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Letter

Novel SnO_2/MnO co-doped phosphate glasses with tunable luminescence properties

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ABSTRACT

In the present work, novel SnO_2/MnO co-doped phosphate glasses are prepared and their tunable luminescence properties are presented. Under excitation at 267 nm, all co-doped glasses exhibit an assembly of SnO_2 blue emission at 420 nm and MnO red emission around 600 nm. With the increasing of MnO concentration, intensity of the SnO_2 blue emission decreases while that of MnO red emission increases. With the increasing of SnO_2 concentration, both SnO_2 and MnO emissions are greatly enhanced, resulting in the white light emitting.

1. Introduction

Luminescent glasses doped with active elements are essential for applications in solid state lasers, fiber amplifiers, color displays, optical memory and solar cells [1–4]. Such applications rely on the luminescence properties of dopants, which, in most cases, are rare earth (RE) ions. Other frequently reported dopants in glasses include semiconducting oxides (SCO) and transition metal (TM) ions. SCO normally shows an intense luminescence in near ultraviolet and visible region due to its strong optical transitions from the valence to the conduction band [5–8], while fluorescence mechanism of TM ions usually involves both parity and spin forbidden transitions with the relatively weak emissions [9]. To enhance luminescence of glasses, energy transfer (ET) mechanisms between dopants have been extensively investigated. While many published work in this respect have traditionally focused on RE pairs [10–12] and recently moved to SCO/RE or RE/TM pairs [6–8,13], ET processes between SCO/TM pairs is scarcely reported.

In the present study, we presented our recent experimental results on novel luminescent phosphate glasses co-doped with SnO_2 and MnO ions. Since SnO_2 shows an intense luminescence around 420 nm in phosphate glass [6] and MnO exhibit green, orange, or red photoluminescence depending on host materials [9], combination of them might produce white light. Besides, both SnO_2 and MnO show the broad emission bands, which are different from majority of RE ions normally with sharp lines. Therefore, SnO_2/MnO pair most likely display unique luminescence behaviors, especially, efficient excitation of MnO via ET from SnO_2 is highly expected. Moreover, compared with RE ions which normally have limited solubility in glasses due to high-field strength and thus easily cause problems with concentrations quenching, SnO_2 and MnO can be incorporated into glass matrix in the relatively high concentration due to their role as an intermediate in glass network [9].

2. Experimental

Glasses were prepared from high purity compounds ($NH_4H_2PO_4$, $SrCO_3$, SnO_2, $MnCO_3$, 99.99%). The molar compositions of glass samples are listed in Table 1. The starting materials in powder form were mixed and ground thoroughly in appropriate proportion then melted at 1250 °C for 1.5 h, Glass melts were poured into the preheated steel mould and then quenched in air. The obtained glass samples were annealed at temperatures about 20 °C below their T_g for 2 h to remove inner stress. Samples were cut into 2 mm in thickness and well polished to mirror smoothness to achieve good optical quality. The emission and excitation spectra were recorded by a Fluorolog-3-P UV–vis-NIR fluorescence spectrophotometer (Jobin Yvon, France), while the transmission spectra were recorded by a Spectrumlab gold S54T UV–vis-NIR spectrometer (China), all measurement are carried out at room temperature.

3. Results and discussion

As an example, the absorption spectrum of the SnO_2/MnO co-doped sample (G4) is shown in Fig. 1. It is clearly seen that the UV cut-off position is located around 240 nm which is due to glass matrix absorption. The inset (zoom in the region from 300 nm to

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Table 1
The composition and color coordinates of samples G0–G8.

Sample	Composition (mol%)				Color coordinates (x, y)
	P_2O_5	SrO	SnO_2	MnO	
G0	75	25	1.5	–	–
G0′	75	25	–	2.0	–
G1	75	25	1.5	0.5	0.2179, 0.2038
G2	75	25	1.5	1.0	0.2646, 0.2382
G3	75	25	1.5	2.0	0.3457, 0.2894
G4	75	25	1.5	4.0	0.4524, 0.3357
G5	75	25	1.0	2.0	0.3415, 0.2870
G6(G3)	75	25	1.5	2.0	0.3457, 0.2894
G7	75	25	2.0	2.0	0.3447, 0.2895
G8	75	25	2.5	2.0	0.3433, 0.2885

