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# A new emission band of $\text{Eu}^{2+}$ and its efficient energy transfer to $\text{Mn}^{2+}$ in $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:\text{Mn}^{2+}$ , $\text{Eu}^{2+}$

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**$\text{Eu}^{2+}$  singly and  $\text{Eu}^{2+}$ ,  $\text{Mn}^{2+}$  co-doped  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}$  exhibit not only the well known blue emission band of  $\text{Eu}^{2+}$  peaking at 448 nm but also a new band at 399 nm in violet. They are attributed to  $\text{Eu}^{2+}$  on different  $\text{Sr}^{2+}$  sites. The  $\text{Eu}^{2+}$  for the violet band can transfer energy to the red emitting  $\text{Mn}^{2+}$  more efficiently than  $\text{Eu}^{2+}$  for the blue band. The new  $\text{Eu}^{2+}$  band could enable  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:\text{Mn}^{2+}$ ,  $\text{Eu}^{2+}$  to be a promising phosphor for enriching the red component of white LEDs.**

The solid state lighting sources based on white light emitting diodes (LED) fabricated using blue and/or near UV LED chips coated with phosphors have been widely studied in recent years.<sup>1–3</sup> The white LEDs employing near UV LED chips with tri-color phosphors have the advantage of less shift of color point against forward current because the white light is completely phosphor converted rather than the case of blue LED combined with a yellow emitting YAG: $\text{Ce}^{3+}$  phosphor.<sup>1</sup>  $\text{Eu}^{2+}$  activated phosphate is a kind of highly efficient blue emitting phosphors for near UV LED excitation.<sup>4–7</sup> However, white light generation suffers from lack of bright red emitting phosphate. To solve this problem,  $\text{Mn}^{2+}$  was codoped into some blue emitting phosphates and an intense red emission of  $\text{Mn}^{2+}$  was additionally achieved through energy transfer from  $\text{Eu}^{2+}$  to  $\text{Mn}^{2+}$ .<sup>6,7</sup>

The blue emission of  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:\text{Eu}^{2+}$  was first reported by Hoffman in 1968.<sup>8</sup> Recently, Ngee *et al.* demonstrated that  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:\text{Eu}^{2+}$  can be excited efficiently by near UV to emit strongly in blue (peaking at 448 nm) and the luminescence temperature characteristics are much better than those of commercial YAG: $\text{Ce}^{3+}$ , implying its promising application as a blue phosphor for white LEDs.<sup>9</sup> Guo *et al.* reported energy transfer from the blue  $\text{Eu}^{2+}$  to red  $\text{Mn}^{2+}$  in  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}$ , showing dual color emissions at 447 nm in blue and 610 nm in red, respectively.<sup>10</sup> On noticing the previous reports on emission of  $\text{Eu}^{2+}$  in  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}$ , we found that these reports exhibited solely a PL band of  $\text{Eu}^{2+}$  in blue.  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}$  has two kinds of  $\text{Sr}^{2+}$  sites, as described by Hong *et al.*<sup>11</sup> One strontium ( $\text{Sr}_1$ ) ion, with an average  $\text{Sr}_1\text{–O}$  bond length of 0.256 nm, occupies the larger cavities

surrounded by O atoms with tenfold coordination. The other strontium ( $\text{Sr}_2$ ) ion is six O atoms coordinated with average  $\text{Sr}_2\text{–O}$  bond length of 0.2265 nm. The two  $\text{Sr}^{2+}$  sites imply the possibility of two emission bands of  $\text{Eu}^{2+}$  in  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}$ .

In this communication, we report, to our knowledge for the first time, the observation of a new strong emission band of  $\text{Eu}^{2+}$  located at 399 nm in  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}$ . It is also significantly observed that the  $\text{Eu}^{2+}$  for the new band can transfer energy to  $\text{Mn}^{2+}$  more efficiently than that for the blue band in  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}$ .

