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White-light generation and energy transfer in $SrZn_2(PO_4)_2$:Eu,Mn phosphor for ultraviolet light-emitting diodes

Woan-Jen Yang and Teng-Ming Chen[a)]

Department of Applied Chemistry, National Chiao Tung University, Hsinchu 30050, Taiwan, Republic of China

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The $SrZn_2(PO_4)_2:Eu^{2+},Mn^{2+}$ phosphor shows two emission bands under ultraviolet radiation; the one observed at 416 nm is attributed to Eu^{2+} occupying the Sr^{2+} sites and the other asymmetric band deconvoluted into two peaks was found to center at 538 and 613 nm, which originate from Mn^{2+} occupying two different Zn^{2+} sites. The energy transfer from Eu^{2+} to Mn^{2+} has been demonstrated to be a resonant type via a dipole-quadrupole mechanism. By utilizing the principle of energy transfer and appropriate tuning of activator contents, we have demonstrated that $SrZn_2(PO_4)_2:Eu^{2+},Mn^{2+}$ is potentially useful as an ultraviolet-convertible phosphor for white-light emitting diodes. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2182026]

The quest for new light-emitting-diode (LED) converted phosphors has triggered active research efforts in the investigation of single-phased white-emitting phosphors. It has been well known that Eu^{2+} may act as an efficient sensitizer transferring energy to Mn^{2+} in several host lattices.[1–3] The energy transfer from Eu^{2+} to Mn^{2+} ($ET_{Eu\rightarrow Mn}$) in luminescent materials has been studied extensively during the past few years.[4–7] The main interest is in the development of new and single-phased (instead of combination of red, green, and blue) phosphors for white-light ultraviolet light-emitting diodes (UVLEDs). In this letter, we have demonstrated that with appropriate tuning of activator contents $SrZn_2(PO_4)_2:Eu^{2+},Mn^{2+}$ (SZP:Eu,Mn) phosphors exhibit great potential to act as a single-phased white-emitting phosphor for UVLEDs. The energy transfer mechanism among the luminescent centers in SZP:Eu,Mn has also been investigated and reported herein.

The compound $SrZn_2(PO_4)_2$ (SZP) was confirmed to exist as a single phase in the $Sr_3(PO_4)_2-Zn_3(PO_4)_2$ system in 1961 by Hummel[8] and, although only unindexed x-ray powder data were reported, the luminescent properties of the SZP:Eu^{2+} were reported in 1968 by Hoffman.[9] Until 1990, the crystal structure of SZP was then determined by Hemon[10] to be a Hurlbutite-type structure with the composition $CaBe_2(PO_4)_2$,[11] which was found to emit blue light by Eu^{2+} doping under 254 nm excitation.[12]

SZP:Eu,Mn phosphors were synthesized through a solid-state reaction route. The starting materials $SrCO_3$, ZnO, $NH_4H_2PO_4$, Eu_2O_3, and $MnCO_3$ with purity of 99.99% were mixed in the requisite proportions and calcined at 900–1000 °C under 5:95 H_2/Ar atmosphere. The phase purity of the as-prepared phosphor samples was checked by powder x-ray diffraction (XRD) analysis by using a Bruker AXS D8 advanced automatic diffractometer with Cu K_α radiation operated at 40 kV and 20 mA. The XRD profile of SZP:Eu,Mn is shown in Fig. 1 and it agrees well with that reported in JCPDS file 80-1062, indicating that codoping Eu^{2+} and Mn^{2+} does not cause any significant change in the host structure. SZP crystallizes in a monoclinic system with the space group of $P2_1/c$ and has five crystallographically independent cation sites in a unit cell, namely, one seven-coordinated Sr^{2+} site, two four-coordinated Zn^{2+} sites, and two four-coordinated P^{5+} sites.[10] Based on the effective ionic radii of cations with different coordination numbers,[13] we have proposed that Eu^{2+} and Mn^{2+} are expected to occupy the Sr^{2+} and Zn^{2+} sites preferably, respectively, since the ionic radii of Eu^{2+} (1.20 Å) and Mn^{2+} (0.66 Å) are close to that of Sr^{2+} (1.21 Å) and Zn^{2+} (0.60 Å), respectively. However, the P^{5+} sites with ionic radius of 0.17 Å are too small for Eu^{2+} and Mn^{2+} to occupy.

