Enhanced and shortened Mn²⁺ emissions by Cu⁺ co-doping in borosilicate glasses for W-LEDs

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Abstract: A novel pair of transition metal ions Cu⁺, Mn²⁺ is co-doped in borosilicate glasses. Both copper and manganese ions exist in lower valence states (Cu⁺, Mn²⁺) in the as-prepared glasses. Around 5-time enhanced Mn²⁺ emission under the UV excitation is observed, which, as demonstrated by excitation spectra and emission decay curves, is due to an energy transfer from Cu⁺ ions resulting in greatly increased absorption of Mn²⁺ ions in the UV region, and relaxation on doubly-forbidden transition of Mn²⁺ leading to the much shortened Mn²⁺ emission lifetime from millisecond to microsecond level. Besides, a composite white emission is generated by combining the blue-green part from Cu⁺ ions with the green-red part from Mn²⁺ ions and it can be effectively tuned from cold to warm by adjusting host glass composition and altering excitation wavelength. Relevant mechanisms are discussed.

OCIS codes: (160.2540) Fluorescent and luminescent materials; (160.4670) Optical materials.

References and links

1. X. Liang, Y. Yang, C. Zhu, S. Yuan, G. Chen, A. Pring, and F. Xia, "PL properties of Tb³⁺-Sm³⁺ co-doped glasses for white light emitted diodes," Appl. Phys. Lett. **91**, 091104 (2007).
2. S. Yuan, Y. Yang, X. Zhang, F. Tessier, F. Cheviré, J. L. Adam, B. Moine, and G. Chen, "Eu²⁺ and Mn²⁺ codoped Ba₂Mg(BO₃)₂--new red phosphor for white LEDs," Opt. Lett. **33**(23), 2865–2867 (2008).
3. N. Da, M. Peng, S. Krolikowski, and L. Wondraczek, "Intense red photoluminescence from Mn²⁺-doped (Na⁺; Zn²⁺) sulfophosphate glasses and glass ceramics as LED converters," Opt. Express **18**(3), 2549–2557 (2010).
4. J. Ren, B. Li, G. Yang, W. Xu, Z. Zhang, M. Secu, V. Bercu, H. Zeng, and G. Chen, "Broadband near-infrared emission of chromium-doped sulfide glass-ceramics containing Ga₂s₃ nanocrystals," Opt. Lett. **37**(24), 5043–5045 (2012).
5. H. Masai, T. Fujiwara, S. Matsumoto, Y. Takahashi, K. Iwasaki, Y. Tokuda, and T. Yoko, "White light emission of Mn-doped SnO-ZnO-P₂O₅ glass containing no rare earth cation," Opt. Lett. **36**(15), 2868–2870 (2011).
6. H. Masai, Y. Yamada, Y. Suzuki, K. Teramura, Y. Kanemitsu, and T. Yoko, "Narrow energy gap between triplet and singlet excited states of Sn²⁺ in borate glass," Sci Rep **3**, 3541 (2013).
7. Y. Liu, X. Zhang, Z. Hao, Y. Luo, X. Wang, L. Ma, and J. Zhang, "Luminescence and energy transfer in Ca₃Sc₂Si₃O₁₂: Ce³⁺, Mn²⁺ white LED phosphors," J. Lumin. **133**, 21–24 (2013).
8. Q. Yan, J. Ren, and G. Chen, "CsCl modified Ge-Ga-S glasses co-doped with Eu²⁺ and Mn²⁺: a potential yellow phosphor for solid-state lighting," J. Am. Ceram. Soc. **95**(12), 3719–3721 (2012).
9. H. S. Bhatti, R. Sharma, N. K. Verma, N. Kumar, S. R. Vadera, and K. Manzoor, "Lifetime shortening in doped ZnS nanophosphors," J. Phys. D Appl. Phys. **39**(9), 1754–1760 (2006).
10. J. Liu, Y. Wang, X. Yu, and J. Li, "Enhanced PL properties of Zn₂SiO₄:Mn²⁺ co-activated with Y³⁺/Li⁺ under VUV excitation," J. Lumin. **130**(11), 2171–2174 (2010).
11. Q. Zhang, G. Chen, G. Dong, G. Zhang, X. Liu, J. Qiu, Q. Zhou, Q. Chen, and D. Chen, "The reduction of Cu²⁺ to Cu⁺ and optical properties of Cu⁺ ions in Cu-doped and Cu/Al-co-doped high silica glasses sintered in an air atmosphere," Chem. Phys. Lett. **482**(4–6), 228–233 (2009).
12. R. Wei, C. Ma, Y. Wei, J. Gao, and H. Guo, "Tunable white luminescence and energy transfer in novel Cu⁺, Sm³⁺ Co-doped borosilicate glasses for W-LEDs," Opt. Express **20**(28), 29743–29750 (2012).