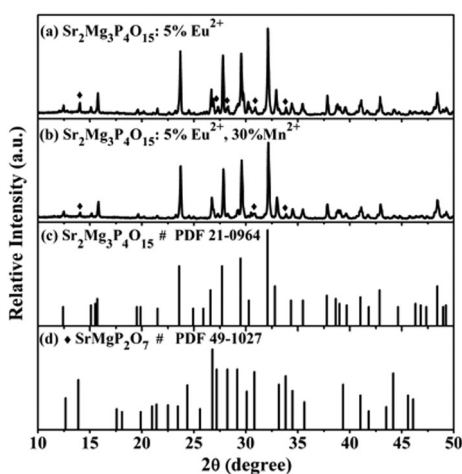
Photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured using an F-4500 spectrometer. The crystalline structure was recorded by an X-ray diffractometer (XRD) (Rigaku D/M AX-2500 V). Fluorescence lifetimes were measured upon the excitation of the third harmonic (355 nm) of a YAG:Nd pulsed laser (Spectra-Physics, GCR130), and the signals were detected with a Tektronix digital oscilloscope (TDS 3052).

Fig. 1 shows the XRD patterns of  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:5\% \text{Eu}^{2+}$  and  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:5\% \text{Eu}^{2+}$ , 30%  $\text{Mn}^{2+}$ . The predominant phase in the samples is the (c)  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}$  phase (JCPDS-No21-0964) with a very small amount of the secondary (d)  $\text{SrMgP}_2\text{O}_7$  phase (JCPDS-No49-1027,  $\blacklozenge$ ).

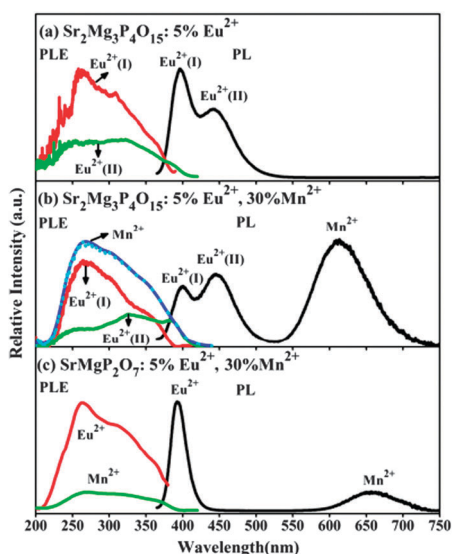
Fig. 2 shows the PL and PLE spectra of (a)  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:5\% \text{Eu}^{2+}$  and (b)  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:5\% \text{Eu}^{2+}$ , 30%  $\text{Mn}^{2+}$ . For clarifying the ineffective role of the secondary  $\text{SrMgP}_2\text{O}_7$  phase in luminescence properties of the primary  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}$  phase, the spectra of (c)  $\text{SrMgP}_2\text{O}_7:5\% \text{Eu}^{2+}$ , 30%  $\text{Mn}^{2+}$  are also presented in Fig. 2. It is observed that the PL spectrum of  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:5\% \text{Eu}^{2+}$  exhibits not only the well known blue band located at 448 nm as previously reported,<sup>9,10</sup> but also a new band located at 399 nm in violet that has never been demonstrated previously. Here, we label the violet band as  $\text{Eu}^{2+}$  (i) and the blue one as  $\text{Eu}^{2+}$  (ii). The violet and blue bands also show different PLE spectrum. The PLE band for the violet emission terminates at around 375 nm and that for the blue one terminates at around 405 nm. This partially gives a reason why the violet band was not detected in Ngee *et al.*<sup>9</sup> and Guo *et al.*'s<sup>10</sup> work because they used 395 nm and 380 nm, respectively, as an excitation wavelength that can only selectively excite  $\text{Eu}^{2+}$  (ii) to emit in blue. One question is if the violet band originates from  $\text{Eu}^{2+}$  in the secondary  $\text{SrMgP}_2\text{O}_7$  phase. To answer this question, we prepared  $\text{SrMgP}_2\text{O}_7:5\% \text{Eu}^{2+}$ , 30%  $\text{Mn}^{2+}$  and

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**Fig. 1** XRD patterns of (a)  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:5\% \text{Eu}^{2+}$ , (b)  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:5\% \text{Eu}^{2+}, 30\% \text{Mn}^{2+}$ , standard (c)  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}$  phase and (d)  $\text{SrMgP}_2\text{O}_7$  phase.



