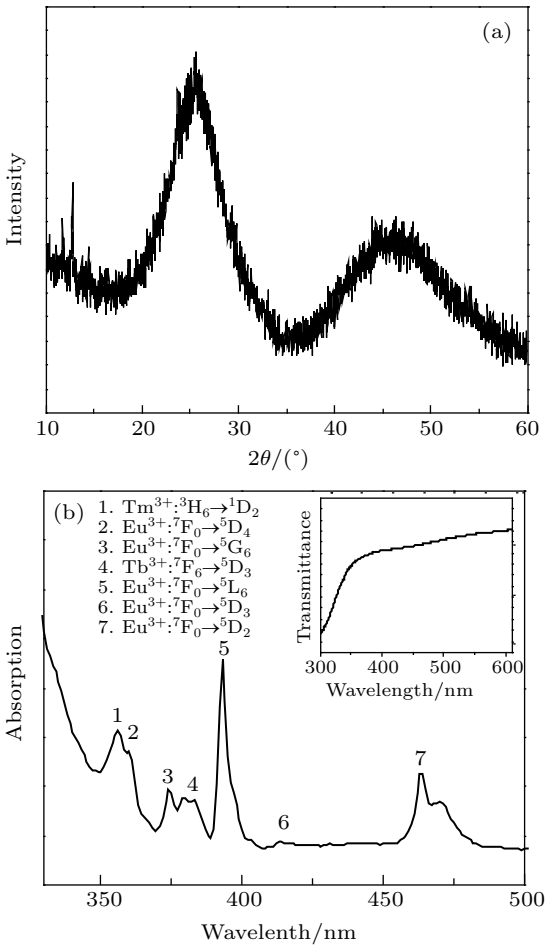


Fig. 1. (a) The XRD pattern of triply-doped $Tm^{3+}{}_1$–$Tb^{3+}{}_{0.1}$–$Eu^{3+}{}_{1.1}$ ZBLAN glass. (b) The absorption spectrum of the sample. Inset shows the transmitted spectrum.

To verify the transition of electrons between levels and white emission mechanism of the sample, the PLE spectra for individual doping RE^{3+} ions in ZBLAN are shown in Fig. 3. For typical transition radiation of Tm^{3+} at 449 nm in Fig. 3(a), the excitation peak for Tm^{3+} single-doped ZBLAN is centered at 356 nm, representing the electronic transitions from the ground-state $^3H_6$ to excited-state $^1D_2$. The absorption band range between 340 and 370 nm means that Tm^{3+} could be excited effectively by 365 nm. For Tb^{3+} single-doped sample, the excitation wavelength for Tb^{3+} 541 nm emission could be related to the several individual sharp peaks (as shown in Fig. 3(b)) including 350 nm ($^7F_6 \rightarrow {}^5D_2$), 367 nm ($^7F_6 \rightarrow {}^5L_{10}$), 376 nm ($^7F_6 \rightarrow {}^5D_3$), and 485 nm ($^7F_6 \rightarrow {}^5D_4$). When the emission wavelength is monitored at 611 nm, the excitation spectrum for Eu^{3+} single-doped sample is depicted in Fig. 3(c). The six sharp excitation peaks are observed owing

to the transition from $^7F_0$ to the excited states $^5D_4$, $^5L_8$, $^5G_6$, $^5L_6$, $^5D_3$, $^5D_2$, etc.