13. Y. Xu, X. Zhang, S. Dai, B. Fan, H. Ma, J. Adam, J. Ren, and G. Chen, "Efficient near-infrared down-conversion in Pr^{3+}-Yb^{3+} co-doped glasses and glass ceramics containing LaF_3 nanocrystals," J. Phys. Chem. C **115**(26), 13056–13062 (2011).
14. D. S. Sumida and T. Y. Fan, "Effect of radiation trapping on fluorescence lifetime and emission cross section measurements in solid-state laser media," Opt. Lett. **19**(17), 1343–1345 (1994).
15. H. Kühn, S. T. Fredrich-Thornton, C. Kränkel, R. Peters, and K. Petermann, "Model for the calculation of radiation trapping and description of the pinhole method," Opt. Lett. **32**(13), 1908–1910 (2007).

1. Introduction

Photoluminescence (PL) materials have been widely applied in versatile fields. Rare earth (RE) ions have long been preferentially used as activators in the PL materials due to their rich emission spectra and inter-ion energy transfer phenomena [1,2]. Transition metal (TM) ions, on the other hand, exhibit fluorescence mechanism usually involving both parity and spin forbidden transitions and have been frequently reported in different crystalline and glassy solids [2–4]. Recently, it appears that non rare earth ions activated luminescent materials are among the cutting-edge researches [5,6].

As an important TM ion, divalent manganese (Mn^{2+}) plays a key role in phosphors for lighting applications. Mn^{2+} can give rise to a broad emission from green to red under the ultraviolet (UV) or near UV excitation, depending on the interaction of crystal field (CF) with the $^4T_1(G)$-$^6A_1(G)$ transition [2,3]. Thus Mn^{2+} ion has become an attractive component in developing novel PL materials as primary phosphor in combination with soft UV and blue excitation sources or as secondary phosphors to improve color rendering index. However, the emission of Mn^{2+} is inefficient with long decay time due to the electric dipole forbidden d–d transition [7]. In fact, in the process of some applications, e.g., plasma display panels, the emission intensity and lifetime of a phosphor are of equal significance. Great efforts have been made to improve the PL performance of Mn^{2+} doped phosphors via energy transfer (ET) from co-doped ions. For example, Ce^{3+} and Eu^{2+} have been successfully used as sensitizers to increase Mn^{2+} emission intensity greatly, but the decay time was not reduced [7,8]. There is also an approach to enhance the Mn^{2+} emission through relaxing limitations on doubly-forbidden transition of Mn^{2+} by introducing co-activators or so-called quenchers, mostly TM ions, such as Ni^{2+} and Y^{3+} with which both short decay time and high PL intensity were achieved [9,10].

In the present work, the novel Cu^+, Mn^{2+} co-doped borosilicate glasses are presented and their PL properties are investigated by optical transmission and PL spectra. The univalent copper (Cu^+) ion exhibits broad excitation in a UV band and wide emission in the visible region overlapping large portions of the Mn^{2+} excitation bands [9]. In the new pair of dopants consisting of two different TM ions, Cu^+ ions, besides absorbing UV energy and emitting in the blue-green region, are expected to act as both activator and sensitizers. As an activator, Cu^+ might split the energy levels of Mn^{2+} due to exchange interaction between them, and change the formerly spin forbidden transition of Mn^{2+} to allowed one, leading to increased transition probability and reducing emission lifetime from millisecond to the microsecond level [9,10]. As a sensitizer, a portion of the absorbed energy by Cu^+ ions is transferred to Mn^{2+} ions, all mechanisms resulting in enhanced Mn^{2+} emission in the green-red spectrum range. Since emissions from Cu^+ and Mn^{2+} ions cover all visible region, it is thus believed possible to realize white-light emission by proper Cu^+, Mn^{2+} co-doping, meeting requirements for white light-emitting diodes (W-LEDs) pumped by UV LED chips.