The measurements of photoluminescence (PL) and photoluminescence excitation (PLE) spectra for SZP:Eu,Mn phosphors were performed by using a Spex Fluorolog-3 spectrofluorometer (Instruments S.A., Edison, N.J.) equipped with a 450 W Xe light source and double excitation monochromators, and the details have been described in our previous work.[7] As shown in Fig. 2, the PLE spectrum of SZP:Eu shows an optimal excitation band centered at 365 nm, consisting of unresolved bands due to the $4f5d$ multiplets of the Eu^{2+} excited state, and the PL spectrum of that shows an intense broad band centered at 416 nm, which could be attributed to the typical $4f^65d^1(t_{2g})\rightarrow 4f^7(^8S_{7/2})$ transition of Eu^{2+}. The PLE spectrum of SZP:Mn consists of several

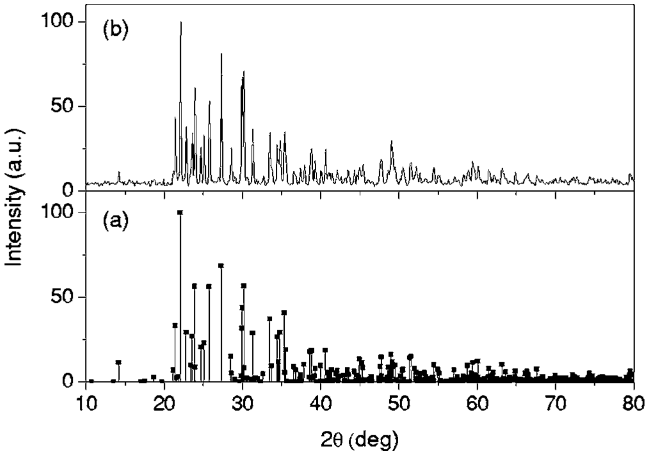

FIG. 1. XRD patterns of (a) $SrZn_2(PO_4)_2$ (JCPDS file No. 80-1062) and (b) $(Sr_{0.99}Eu^{2+}_{0.01})(Zn_{1.99}Mn^{2+}_{0.01})(PO_4)_2$ phosphor.

[a)] Author to whom correspondence should be addressed; electronic mail: tmchen@mail.nctu.edu.tw

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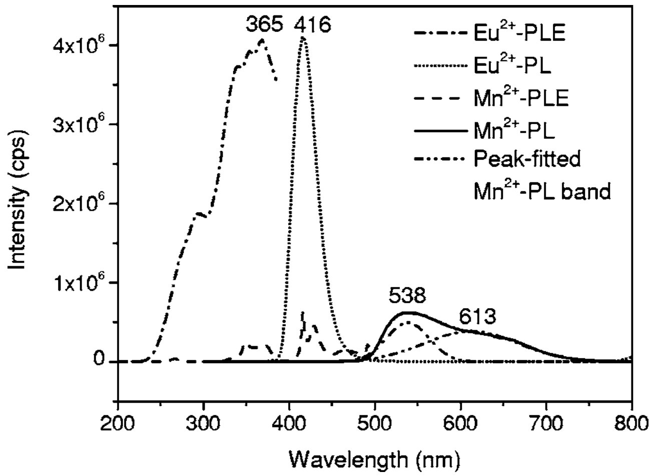

FIG. 2. PLE and PL spectra for $(Sr_{0.99}Eu^{2+}_{0.01})Zn_2(PO_4)_2$ (PLE monitored at 416 nm and PL exited at 365 nm) and $Sr(Zn_{1.96}Mn^{2+}_{0.04})(PO_4)_2$ (PLE monitored at 538 nm and PL excited at 416 nm) and peak-fitting spectra for PL band of $Sr(Zn_{1.96}Mn^{2+}_{0.04})(PO_4)_2$.