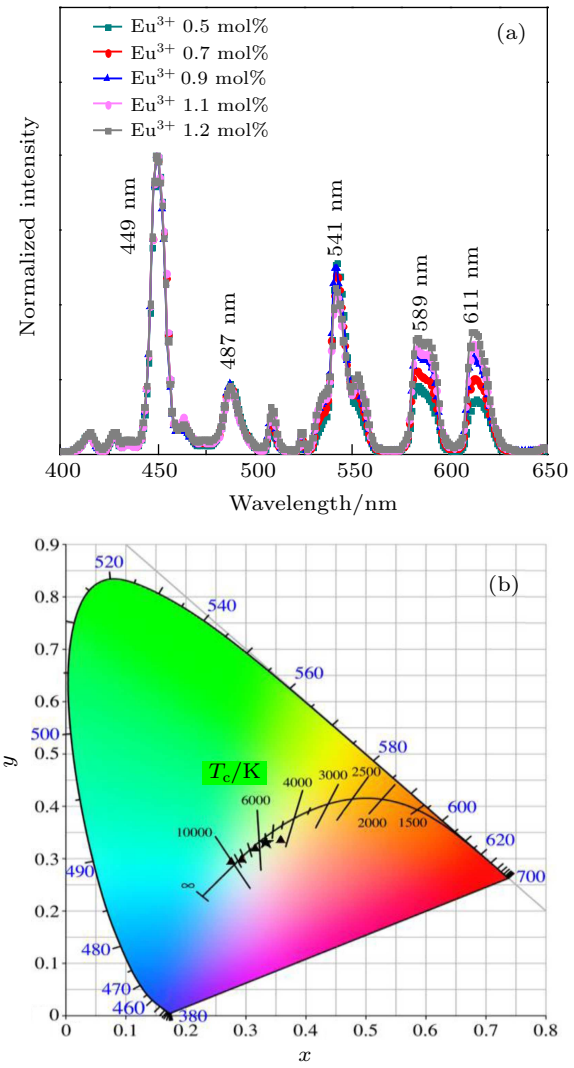


Fig. 2. (color online) (a) Emission spectrum and (b) the CIE chromaticity diagram for $Tm^{3+}{}_1$–$Tb^{3+}{}_{0.1}$–Eu^{3+}_x ($x = 0.5$, 0.7, 0.9, 1.1, 1.2 mol%) doped samples, the CIE values are labeled with triangles and the standard value for white light is labeled as a star by Eu^{3+}-doped concentration of 1.1 mol%.

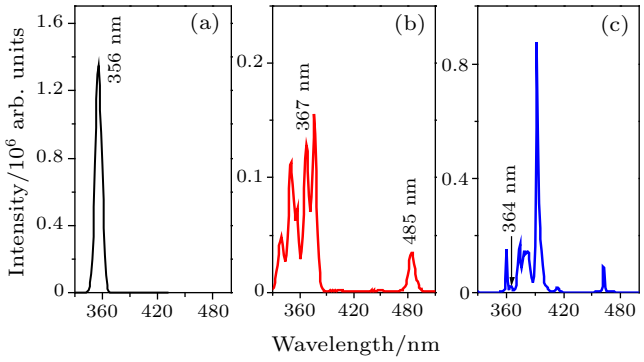


Fig. 3. (color online) The PLE spectra for single-doped (a) Tm^{3+}, (b) Tb^{3+}, and (c) Eu^{3+} sample.

The excitation energy for Eu^{3+} transition radiation can be provided by the direct absorption of photons or by the energy transfer from matrix or other rare earth ions. From Fig. 3, it is believed that Tm^{3+} and Tb^{3+} are simultaneously excited by 365 nm effectively, but Eu^{3+} is excited weakly. Considering PLE and PL spectra of Eu^{3+} single-doped and $Tm^{3+}/Tb^{3+}/Eu^{3+}$ triply-doped ZBLAN in Fig. 4, the emission intensity of Eu^{3+} at 611 nm in the triply-doped sample is increased three times more than that of the Eu^{3+} single-doped sample (see Fig. 4(b)). An additional excitation wavelength for Eu^{3+} 611-nm emission in triply-doped sample (see Fig. 4(a)) is found at 487 nm, which is reasonable to associate with the transition Tb^{3+} $^5D_4 \rightarrow {}^7F_6$. It implies that the radiation energy for Eu^{3+} at 611 nm is probably both from the co-doped energy transfer by Tb^{3+} and its self-excitation. In particular, there is no evidence confirming the possible energy transfer between Tm^{3+} and Eu^{3+}. The discussion is different from the conclusion by Kuznetsov *et al.*, in which no energy transfer process was concerned for white emission generation in $Tm^{3+}/Tb^{3+}/Eu^{3+}$ triply-doped oxyfluoride glass when regarding Pb and Cd heavy atoms as addition agents.[11]

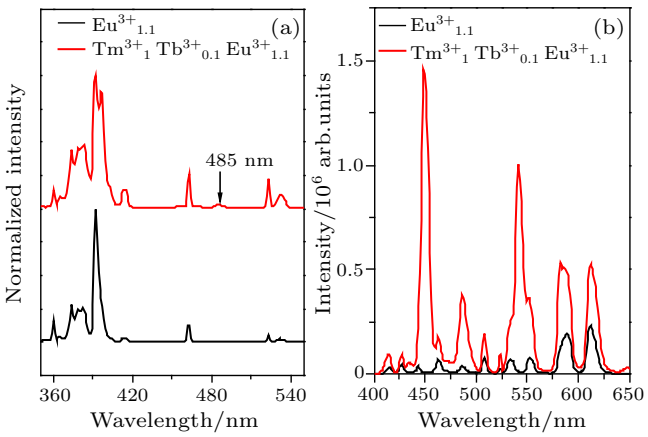


Fig. 4. (color online) (a) Excitation and (b) emission spectra for Eu^{3+} single-doped and $Tm^{3+}/Tb^{3+}/Eu^{3+}$ triply-doped glass.