2. Experimental

Mn^{2+} and Cu^+ singly and co-doped borosilicate glasses were prepared by the melt-quenching process using chemical purity SiO_2, H_3BO_3, Na_2CO_3, $BaCO_3$, CuO, MnO_2 as starting materials and $SnCl_2$ as the reducing agent with the molar ratio to CuO as 4:1. Glass batches were prepared according to the nominal compositions in Table 1, including the host glass

(G1), Mn^{2+}, Cu^+ singly doped glasses (G2, G3) and Cu^+, Mn^{2+} co-doped glasses with different host glass composition (G4, G5, G6).

Table 1. Nominal Compositions of As-prepared Glasses (mol %).

Sample code	Na_2O	BaO	B_2O_3	SiO_2	CuO	MnO_2	$SnCl_2$
G1	20	10	10	60	0	0	0
G2	20	10	10	60	0	1.5	2
G3	20	10	10	60	0.5	0	2
G4	20	10	10	60	0.5	1.5	2
G5	17	8	15	60	0.5	1.5	2
G6	20	15	10	55	0.5	1.5	2

The prepared batches were poured into Al_2O_3 crucibles and moved to an electric furnace for melting in air at 1450-1550 °C for 3-4 hrs and annealed at 550 °C for 2-3 hrs. The glasses obtained were transparent in UV and visible region. All samples were cut into rectangular shapes with 2 mm in thickness and well polished to mirror smoothness to achieve good quality for optical measurements.

Transmission spectra were recorded by a double-beam Lambda 950 UV-VIS Spectrometer (Perkin-Elmer, USA). The PL and PLE spectra were collected by a high-resolution spectrofluorometer (Fluorolog-3, Horiba Jobin Yvon Inc., Edison, NJ) using a 450 W Xe-lamp as the excitation source. The pump light beams were incident and the emitted light beams were collected both at a 45 degree angle to the plate normal with the same slit width for all samples, while reported data were corrected for instrumental response. The PL decay lifetime was measured by FLSP920 (Edinburgh Instruments, Livingston, UK) using nF900 microsecond pulsed Xe-lamp as source with the pulsed width of 2-3 microseconds. An angle of 90 degrees was applied between the light source and the detector. The reflected light signal was detected by the PMT visible light detector after excitation of the sample.