**Fig. 2** PL and PLE spectra for (a)  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:5\% \text{Eu}^{2+}$ .  $\lambda_{\text{ex}} = 355 \text{ nm}$ ,  $\lambda_{\text{em}} = 399, 448 \text{ nm}$ . (b)  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:5\% \text{Eu}^{2+}, 30\% \text{Mn}^{2+}$ .  $\lambda_{\text{ex}} = 355 \text{ nm}$ ,  $\lambda_{\text{em}} = 399, 448$  and  $610 \text{ nm}$ . (c)  $\text{SrMgP}_2\text{O}_7:5\% \text{Eu}^{2+}, 30\% \text{Mn}^{2+}$ .  $\lambda_{\text{ex}} = 355 \text{ nm}$ ,  $\lambda_{\text{em}} = 392, 655 \text{ nm}$ .

present its spectra in Fig. 2(c) for comparing with Fig. 2(a) and (b).  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:5\% \text{Eu}^{2+}, 30\% \text{Mn}^{2+}$  exhibits a typical red PL band peaking at  $610 \text{ nm}$ , originating from  ${}^4\text{T}_1-{}^6\text{A}_1$  transition of  $\text{Mn}^{2+}$  in  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}$  as previously reported.<sup>10</sup>

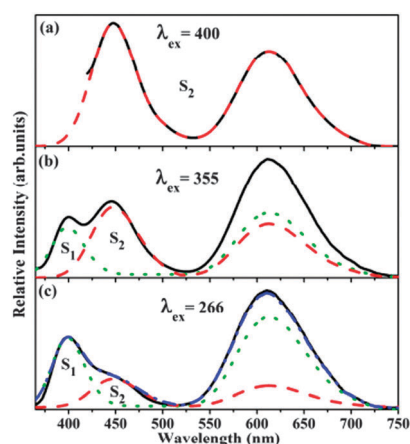
From Fig. 2(b) one can see that the shape of the PLE band for  $\text{Mn}^{2+}$  is neither identical to that for individual  $\text{Eu}^{2+}(\text{I})$  nor  $\text{Eu}^{2+}(\text{II})$ , but consistent with the linear combination of  $\text{Eu}^{2+}(\text{I})$  and  $\text{Eu}^{2+}(\text{II})$  (dotted line). This result indicates that both  $\text{Eu}^{2+}(\text{I})$  and  $\text{Eu}^{2+}(\text{II})$  are able to effectively transfer energy to  $\text{Mn}^{2+}$ . In general, it is considered that effective non-radiative energy transfer among ions cannot occur between two different crystal phases because of the long distance. It is therefore evidenced that  $\text{Eu}^{2+}(\text{I})$ ,  $\text{Eu}^{2+}(\text{II})$  and  $\text{Mn}^{2+}$  are located within the same  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}$  phase. As can be seen in the PL spectrum of  $\text{SrMgP}_2\text{O}_7:5\% \text{Eu}^{2+}, 30\% \text{Mn}^{2+}$ , there is a violet band of  $\text{Eu}^{2+}$  peaking at  $392 \text{ nm}$  different from the

one at  $399 \text{ nm}$  for  $\text{Eu}^{2+}(\text{I})$  in  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}$ , while, the red emission band of  $\text{Mn}^{2+}$  in  $\text{SrMgP}_2\text{O}_7$  peaks at  $655 \text{ nm}$  quite different from the one at  $610 \text{ nm}$  for  $\text{Mn}^{2+}$  in  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}$ . The evidenced  $\text{Mn}^{2+}$  emission in  $\text{SrMgP}_2\text{O}_7$  also results from energy transfer from  $\text{Eu}^{2+}$  because their PLE bands are consistent with each other very well. As a result, the spectra in Fig. 2(b) reflect the nature of  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:5\% \text{Eu}^{2+}, 30\% \text{Mn}^{2+}$  without influence of the secondary  $\text{SrMgP}_2\text{O}_7$  phase. According to Hong *et al.*'s work,<sup>11</sup> there exist  $\text{Sr}_1$  and  $\text{Sr}_2$  sites in  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}$  with ten and six oxygens coordinated, respectively. As a result, we attribute the violet and blue band to  $\text{Eu}^{2+}$  on the  $\text{Sr}_1$  site and  $\text{Sr}_2$  site, respectively, because  $\text{Eu}^{2+}$  with a higher coordination number generally emits at higher energy than that with a lower coordination number as described by Van Uiter.<sup>12</sup>