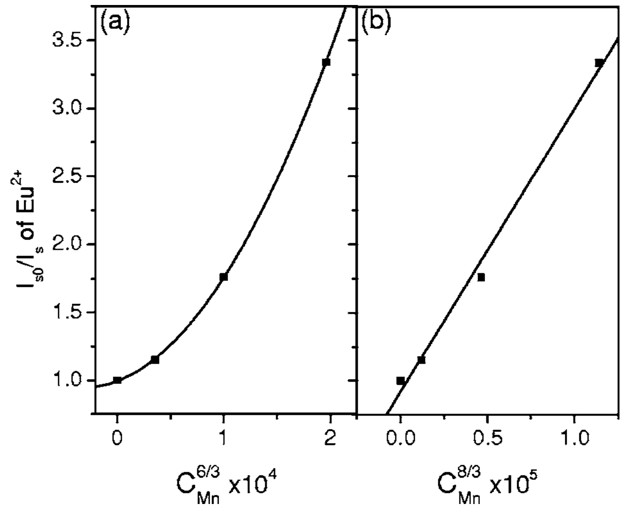

FIG. 4. Dependence of I_{S0}/I_S of Eu^{2+} on (a) $C^{6/3}$ and (b) $C^{8/3}$.

bands centered at 350, 372, 416, 429, and 468 nm, corresponding to the transitions of Mn^{2+} from $^6A_1(^6S)$ to $^4E(^4D)$, $^4T_2(^4D)$, $[^4A_1(^4G), ^4E(^4G)]$, $^4T_2(^4G)$, $^4T_1(^4G)$ levels, respectively. The broad and asymmetric emission band of SZP:Mn is attributed to the spin-forbidden $^4T_1(^4G) \rightarrow {}^6A_1(^6S)$ transition of Mn^{2+} occupying two crystallographically distinct Zn^{2+} sites. Therefore, by deconvoluting the observed emission band of Mn^{2+}, we could obtain two peaks centered at 538 and 613 nm, respectively.

As shown in Fig. 2, a significant spectral overlap was observed between the emission band of Eu^{2+} centered at 416 nm and the Mn^{2+} excitation transition multiplets of $^6A_1(^6S) \rightarrow {}^4T_1(^4G)$, $^4T_2(^4G)$, $[^4A_1(^4G), ^4E(^4G)]$. Therefore, the effective resonance-type $ET_{Eu\rightarrow Mn}$ is expected. Figure 3 shows the PLE and PL spectra for $(Sr_{0.99}Eu^{2+}_{0.01}) \times (Zn_{2-n}Mn^{2+}_n)(PO_4)_2$ phosphors with different Mn^{2+} dopant contents n of 0, 0.006, 0.010, and 0.014, respectively. Interestingly and reasonably, with increasing Mn^{2+} dopant content, the PL intensity of Mn^{2+} activator (or energy acceptor) was observed to increase, whereas that of Eu^{2+} sensitizer (or energy donor) was simultaneously found to decrease monotonically. The energy transfer efficiency (η_T) from Eu^{2+} to Mn^{2+} can be expressed by[14]

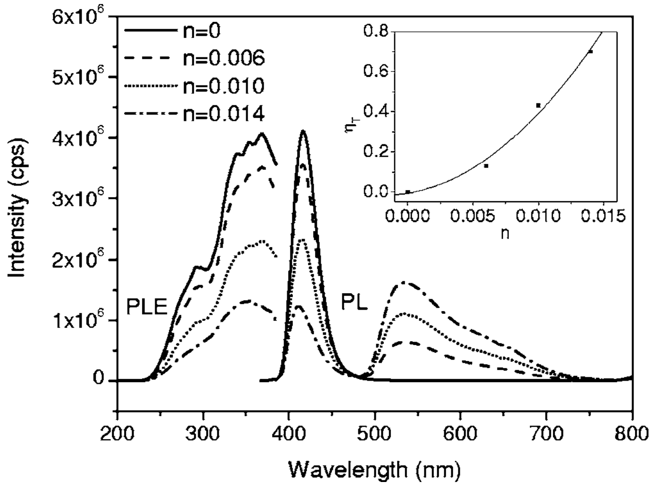

FIG. 3. PLE and PL spectra for $(Sr_{0.99}Eu^{2+}_{0.01})(Zn_{2-n}Mn^{2+}_n)(PO_4)_2$ phosphors (PLE monitored at 416 nm and PL excited at 365 nm), and dependence of the energy transfer efficiency η_T on Mn^{2+} content n.

$$\eta_T = 1 - \frac{I_S}{I_{S0}}, \tag{1}$$

where I_{S0} and I_S are the luminescence intensity of sensitizer (Eu^{2+}) in the absence and presence of activator (Mn^{2+}). The η_T from Eu^{2+} to Mn^{2+} in $(Sr_{0.99}Eu^{2+}_{0.01})(Zn_{2-n}Mn^{2+}_n)(PO_4)_2$ was calculated as a function of n and is illustrated in Fig. 3. With increasing Mn^{2+} dopant content, the η_T was found to increase gradually.