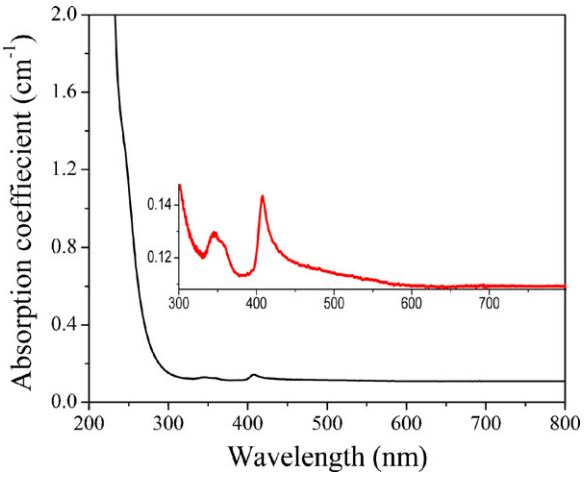

Fig. 1. Absorption spectrum of G4.

800 nm) shows two main peaks located around 350 nm and 407 nm. The peak at 350 nm is a combination of 346 nm and 356 nm corresponding to the electronic transition of Mn^{2+} from the ground state $^6A_1(S)$ to the excited state $^4E(D)$ and $^4T_2(D)$ transition, respectively. While 407 nm is a combination of 407 nm and 422 nm and that correspond to the transition of Mn^{2+} from ground state $^6A_1(S)$ to the excited state $^4E(G)/^4A_1(G)$ and $^4T_2(G)$, respectively [9]. Meanwhile, the broad peaks centered around 500 nm is also distinguishable which is attributed to the electronic transition of Mn^{2+} ions from the $^6A_1(S)$ to $^4E(D)$ [9,14].

Fig. 2 presents emission spectra of singly doped glass samples. The SnO_2 doped sample (G0) shows a broad luminescence

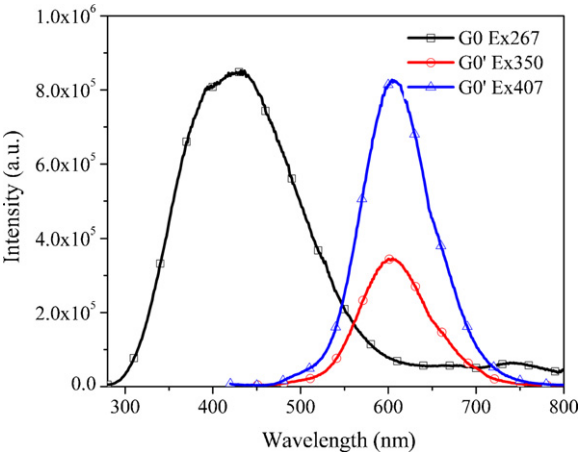

Fig. 2. Emission spectra of glasses singly doped with SnO_2 or MnO.

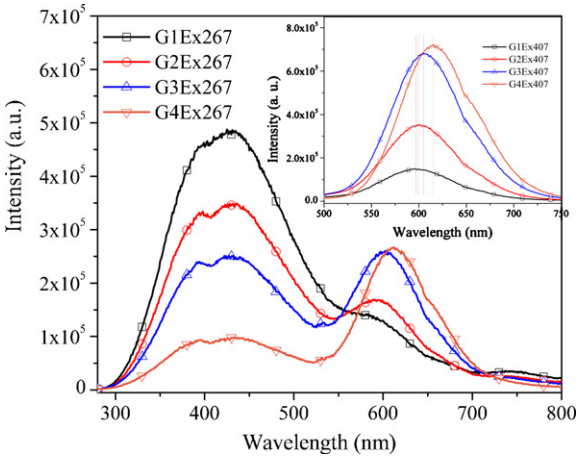

Fig. 3. Emission spectra of samples G1–G4 with 267 nm and 407 nm (inset) excitation.

band peaking at 420 nm under excitation at 267 nm while the MnO doped sample (G0′) exhibits a characteristic red emission at about 600 nm under excitation at both 350 nm and 407 nm. The emission at 420 nm is generally believed due to the T_1 to S_0 transition of SnO_2 [5,6] while the 600 nm emission band is caused by the $^4T_1(G)$ to $^6A_1(S)$ transition of Mn^{2+} ions [9,14].