In view of occurrence of energy transfer from both  $\text{Eu}^{2+}(\text{I})$  and  $\text{Eu}^{2+}(\text{II})$  to  $\text{Mn}^{2+}$ , the PL spectrum (Fig. 2b) of  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:5\% \text{Eu}^{2+}, 30\% \text{Mn}^{2+}$  in fact is the combination of the  $\text{Eu}^{2+}(\text{I})/\text{Mn}^{2+}$  individual spectrum ( $S_1$ ) and the  $\text{Eu}^{2+}(\text{II})/\text{Mn}^{2+}$  individual spectrum ( $S_2$ ), which in principle is independent of excitation wavelengths because of fixed  $\text{Mn}^{2+}$  concentration. Based on the different PLE spectra of  $\text{Eu}^{2+}(\text{I})$  and  $\text{Eu}^{2+}(\text{II})$ , the distribution of PL spectra varies with excitation wavelengths. Fig. 3 shows the PL spectra of  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:5\% \text{Eu}^{2+}, 30\% \text{Mn}^{2+}$  upon excitation at (a)  $400 \text{ nm}$ , (b)  $355 \text{ nm}$  and (c)  $266 \text{ nm}$ .

For excitation at  $400 \text{ nm}$ , only  $\text{Eu}^{2+}(\text{II})$  is selectively excited, resulting in the  $\text{Eu}^{2+}(\text{II})/\text{Mn}^{2+}$  individual spectrum ( $S_2$ ). The  $\text{Eu}^{2+}(\text{I})/\text{Mn}^{2+}$  individual spectrum ( $S_1$ ) can be obtained by subtracting  $S_2$  from the spectrum for  $355 \text{ nm}$  excitation (Fig. 3b). One can clearly find that  $S_1$  shows a larger area intensity ratio of  $\text{Mn}^{2+}$  to  $\text{Eu}^{2+}$  than  $S_2$ , implying more effective energy transfer from  $\text{Eu}^{2+}(\text{I})$  to  $\text{Mn}^{2+}$ . Using  $S_1$  and  $S_2$  as basis spectra, the PL spectrum for  $266 \text{ nm}$  excitation is well reconstructed, as shown in Fig. 3(c). It should be noted that in spectral simulation, the emission bands of  $\text{Eu}^{2+}(\text{I})$ ,  $\text{Eu}^{2+}(\text{II})$  and  $\text{Mn}^{2+}$  are fitted very well with Gaussian functions in wavenumber.

On comparing the PL spectra of  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:5\% \text{Eu}^{2+}$  and  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:5\% \text{Eu}^{2+}, 30\% \text{Mn}^{2+}$ , it can be seen that the PL intensity ratio of  $\text{Eu}^{2+}(\text{I})$  to  $\text{Eu}^{2+}(\text{II})$  becomes lower in  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:5\% \text{Eu}^{2+}, 30\% \text{Mn}^{2+}$ . This further reflects a more effective  $\text{Eu}^{2+}(\text{I})-\text{Mn}^{2+}$  energy transfer. To know the energy



**Fig. 3** PL spectra of  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:5\% \text{Eu}^{2+}, 30\% \text{Mn}^{2+}$  upon excitation at (a)  $400 \text{ nm}$ , (b)  $355 \text{ nm}$  and (c)  $266 \text{ nm}$ .

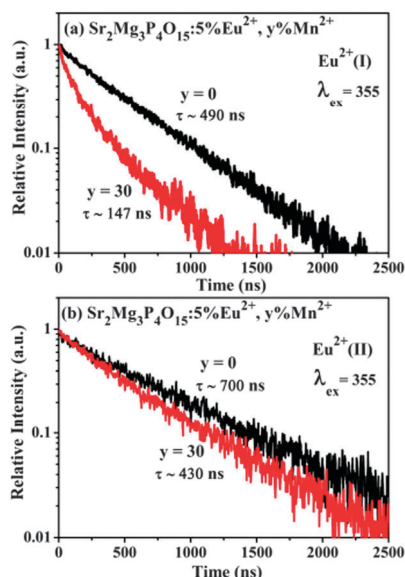
transfer efficiency, the fluorescence decays of (a)  $\text{Eu}^{2+}(\text{I})$  and (b)  $\text{Eu}^{2+}(\text{II})$  in  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:5\% \text{Eu}^{2+}$  and  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:5\% \text{Eu}^{2+}$ , 30%  $\text{Mn}^{2+}$  are measured and plotted in Fig. 4.