On the basis of Dexter's energy transfer formula of multipolar interaction and Reisfeld's approximation, the following relation can be obtained:[15]

$$\frac{\eta_0}{\eta} \propto C^{n/3} \tag{2}$$

where η_0 and η are the luminescence quantum efficiency of Eu^{2+} in the absence and presence of Mn^{2+}, respectively; the values η_0/η can be approximately calculated by the ratio of related luminescence intensities (I_{S0}/I_S); C is the content of Mn^{2+}; n=6, 8, and 10, corresponding to dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions, respectively. The I_{S0}/I_S-$C^{n/3}$ plots are represented in Figs. 4(a) and 4(b), and only when n=8 does it exhibit a linear relation, indicating clearly that $ET_{Eu\rightarrow Mn}$ is the dipole–quadrupole mechanism, which is similar to that observed in $CaAl_2Si_2O_8$:Eu,Mn previously investigated in our group.[7]

For the dipole–quadrupole mechanism, the critical distance (R_c) of $ET_{Eu\rightarrow Mn}$ can be expressed by[7]

$$R_c^8 = 0.63 \times 10^{28} \frac{f_q \lambda_S^2 Q_A}{f_d E_S^4} \int F_S(E) F_A(E) dE, \tag{3}$$

where $Q_A = 4.8 \times 10^{-16} f_d$ is the absorption cross section of Mn^{2+}, $f_d = 10^{-7}$ and $f_q = 10^{-10}$ are the oscillator strengths of the dipole and quadrupole electrical absorption transitions for Mn^{2+}; λ_S (in Å) and E (in eV) are emission wavelength and emission energy of Eu^{2+}; $\int F_S(E) F_A(E) dE$ represents the spectral overlap between the normalized shapes of Eu^{2+} emission $F_S(E)$ and Mn^{2+} excitation $F_A(E)$, and it is estimated at about 4.35 eV^{-1}. So the R_c of $ET_{Eu\rightarrow Mn}$ in SZP:Eu,Mn was calculated to be about 11.4 Å, which is slightly

TABLE I. Comparison of CIE chromaticity coordinates for $(\mathrm{Sr}_{1-m}\mathrm{Eu}_m^{2+})\times(\mathrm{Zn}_{2-n}\mathrm{Mn}_n^{2+})(\mathrm{PO}_4)_2$ phosphors and simulated white light using commercial YAG:Ce phosphor.

λ_{ex} (nm)	Sample		(x,y)
365	$m=0.01$	$n=0$	(0.17,0.06)
365	$m=0.01$	$n=0.006$	(0.26,0.22)
365	$m=0.01$	$n=0.010$	(0.32,0.31)
365	$m=0.01$	$n=0.014$	(0.37,0.37)
416	$m=0$	$n=0.04$	(0.46,0.46)
467	Simulated white light with YAG:Ce		(0.31,0.27)

longer than that (i.e., 10.8 Å) reported for $\mathrm{CaAl_2Si_2O_8:Eu,Mn}$.[7]

