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Enhanced Luminescent Properties in Tm^{3+}/Dy^{3+} Co-doped Transparent Phosphate Glass Ceramic

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Abstract. Novel Tm^{3+}/Dy^{3+} co-doped phosphate glass and glass ceramic samples for white light emitting diodes were prepared by melt quenching method. Under 353 nm excitation, the colors of the luminescence of the glass and glass ceramic samples are white. The CIE chromaticity coordinates (0.338, 0.328) of the emission from the glass ceramic is close to the standard white-light illumination (0.333, 0.333). Compared to the glass, the fluorescence intensity in the glass ceramic is greatly enhanced.

1 Introduction

Nowadays, white light-emitting diodes have attracted significant attention and replaced conventional fluorescent lamps owing to their high brightness, reliability, lower power consumption and long lifetimes [1–3]. Generally, W-LEDs can be fabricated by combining GaN-based blue chips with YAG: Ce^{3+} yellow phosphors [4]. However, this combination still have some inherent drawbacks such as poor heat resistance, high correlated color temperature and low color rendering index due to their low thermal quenching temperature and lack of red emitting element [5]. In order to overcome the problems thoroughly, the rare-earth (RE) doped phosphors have been achieved great important applications in the development of W-LEDs [6-11]. Considering energy and environment problems, it is urgent to develop pollution-free, cheap, highly efficient white-light-emitting (WLE) materials. It is generally known that the homogenization of the emission in the single phosphor is better than that of the mixed phosphors, and the product cost of the single phosphor is also lower compared to that in the mixed phosphors. So, it is most valuable to explore the single phosphor. Currently, in order to enhance the luminous efficiency, the hosts with lower phonon energy are usually chosen [12-14]. However, this way does not thoroughly solve the problem of low luminous efficiency. It is found that the emission efficiency of the visible light is higher at ultraviolet light excitation. Under 350 nm excitation, the Dy^{3+} doped glass and glass ceramic materials were discovered to be in the vicinity of white light

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zone [15-16] and the materials with Tm^{3+} ion were found to be of the blue phosphor [12].

For all we know, there is less report on the WLE of Tm^{3+}/Dy^{3+} co-doped glass phosphor [17]. In order to obtain enhanced white light phosphor, the Tm^{3+}/Dy^{3+} co-doped phosphate glass and glass ceramic samples were prepared. The emission spectra and the CIE chromaticity coordinates of the samples are studied and discussed.

2 Experimental

Glasses with composition of (in mol %) $(38P_2O_5$-$44ZnO$-$16SrO$- $2ZrO_2)$-$0.3Tm_2O_3$, $(38P_2O_5$-$44ZnO$-$16SrO$-$2ZrO_2)$-$0.4Dy_2O_3$, $(38P_2O_5$-$44ZnO$-$16SrO$-$2ZrO_2)$-$0.3Tm_2O_3$-$0.4Dy_2O_3$ were prepared by the melt quenching method using analytical grade $SrCO_3$, $NH_4H_2PO_4$, ZnO and ZrO_2 and high purity (≥99.99%) Tm_2O_3, Dy_2O_3. The weighed raw materials in requisite proportions were ground and mixed thoroughly in an attrition mill. The mixtures were melted in an electrical furnace and kept at 1300℃ in air for 2 h. Glass melts were poured on a preheated copper mold to make glass blocks. The glass samples were heated at 480℃ for 4 h to release thermal stress. To obtain glass ceramic, the Tm^{3+}/Dy^{3+} co-doped phosphate glass was heated at 570℃ ascertained by DTA for 10 h. Finally, the samples were cut and polished for optical measurements.

The structural analysis of the glass samples was identified by a model D8-Advance X-ray powder diffractometer with Cu Ka radiation at room temperature. To investigate the optical measurements of the glasses, all samples were incised and surface-polished polished for optical measurements and all the measurements were performed with the same instrument parameters at room temperature. The emission and excitation spectra were recorded on FL3-TCSPC fluorescent spectrometer (Horiba Jobin–Yvon, France), using Xenon lamp as the excitation source. The chromaticity coordinates (x, y) were calculated based on the photoluminescent spectra by using software.