Emission spectra of SnO_2/MnO co-doped samples are shown in Fig. 3 (G1–G4) and Fig. 4 (G5–G8), respectively. It is seen that all co-doped samples show an assembly of SnO_2 blue and MnO red emissions. Moreover, the MnO emission suffers a red shift from 596 nm (G1) to 616 nm (G4), which, according to the reference, is caused by the increasing interaction of Mn^{2+}–Mn^{2+} pairs due to the increasing of MnO concentration [9,14]. The most interesting observations are the different luminescence behaviors of these glasses resulting from the different concentrations of activators. With the constant SnO_2 (1.5 mol%) and increased MnO concentrations (Fig. 3), the intensity of SnO_2 emission around 420 nm decreases tremendously while the intensity of MnO emission around 600 nm increases steadily. With the constant MnO (2.0 mol%) and increased SnO_2 concentrations, however, both SnO_2 blue emission and MnO red emission are enhanced significantly. We can thus reasonably suggest that an energy transfer from SnO_2 to MnO most likely occurs.

To understand the possible energy transfer process, the excitation spectra of singly doped (G0 and G0′) and co-doped (G3) samples are compared in Fig. 5. The SnO_2 doped sample shows

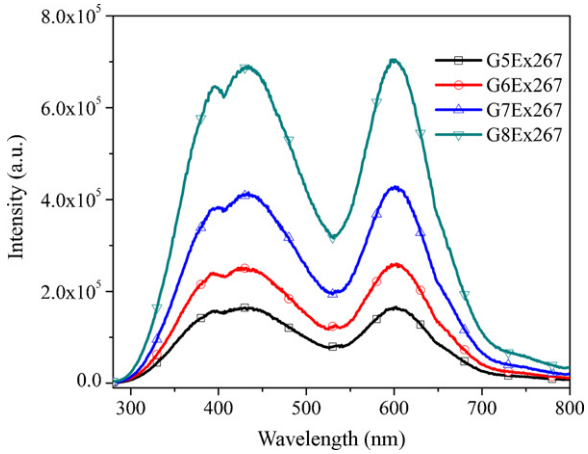

Fig. 4. Emission spectra of samples G5-G8 with a 267 nm excitation.

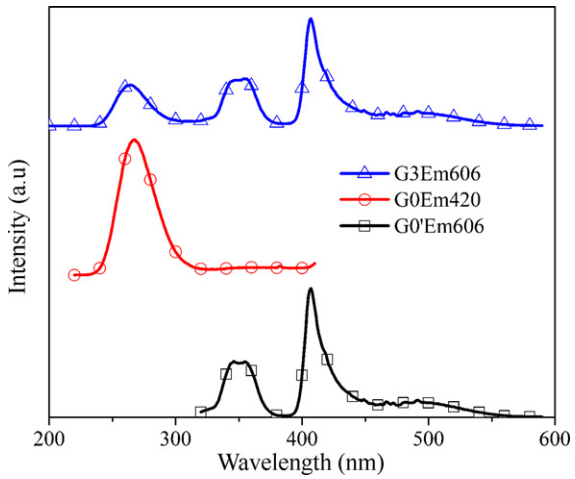

Fig. 5. Excitation spectra of G0, G0′ and G3 samples.

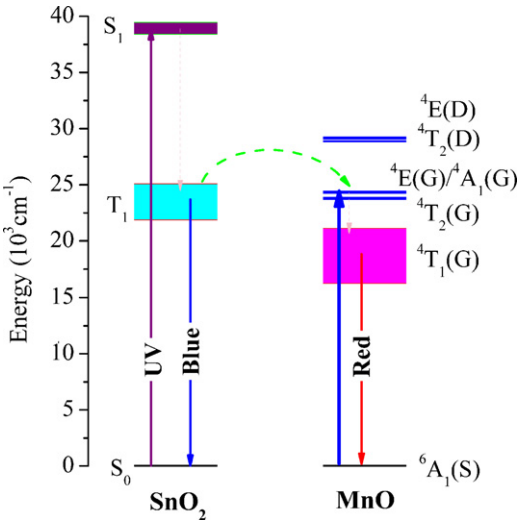

Fig. 6. Energy levels diagram of SnO_2 and MnO.