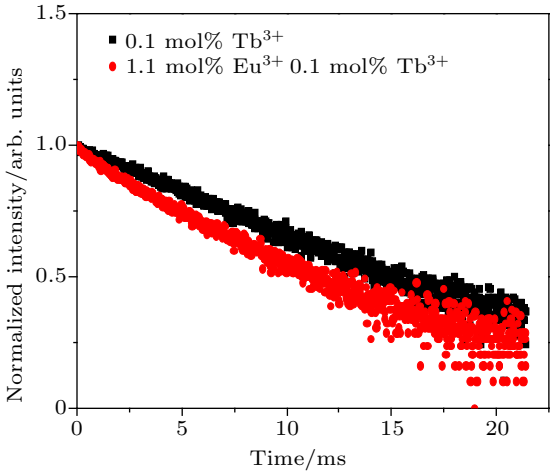


Fig. 5. (color online) Decay curves of Tb^{3+} at 487 nm in single-doped glass and Tb^{3+}/Eu^{3+} co-doped samples.

The energy transfer process and its dynamics in the doped ZBLAN can be discussed by measuring the decay time of the

luminescence radiation. Figure 5 shows the light emission decay curves for Tb^{3+} 487 nm emission in Tb^{3+}/Eu^{3+} co-doped and Tb^{3+} single-doped ZBLAN, respectively. Fitted by the first-order exponential equation $I(t) = I_0 + A\exp(-t/\tau)$,[17] the Tb^{3+} $^5D_4 \rightarrow {}^7F_6$ (487 nm) transition in its single-doped ZBLAN has a lifetime of about 4.575 ms, but it is found to reduce to 3.219 ms in Tb^{3+}/Eu^{3+} co-doped ZBLAN. The energy transfer efficiency is estimated to be 30% by using the formula $\eta(\mathrm{ET}) = 1 - \tau_{\mathrm{AD}}/\tau_{\mathrm{D}}$,[18] in which τ_{AD} and τ_{D} represent amplitude-average lifetimes of donor (Tb^{3+}) in the presence and absence of acceptor (Eu^{3+}).

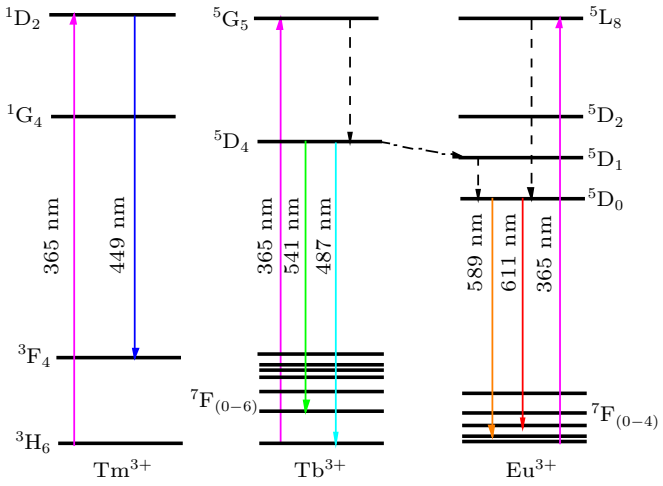


Fig. 6. (color online) Energy level diagram for the $Tm^{3+}/Tb^{3+}/Eu^{3+}$ triply-doped ZBLAN glass.

The explanation for excitation and emission paths for the $Tm^{3+}/Tb^{3+}/Eu^{3+}$ triply-doped ZBLAN can be expressed by the energy level diagram in Fig. 6. By the direct absorption of the energy of 365 nm, the ground-state electron of Tm^{3+} is excited to $^1D_2$, and then down to $^3F_4$ by radiative transition for 449 nm emission. Simultaneously, the ground-state electrons of Tb^{3+} are excited to $^5G_5$ and then relax to the $^5D_4$ energy level. When the electron returns back to the low energy states of Tb^{3+}, the transition radiation due to $^5D_4 \rightarrow {}^7F_6$ and $^5D_4 \rightarrow {}^7F_5$ can be observed. The directly excited electrons at the $^5L_8$ level of Eu^{3+} would relax to the $^5D_0$ energy level and turn to the $^7F_1$ and $^7F_2$ levels of Eu^{3+}, having the radiative transition wavelength at 589 nm and 611 nm. The cross energy transfer processes occuring between $^5D_4$ of Tb^{3+} and the $^5D_1$ level of Eu^{3+} improves the PL intensity for Eu^{3+} 611 nm under 365 nm excitation.

4. Conclusions

In conclusion, $Tm^{3+}/Tb^{3+}/Eu^{3+}$ triply-doped ZBLAN glass is synthesized by the melt-quenching method. Under excitation of 365 nm light, the PL spectra show the red (Eu^{3+}), green (Tb^{3+}), and blue (Tm^{3+}) band emission, simultaneously. With increasing the Eu^{3+} doping concentration, the color tones of triply-doped ZBLAN change from blue to white, in which the standard white CIE coordinates ($x = 0.33$, $y = 0.33$) are obtained at 1.1 mol%. In assistance of PLE and the decay time spectra, the energy transfer process from Tb^{3+} to Eu^{3+} is responsible for the effective 611-nm emission of Eu^{3+}.

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