3 Results and Discussion

Fig. 1(a) shows the excitation spectra of the Tm^{3+} (λ_{em}=452 nm) and Dy^{3+} (λ_{em}=574 nm) single-doped phosphate glass samples. For the Tm^{3+} doped sample, the excitation band at 350-375 nm for the 452 nm blue emission is discovered. The main excitation band peaking at 356 nm is assigned to the Tm^{3+}: $^3H_6 \rightarrow {}^1D_2$ transition monitored at 452 nm. For the Dy^{3+} doped sample, monitoring the Dy^{3+} emission at 574 nm, corresponding to the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition, the excitation maximum is located around 347 nm corresponding to $^6H_{15/2} \rightarrow {}^6P_{7/2}$ transition. The other secondary excitation peaks, detected around 321 nm, 363 nm and 385 nm comply with the transitions $^6H_{15/2} \rightarrow {}^6P_{3/2}$, $^6H_{15/2} \rightarrow {}^6P_{5/2}$ and $^6H_{15/2} \rightarrow {}^4F_{7/2}$, respectively [18]. Based on the excitation spectra, the 353 nm light is chosen as the pumping source. The emission spectra of the two samples at 353 nm light excitation are shown in Fig. 1(b). The Tm^{3+} doped sample displays one intense blue emission band centered at 452 nm derived from the Tm^{3+}: $^1D_2 \rightarrow {}^3F_4$ transition. The Dy^{3+} doped sample exhibits two intense bands centered around 482 nm (blue), 574 nm (yellow) and a weak band around 663 nm (red), corresponding to the $^4F_{9/2} \rightarrow {}^6H_J$ (J = 15/2, 13/2, 11/2) transitions, respectively [19].

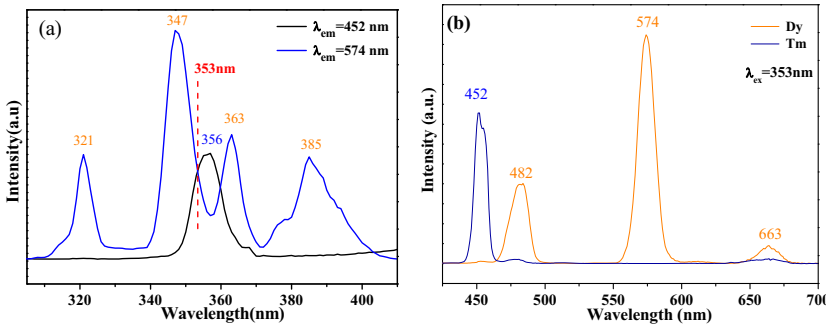


Fig. 1 (a) Excitation spectra of the Tm^{3+} (λ_{em}=452 nm) and Dy^{3+} (λ_{em}=574 nm) single-doped phosphate glasses. (b) Emission spectra of the Tm^{3+} and Dy^{3+} single-doped phosphate glasses at 353 nm light excitation.

Fig.2 indicates the DTA curve of the mother glass at heating rate of 10 k/min. It is observed that the glass transition temperature (T_g) is 480℃, the starting crystallization temperature (T_x) is 570℃ and the peak crystallization temperature (T_p) is 620℃. Glass ceramic was prepared by annealing at 570℃ for 10 h and the corresponding glass ceramic was hereinafter denoted as GC.