3. Result and discussion

3.1 Transmission and PL spectra

Transmission spectra of G1-G4 are jointly presented in Fig. 1 (a). Compared with G1, G2 exhibits two typical Mn^{2+} absorption bands at 353 nm ($^6A_1(S) \rightarrow {}^4E(D)/ {}^4T_2(D)$) and 419 nm ($^6A_1(S) \rightarrow {}^4E(G)/{}^4A_1(G)$ and $^4T_2(G)$) [8], G3 suffers a significant red shift of the absorption edge relative to G1, corresponding to the transition of Cu^+ from ground d state to excited s states [11,12], while G4 is characterized by absorptions of both Cu^+ and Mn^{2+}. For all doped samples, there appear no obvious absorption bands of Cu nanoparticles or Cu^{2+} from 510 nm to 800 nm [11,12], and/or characteristic Mn^{3+} absorption band at around 490 nm [3], indicating that $SnCl_2$ is an effective reducing agent to make copper and manganese ions exist both in the lower oxide states (Cu^+, Mn^{2+}) in the present glass samples.
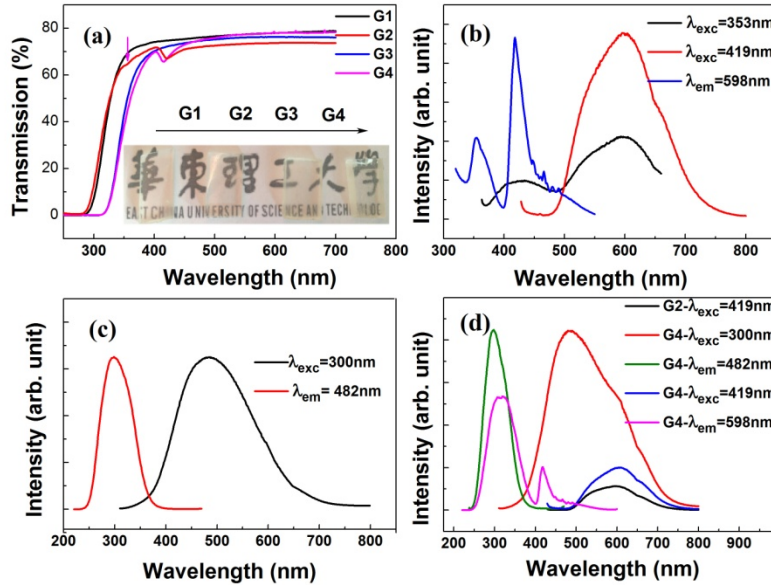
Fig. 1. Transmission spectra of samples G1-G4 (a) and PL and PLE spectra of glasses G2 (b), G3 (c) and G4 (d). Inset in (a): the digital photos of the samples G1-G4.

Figures 1(b)-1(d) present PL and PLE spectra of G2-G4. When excited at 419 nm, G2 exhibits a characteristic green-red emission of Mn^{2+} peaking around 598 nm ($^4T_1(G) \rightarrow ^6A_1(S)$), and so does at 353 nm but much weaker (b). Consistently, the PLE spectrum for the 598 nm emission shows an intense band around 419 nm and a comparatively weak band around 353 nm. For the PL spectrum of G3 excited at 300 nm, a blue-green emission of Cu^+ ions (s→d) appears peaking at around 482 nm (c), and by reversely monitoring the Cu^+ emission, a broad excitation band covering 260 nm to 360 nm is observed with a maximum around 300 nm. In the case of G4, it is impressively noted that pumping Cu^+ at 300 nm produces a super-broad emission band which combines exactly the Cu^+ blue-green (482 nm) and Mn^{2+} green-red (598 nm) emission bands (d), composing the quasi white-light emission with the chromaticity coordinate of emission as (0.29, 0.34). In particular, the Mn^{2+} emission at 598 nm is enhanced by about 5 times compared with G2 excited at 419 nm, while the Cu^+ emission at 482 nm is reduced around one time relative to G3. In order to obtain more information on Mn^{2+} emission via Cu^+ excitation, PLE spectra of G4 for Cu^+ and Mn^{2+} emissions are compared. The PLE spectrum for Cu^+ emission at 482 nm in G4 resembles that in G3, while for the Mn^{2+} emission at 598 nm, the UV excitation band is much enhanced relative to the originally stronger visible excitation band at 419 nm, and broadened as well as blue shifted to around 320 nm, close to the Cu^+ excitation band. Nevertheless, the Mn^{2+} green-red emission under excitation at 419 nm is still nearly one-time enhanced in G4 compared with that in G2.

Hence, the data consistently presents evidence of an enhanced Mn^{2+} emission in association with the presence of Cu^+ ions in the host glass. There are two possible explanations for the above observations, one is via an ET process from Cu^+ by absorption energy transfer to Mn^{2+} ions in the UV region, and another is due to an exchange interaction between Cu^+ and Mn^{2+} ions leading to change of doubly-forbidden transition of Mn^{2+} ions.