The Commission International de I'Eclairage (CIE) chromaticity coordinates for $(\mathrm{Sr}_{1-m}\mathrm{Eu}_m^{2+})(\mathrm{Zn}_{2-n}\mathrm{Mn}_n^{2+})(\mathrm{PO}_4)_2$ phosphors were measured and summarized in Table I and the CIE coordinates are also represented as series A in Fig. 5. We have observed that the (x,y) coordinates vary systematically from (0.17, 0.06), (0.26, 0.22), (0.32, 0.31), (0.37, 0.37) to (0.46, 0.46), corresponding to hues of blue, aqua, white, and eventually to yellow; and the PL image of white-light emission is also shown in inset (a) of Fig. 5. To demonstrate that $(\mathrm{Sr}_{0.99}\mathrm{Eu}_{0.01}^{2+})(\mathrm{Zn}_{1.99}\mathrm{Mn}_{0.01}^{2+})(\mathrm{PO}_4)_2$ is a single-phased white-emitting phosphor, we have investigated the photoluminescence of the phosphor particles by using a fluorescence microscope (Olympus IX70) with a mercury light source and the fluorescence image obtained with 365 nm radiation is shown in inset (b) of Fig. 5. The observed golden rather than white colored image has been attributed to possible chromatic aberration of the microscope system, indicating that our SZP:Eu,Mn phosphor is truly a single-phased phosphor. Therefore, our observation confirms the fact that both Eu^{2+} and Mn^{2+} simultaneously codoped into $\mathrm{SrZn_2(PO_4)_2}$ rather than the respective doping. Furthermore, to evaluate the potential of the wavelength-tunable SZP:Eu,Mn as white-emitting phosphors, we have investigated and compared the chromaticity characteristics of the simulated white light generated from commercial $\mathrm{Y_3Al_5O_{12}:Ce}$ (YAG:Ce, Nichia Co., Japan) excited with monochromatic blue light of 467 nm with coordinates of (0.15, 0.04) represented as series B in Fig. 5. The experimentally determined chromaticity coordinates were found to be (0.48, 0.50) for YAG:Ce and (0.31, 0.27) for simulated white light, respectively, and the color saturation was found to be inferior to that generated from our SZP:Eu,Mn phosphor. In practice, with an increasing amount of electrical current, the hue of a white-light LED changes from yellow to white and to blue. Therefore, the white-light LED based on YAG:Ce excited by a blue-emitting chip tends to produce color aberration when the LED chip is degrading. In contrast, our SZP:Eu,Mn phosphors excited with UV light will not have that problem because the excited light is invisible. The above observations hint at the promising application of SZP:Eu,Mn as a single-phased white-emitting phosphor for UVLEDs.

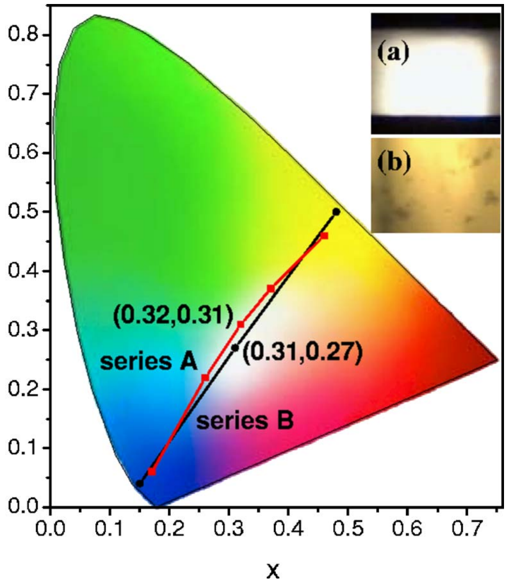

FIG. 5. (Color online) CIE chromaticity diagram for $(\mathrm{Sr}_{1-m}\mathrm{Eu}_m^{2+})\times(\mathrm{Zn}_{2-n}\mathrm{Mn}_n^{2+})(\mathrm{PO}_4)_2$ phosphors with different Mn^{2+} dopant contents represented as series A ($m=0.01$ excited at 365 nm, $m=0$ excited at 416 nm) and simulated white light generated with YAG:Ce represented as series B (excited at 467 nm); inset (a) PL image and (b) fluorescence image under 40× magnification of $(\mathrm{Sr}_{0.99}\mathrm{Eu}_{0.01}^{2+})(\mathrm{Zn}_{1.99}\mathrm{Mn}_{0.01}^{2+})(\mathrm{PO}_4)_2$.

In conclusion, the white-light generation has been realized through tuning of Eu^{2+} and Mn^{2+} contents in $\mathrm{SrZn_2(PO_4)_2}$ under UV radiation. We have also demonstrated that the energy transfer from Eu^{2+} to Mn^{2+} in $\mathrm{SrZn_2(PO_4)_2:Eu^{2+},Mn^{2+}}$ phosphors is a resonant type via a dipole–quadrupole mechanism. Therefore, by utilizing the principle of energy transfer and adjusting activator contents properly, we have shown that $\mathrm{SrZn_2(PO_4)_2:Eu^{2+},Mn^{2+}}$ can act as a potential single-phased white-emitting phosphor for UVLEDs.

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