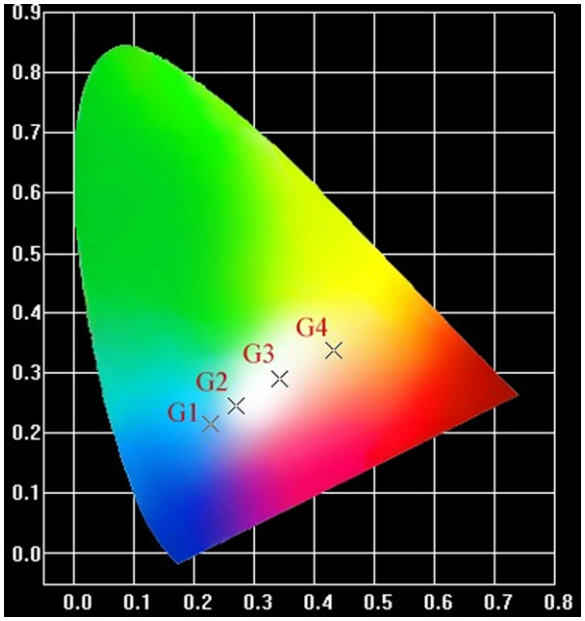

Fig. 7. The CIE chromaticity coordinates diagram for G1–G4.

an excitation band at 267 nm when monitored by 420 nm emission band, which is caused by the electronic transition of SnO_2 from the ground state S_0 to excited state S_1 [5,6]. This band is not observed in the absorption spectrum (Fig. 1) due to UV cut-off absorption from glass matrix. The MnO doped sample, when with the 606 nm monitoring wavelength, shows two main excitation bands at 350 and 407, and their origins are as discussed in absorption spectrum (Fig. 1). In the case of the SnO_2/MnO co-doped sample, when monitoring at the MnO red emission wavelength (606 nm), we impressively noticed an appearance of the SnO_2 excitation band at 267 nm, which offers the evidence that the MnO red emission correlates to the UV excitation on SnO_2, thus supporting our suggestion that an energy transfer from SnO_2 to MnO possibly exists in the SnO_2/MnO co-doped samples.

Further evidence comes from the emission spectra of co-doped samples (Figs. 3 and 4) where an obvious downward peak appears in the SnO_2 emission region at 407 nm and becomes more pronounced with the increased SnO_2 concentration (Fig. 4). It is known from Fig. 5 that 407 nm is one of the MnO excitation wavelengths. We then measured emission spectra of co-doped samples (G1–G4) specially with 407 nm light excitation (Fig. 3 inset) and found that they all resemble those under excitation on SnO_2 at 267 nm (Fig. 3), that is, the emission intensity increases and the peak shifts to longer wavelength with the increasing of MnO concentration. Therefore, we regard the appearance and evolution of the downward peak at 407 nm in the emission spectra of co-doped samples as an indication of the energy transfer occurring from the SnO_2 to MnO.

To describe the aforementioned luminescence phenomena, we schematically plotted the energy levels diagram of SnO_2 and MnO as shown in Fig. 6. Under 267 nm UV excitation, the electrons of SnO_2 in the ground state S_0 were excited to the excited state S_1, followed by non-radiation relaxation to the state T_1. Then partial electrons fall back to the state S_0, yielding the blue light around 420 nm. The rest of electrons transfer their energy to the MnO due to the close energy difference between T_1 and S_0 of SnO_2 and $^4E(G)/^4A_1(G)/^4T_2(G)$ to $^6A_1(S)$ of MnO, resulting in the excitation of the electrons in the ground state $^6A_1(S)$ of MnO to the excited state $^4E(G)/^4A_1(G)$ or $^4T_2(G)$. These excited electrons finally fall down to the ground state $^6A_1(S)$ after non-radiation relaxation to the state $^4T_1(G)$, yielding the red light around 600 nm.

We also calculated CIE chromaticity coordinates for all co-doped samples and results are listed in Table 1 and illustrated in Fig. 7. It is noticed that the emission color of samples G1–G4 varies from blue to yellow with the increasing of MnO concentration where G2 and G3 locate in the white region. On the basis of G3 sample by increasing SnO_2 concentration (G5–G8), the CIE chromaticity coordinates of these samples change little and all remain in the white region. From the above, we could find that the present SnO_2/MnO co-doped samples show a tunable blue and red luminescence which results in a blue, white or yellow light emitting, depending on the MnO concentration. In particular, the white light emission could be enhanced greatly by increasing the SnO_2 concentration while MnO concentration remains constant.

4. Conclusions

In conclusion, we have presented experimental results of the novel SnO_2/MnO co-doped phosphate glasses. Under excitation at 267 nm, the co-doped glasses exhibit a tunable blue and red luminescence which results in a blue, white or yellow light emitting, depending on the MnO concentration. In particular, the white light emission could be enhanced greatly by increasing the SnO_2 concentration. The present work presents will find application in illumination devices.

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