3.2. PL decay curves

To demonstrate above speculations, samples G2-G4 are characterized by PL decays as shown in Fig. 2. All the decay curves show strong non-single exponential character; for singly doped samples as G2 and G3, this is a clear evidence of either the presence of different emitting centers or of energy migration due to interaction among them.
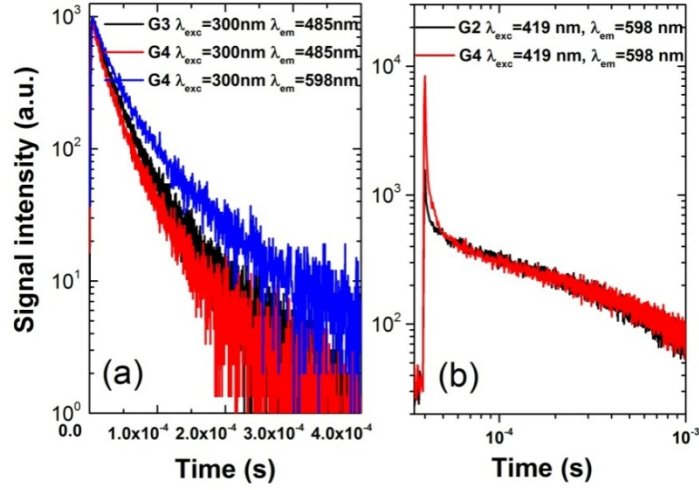

Fig. 2. PL decay curves of G2-G4: pumped at 300 nm for G3 and G4 (a); pumped at 419 nm for G4 and G2 (b). Note the log-log scale in (b) is used to evidence the fast initial decay of G4.

Investigation of the real nature of these processes is beyond the scope of this work. Nevertheless, it is useful to introduce a phenomenological quantification of the decay times of the examined samples. Here we use the equivalent decay time τ_{eq} defined as [13]

$$\tau_{eq} = \frac{\int I(t)\,dt}{I_0} \tag{1}$$

where $I(t)$ is the time-dependent luminescence intensity and I_0 its maximum value. It is known that the PL decay can be easily modulated if there is the absorption in measured samples around the wavelength of emission [14,15]. For the studied samples, however, the absorption/excitation bands do not significantly overlap with the emission bands. Thus, the radiation trapping is assumed not to impose much influence on the measured emission lifetimes although it cannot be completely excluded. The values of τ_{eq} calculated for all the decay curves reported in Fig. 2 are shown in Table 2 together with the excitation and emission wavelengths. Under 300 nm excitation, the Cu^+ emission of the co-doped sample G4 at 482 nm is substantially shorter ($\tau_{eq} = 0.026$ ms) than that of the singly-doped G3 sample ($\tau_{eq} = 0.031$ ms), implying an ET from Cu^+ to Mn^{2+}.

Table 2. Equivalent decay times of the Mn^{2+} (598 nm) and Cu^+ (482 nm) emissions for samples G2-G4.

Sample	λ_{exc}(nm)	λ_{em} (nm)	τ_{eq} (ms)
G2	419	598	0.930
G3	300	482	0.031
G4	300	482	0.026
	300	598	0.040
	419	598	0.170

The ET efficiency (η_T) can be evaluated using the empirical equation: $\eta_T = 1-\tau_s/\tau_{s0}$, where τ_s and τ_{s0} are the decay lifetimes of the sensitizer Cu^+ with and without the activator Mn^{2+} [8]. The calculated η_T is around 16%, which seems not high enough to account for the drastically enhanced Mn^{2+} emission.