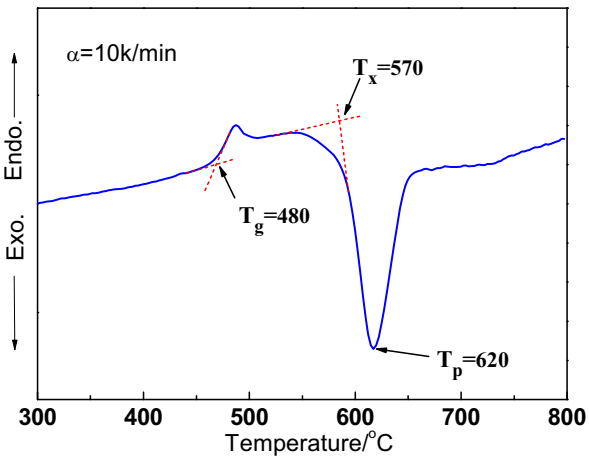


Fig. 2 DTA curve of the mother glass at heating rate of 10k/min

Fig. 3 shows the emission spectra of the Tm^{3+}/Dy^{3+} co-doped phosphate glass and glass ceramic and the XRD patterns. The 452 nm blue emission comes from the $^1D_2 \rightarrow {}^3F_4$ transition of Tm^{3+} and the population of $^1D_2$ is the result of ground state absorption (GSA)1: $^3H_6+hv \rightarrow {}^1D_2$. The 482, 574 and 663 nm emissions are attributed to the transitions of Dy^{3+}: $^4F_{9/2} \rightarrow {}^6H_J$ (J = 15/2, 13/2, 11/2). The population processes of $^6P_{7/2}$ can be described as follows: by GSA2: $^6H_{15/2}+hv \rightarrow {}^6P_{7/2}$, the Dy^{3+} ions in the ground state are excited to $^6P_{7/2}$ state, then the ions are relaxed to $^4F_{9/2}$ state by a non-radiative transition. The results of XRD patterns indicate that the glass sample is structurally amorphous characterized by diffused humps and absence of sharp peaks due to any crystalline state, and $SrZnP_2O_7$ crystallites are precipitated in the transparent glass ceramic. The crystallites size in glass ceramic sample is about 12 nm calculated according to the Scherrer equation [13].

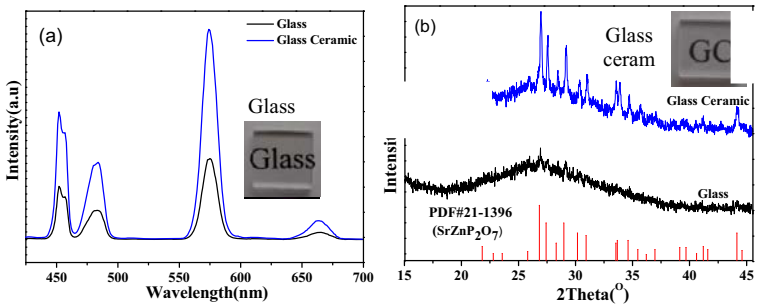
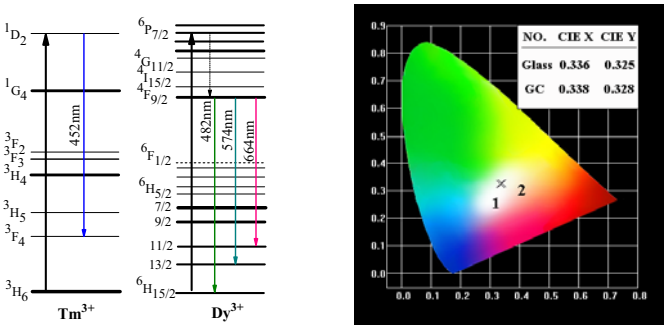


Fig. 3 (a) Emission spectra of the Tm^{3+}/Dy^{3+}co-doped phosphate glass and glass ceramic under 353 nm excitation and (b) XRD patterns of the co-doped glass and glass ceramic (GC).



(a) (b)

Fig. 4 (a)Energy diagrams of the Tm^{3+} and Dy^{3+} ions, and (b) CIE(X, Y) coordinate diagram that shows the chromaticity points of the emissions in the phosphate glass (1) and GC (2) at 353 nm light excitation.

The energy diagrams of the Tm^{3+} and Dy^{3+} ions are shown in Fig. 4(a).The CIE chromaticity coordinates of the emissions from the glass and glass ceramic are (X=0.336, Y=0.325) and (X=0.337, Y=0.328), as shown in Fig. 4(b). The coordinates are close to the standard equal energy white-light illumination (X=0.333, Y=0.333). The emission color of the glass and glass ceramic is white for the naked eye seen in the inset of Fig. 4(a). Particularly, the white light appears in the glass ceramics is bright and dazzling along with light scattering. The emission spectrum of the glass ceramic has covered the whole visible light range. The emission intensity of the glass ceramic is stronger than that of the glass.

4 Conclusions

Tm^{3+}/Dy^{3+} co-doped phosphate glass and glass ceramic samples were prepared and characterized. Under 353 nm light excitation, the colors of the luminescent glass and glass ceramic samples appear white. Especially, a very dazzling white appears on the glass ceramic sample. The emission intensity of the glass ceramic is much stronger than that of the glass. Hence, the results of these investigations indicate that these materials can be useful for white LEDs.

5 Acknowledgements

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