It is observed that either  $\text{Eu}^{2+}(\text{I})$  or  $\text{Eu}^{2+}(\text{II})$  fluorescence displays a single exponential decay in the absence of  $\text{Mn}^{2+}$ . As 30%  $\text{Mn}^{2+}$  is doped, the decays become faster and non-exponential, reflecting the characteristics of donors due to energy transfer. For  $\text{Eu}^{2+}(\text{I})$ , the lifetime ( $\tau_{10}$ ) of 490 ns in the absence of  $\text{Mn}^{2+}$  is shortened to 147 ns ( $\tau_1$ ) in the presence of 30%  $\text{Mn}^{2+}$ . For  $\text{Eu}^{2+}(\text{II})$ , the lifetime ( $\tau_{20}$ ) of 700 ns is shortened to 430 ns ( $\tau_2$ ). The lifetime of  $\text{Mn}^{2+}$  fluorescence is 17 ms. The values of all lifetimes are obtained by integrating the decay curves with normalized initial intensities. The energy transfer efficiency ( $\eta_1$ ) for  $\text{Eu}^{2+}(\text{I})$  can be calculated by  $\eta_1 = 1 - \tau_1/\tau_{10}$ . Accordingly,  $\eta_2 = 1 - \tau_2/\tau_{20}$  for  $\text{Eu}^{2+}(\text{II})$ . For  $\text{Mn}^{2+}$  concentration of 30%, the calculated transfer efficiency  $\eta_1 = 70\%$  for  $\text{Eu}^{2+}(\text{I})$  and  $\eta_2 = 39\%$  for  $\text{Eu}^{2+}(\text{II})$ , showing that  $\text{Eu}^{2+}(\text{I})$  transfers more efficiently than  $\text{Eu}^{2+}(\text{II})$ . This is interpreted by larger spectral overlap between  $\text{Eu}^{2+}(\text{I})$  emission and  $\text{Mn}^{2+}$  excitation within its  $3d^5$  configuration than that between  $\text{Eu}^{2+}(\text{II})$  and  $\text{Mn}^{2+}$ , as shown in Fig. 5.

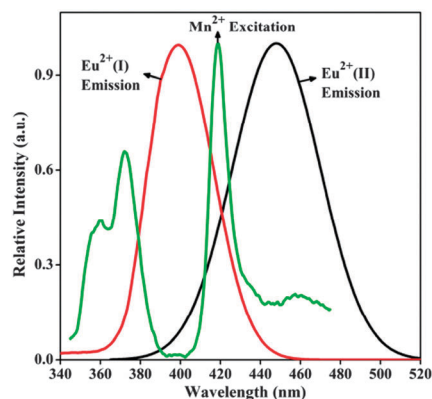
From the PL spectra shown in Fig. 3, for 355 nm excitation, 55% of  $\text{Mn}^{2+}$  emission comes from  $\text{Eu}^{2+}(\text{I})$  transfer, 45% from  $\text{Eu}^{2+}(\text{II})$ . For 266 nm excitation, 79% of  $\text{Mn}^{2+}$  emission comes from  $\text{Eu}^{2+}(\text{I})$  transfer, 21% from  $\text{Eu}^{2+}(\text{II})$ . Denoting the area intensity of the  $\text{Eu}^{2+}(\text{I})$  band and the  $\text{Eu}^{2+}(\text{II})$  band by  $I_1$  and  $I_2$ , respectively, and that of  $\text{Mn}^{2+}$  band from  $\text{Eu}^{2+}(\text{I})$  transfer and  $\text{Eu}^{2+}(\text{II})$  transfer by  $M_1$  and  $M_2$ , respectively, we have

$$M_1/M_2 = \eta_1 I_1 (1 - \eta_2) / \eta_2 I_2 (1 - \eta_1) \quad (1)$$

Using  $\eta_1 = 0.7$  and  $\eta_2 = 0.39$ , eqn (1) gives  $M_1/M_2 = 3.6(I_1/I_2)$ . Using the values of  $I_1/I_2$  obtained from PL spectra, we can calculate the values of  $M_1/(M_1 + M_2)$ . The calculated results show that the percentage of  $\text{Mn}^{2+}$  emission fed by  $\text{Eu}^{2+}(\text{I})$  is 60% for 355 nm excitation and 83% for 266 nm excitation that agreed well with the values of 55% and 79% obtained directly



**Fig. 4** Fluorescence decays of (a)  $\text{Eu}^{2+}(\text{I})$  and (b)  $\text{Eu}^{2+}(\text{II})$  in  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:5\% \text{Eu}^{2+}$  and  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:5\% \text{Eu}^{2+}$ , 30%  $\text{Mn}^{2+}$ .