Also, the emission at 598 nm from the co-doped sample G4 excited at 300 nm is short (τ_{eq} = 0.040 ms); however, pumping at 300 nm excites both Cu^+ and Mn^{2+} ions as Cu^+ has a small but sizeable emission at 598 nm while Mn^{2+} overlaps much excitation source at 300 nm. To disentangle the effect of Cu^+ emission on Mn^{2+} emission lifetime, the decay of the Mn^{2+} emission in G4 was measured under 419 nm excitation [Fig. 2(b)]. It is observed that in this case the equivalent decay time τ_{eq} of the Mn^{2+} emission in the co-doped G4 sample (τ_{eq} = 0.17 ms) is much shortened with respect to that of the singly-doped G2 sample (τ_{eq} = 0.93 ms) as shown in Table 2. This situation can be explained by considering that the Mn^{2+} luminescent emission is produced by the spin-forbidden transition $^4T_1$-$^6A_1$, thus the associated probability is low, giving long (millisecond) lifetime. With Cu^+ co-doping it is most likely that an exchange interaction between Mn^{2+} and Cu^+ occurs, changing the nature of the forbidden Mn^{2+} transition to allowed one [9,10]. Consequently, high Mn^{2+} emission intensity together with fast decay time down to tens of microsecond level were concurrently achieved. Similar phenomena have been observed in Ni co-doped $ZnS:Mn^{2+}$ and Y^{3+}/Li^+ co-activated $Zn_2SiO_4:Mn^{2+}$ phosphors [9,10], but scarcely reported for glasses. With this evidence it is convincing that the fivefold time enhanced Mn^{2+} emission of G4 under excitation at 300 nm is due to the joint effects of the ET from Cu^+ and exchange interaction with Cu^+.

As the energy level structure of Cu^+ is related to distances of Cu^+ ions due to the change of surrounding CF [12], Cu^+ (S-S) and Cu + (L-W) models are used herein to stand for the long wavelength emission of Cu^+ with short distance in strong CF and the short wavelength emission with long distance in weak CF, respectively (Fig. 3). ET1 from Cu^+ to Mn^{2+} ions can easily occur via the excited state of Cu^+ which is energetically close to the $^4T_1(P)$ level of Mn^{2+} ions, resulting in population of the Mn^{2+} excited state $^4T_1(P)$ from the ground state. Mn^{2+} ions then undergo multi-phonon relaxation to the emitting level $^4T_1(P)$ followed by radiative relaxation to the ground state, emitting at 598 nm. ET2 is also possibly proceeded via the following way: part of the emitted photons from Cu^+ pumps Mn^{2+} from the ground state to the $^4T_2(G)$ and $^4A_1(G)$ excited states, and the Mn^{2+} ions in the populated state relax nonradiatively to the emitting state $^4T_1(P)$, resulting in the characteristic emission of Mn^{2+} at 598 nm.
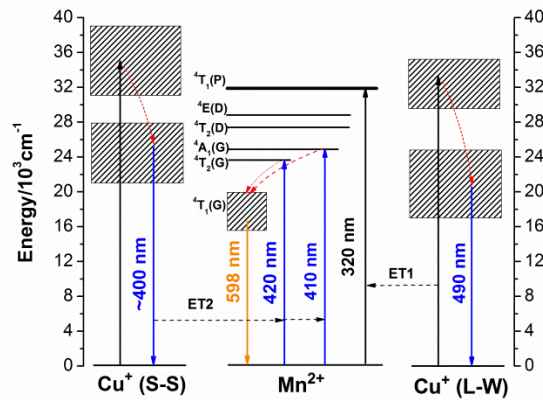

Fig. 3. Simplified energy-level diagrams of Cu^+ and Mn^{2+} ions and possible ET processes.

3.3. CIE chromaticity coordinate

As characterized by CIE chromaticity coordinate of emission (0.29, 0.34), G4 emits at the edge between green and white lights. To tune the PL of the co-doped sample to the white-light region, the CF on Cu^+ ions was adjusted by modifying the host glass composition. PLE spectra of G5 and G6 for Cu^+ and Mn^{2+} emissions show the similarity to G4 (not presented herein) while the PL spectra of G4-G6 are given in Fig. 4(a). G5 containing the higher B_2O_3 content than G4 for substituting Na_2O and BaO suffers an obvious blue shift of the Cu^+ emission from 482 nm of G4 to 470 nm with the intensity ratio of Mn^{2+}/Cu^+ emissions increasing from 0.65 to 0.70. On the contrary, substitution of BaO for SiO_2 (G6) results in a red shift of Cu^+ emission to 525 nm while the Mn^{2+}/Cu^+ intensity ratio decreases to 0.60. Correspondingly, the CIE chromaticity coordinate of emission [Fig. 4(b)] moves from G4 green-white edge (0.29, 0.34) to G6 green region (30, 40) and G5 white-light region (0.30, 0.31) (as shown by the inset image of luminescence from G5 in Fig. 4(a), respectively. According to Cu^+ (S-S) and (L-W) models it is supposed that G5 offers the weaker CF than G4 on Cu^+ ions while Cu^+ ions in G6 are in the stronger CF. In other words, the Cu^+ emission can be tuned effectively by modifying the host glass composition.
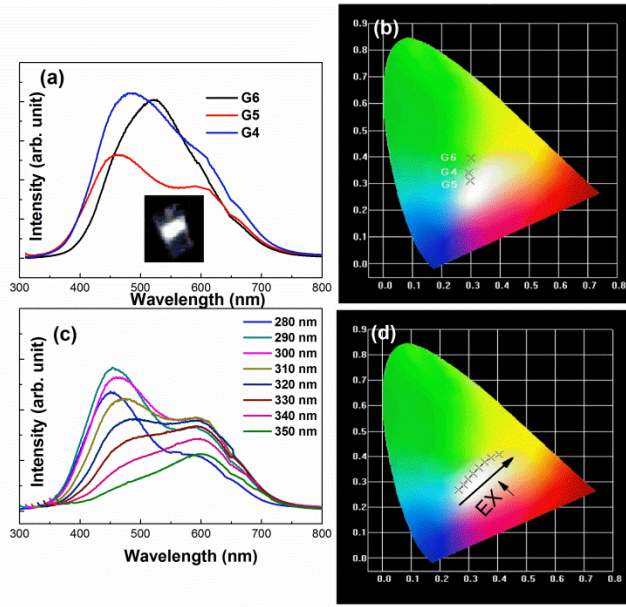

Fig. 4. PL spectra of (a, the inset shows an image of white emission from G5 excited at 300 nm) G4-G6 and (c) G5, (b) and (d) are their CIE chromaticity diagrams, respectively.

Previous work shows that effect of CF on the Cu^+ emission can also be exerted via change of excitation wavelength (EW) [12]. Thus with the help of an efficient ET from Cu^+ to Mn^{2+} in G5, the tunable PL in the white-light region might be possible by altering the EW successively. Figures 4 (c) and d present PL spectra of G5 excited by the light from 280 nm to 350 nm with 10 nm steps and the CIE chromaticity diagram indexing an evolution of PL colors. With the EW shifting to the longer wavelength, the Cu^+ emission suffers red shift with the intensity reaching the maximum at 290 nm and then decreasing while the intensity ratio of Mn^{2+}/Cu^+ emission becomes much increased. In particular, Cu^+ and Mn^{2+} emissions become of equal intensity at 320 nm, while moving to 350 nm, the Cu^+ emission disappears. The CIE chromaticity diagram shows that emissions are almost all within the white-light region and tuned from cold white moving along the green-white edge to the warm white and finally into the yellow region. Thus the tunable white-light emissions are realized in G5 with the lower

alkaline earth and alkali oxides by altering the EW, indicating that Cu^+, Mn^{2+} co-doped borosilicate glasses may be used as converting phosphors for UV LED chips to generate W-LEDs.

4. Conclusion

Enhanced and shortened Mn^{2+} green-red emission is obtained in the Mn^{2+} doped borosilicate glasses by co-doping Cu^+, composing a super-broad band emission via combination of the Cu^+ blue-green emission. PLE and decay lifetime data consistently present evidences of an enhanced Mn^{2+} emission in presence of Cu^+ ions via energy transfer from Cu^+ to Mn^{2+} ions. Moreover, the Mn^{2+} emission is much shortened from 0.93 ms to 0.17 ms, indicating the change of the spin forbidden transition of Mn^{2+} to allowed one due to an exchange interaction with the co-doped Cu^+. White-light emission is realized in the co-doped borosilicate glass with comparatively lower alkali and alkaline earth oxides, and can be continuously tuned from cold to warm white by altering the excitation wavelength. Our work indicates potential applications of Cu^+, Mn^{2+} co-doped borosilicate glasses as converting phosphors for white LEDs pumped by UV LED chips.