**Fig. 5** Normalized PL spectra for  $\text{Eu}^{2+}(\text{I})$ ,  $\text{Eu}^{2+}(\text{II})$  and PLE spectrum for  $\text{Mn}^{2+}$  obtained in  $\text{Eu}^{2+}$  and  $\text{Mn}^{2+}$  singly doped  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}$ .

from PL spectra. Using the values of transfer efficiency, it is also possible to estimate the reduction of the intensity ratio  $I_1/I_2$  in  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:5\% \text{Eu}^{2+}$ , 30%  $\text{Mn}^{2+}$  in comparison with that in  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:5\% \text{Eu}^{2+}$ . From the PL spectra obtained upon 355 nm excitation, the ratio  $I_1/I_2$  in  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:5\% \text{Eu}^{2+}$ , 30%  $\text{Mn}^{2+}$  is as 52% as that in  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:5\% \text{Eu}^{2+}$ . The transfer efficiency yields the ratio to be 0.5 by  $(1 - \eta_1)/(1 - \eta_2)$ , which is in good agreement with the PL data.

In summary,  $\text{Eu}^{2+}$  singly and  $\text{Eu}^{2+}$ ,  $\text{Mn}^{2+}$  co-doped  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}$  exhibit not only the well known blue band of  $\text{Eu}^{2+}$  peaking at 448 nm but also a new emission band peaking at 399 nm in violet, attributed to  $\text{Eu}^{2+}$  on the six- and ten-coordinated  $\text{Sr}^{2+}$  sites in  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}$ , respectively. The  $\text{Eu}^{2+}$  band in violet transfers energy to  $\text{Mn}^{2+}$  more efficiently than that in blue. For  $\text{Mn}^{2+}$  fractional concentration of 0.3, the transfer efficiency is 70% for the violet  $\text{Eu}^{2+}(\text{I})$ , but only 39% for the blue  $\text{Eu}^{2+}(\text{II})$ . The luminescence spectral distributions for various excitation wavelengths are well fitted by the values of energy transfer efficiencies. The new  $\text{Eu}^{2+}$  band could enable  $\text{Mn}^{2+}$  and  $\text{Eu}^{2+}$  co-doped  $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}$  to be a promising phosphor for enriching the red component of white LEDs.

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## Notes and references

- S. Nakamura and G. Fasol, *Proc. SPIE-Int. Soc. Opt. Eng.*, 1997, **3002**, 26.
- J. S. Kim, P. E. Jeon, J. C. Choi and H. L. Park, *Appl. Phys. Lett.*, 2004, **84**, 15.
- Z.-y. Mao, D.-j. Wang, Q.-f. Lu, W.-h. Yu and Z.-h. Yuan, *Chem. Commun.*, 2009, 346–348.
- Z. C. Wu, J. X. Shi, J. Wang, M. L. Gong and Q. Su, *J. Mater. Chem.*, 2006, **179**, 2356–2360.
- Y. S. Tang, S. F. Hu, C. C. Lin, N. C. Bagkar and R. S. Liu, *Appl. Phys. Lett.*, 2007, **90**, 151108.
- S. Ye and Z. S. Liu, *Mater. Res. Bull.*, 2008, **43**, 1057.
- Z. D. Hao, J. H. Zhang, X. Zhang, X. Y. Sun, Y. S. Luo and S. Z. Lu, *Appl. Phys. Lett.*, 2007, **90**, 2611.
- M. V. Hoffman, *J. Electrochem. Soc.*, 1968, **115**, 560–563.
- H. L. Ngee, *et al.*, *Phys. Procedia*, 2009, **2**, 171–183.
- C. F. Guo, X. Ding, L. Luan and Y. Xu, *Sens. Actuators, B*, 2010, **143**, 712–715.
- J. H. Hong, S. Wan Song and S. Tae Hong, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2011, **67**, i1–i3.
- L. G. Van Uitert, *J. Lumin.*, 1984, **29**, 1–9.