

White light generation under violet-blue excitation from tunable green-to-red emitting $\text{Ca}_2\text{MgSi}_2\text{O}_7 : \text{Eu}, \text{Mn}$ through energy transfer

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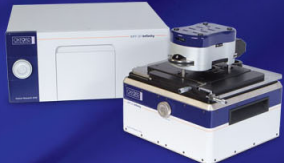
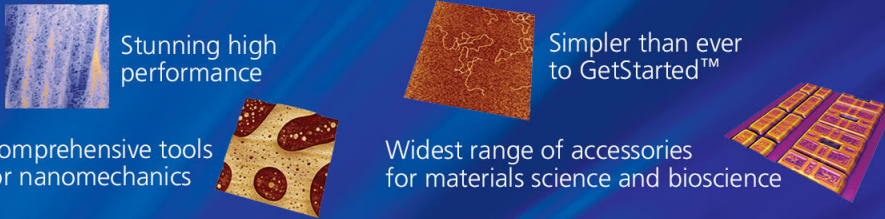
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White light generation under violet-blue excitation from tunable green-to-red emitting $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu},\text{Mn}$ through energy transfer

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Yellowish green-to-orange red emission can be generated by energy transfer from Eu^{2+} to Mn^{2+} in the $\text{Ca}_2\text{MgSi}_2\text{O}_7$ host matrix. Eu^{2+} -doped $\text{Ca}_2\text{MgSi}_2\text{O}_7$ shows a broad green emission band centering at 528 nm and Mn^{2+} -doped $\text{Ca}_2\text{MgSi}_2\text{O}_7$ exhibits a red emission at around 602 nm. The authors have demonstrated that the mechanism of energy transfer from Eu^{2+} to Mn^{2+} in $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu},\text{Mn}$ phosphor is a resonant type via a dipole-quadrupole mechanism. They have also shown that the white light with varied hue, depending on contents of Mn^{2+} , is generated by combination of predesigned emission wavelength-tunable $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu},\text{Mn}$ phosphors and violet-blue light source. © 2007 American Institute of Physics. [DOI: 10.1063/1.2722670]

White light can be produced by many approaches; one of the most common and easiest ways is the combination of the yellow-emitting phosphor made of cerium doped yttrium aluminum garnet ($\text{YAG}:\text{Ce}^{3+}$) (Ref. 1) and blue-emitting GaN chips. Although this kind of white-light blending method has been well used for a few years, some problems have existed; one of them is that the variety of hue is insufficient compared with the white light mixed from three primary colors. To circumvent this disadvantage, the red, green, and blue multiphased phosphors or single-phased dichromatic phosphor consisting of two emission bands in the green and red spectral regions are employed to generate white light under ultraviolet (UV) or blue light-emitting diode (LED) chip excitation, respectively. However, in the three-converter system, the blue emission efficiency is poor because of the strong reabsorption of the blue light by the red or green-emitting phosphors. Therefore, many efforts have been made to develop the single-phased white-emitting phosphors which are based on the mechanism of energy transfer from Eu^{2+} to Mn^{2+} (abbreviated as $\text{ET}_{\text{Eu} \rightarrow \text{Mn}}$ hereafter) that has been studied actively in the past few years.²⁻⁶ In this letter, we have demonstrated that the white light could be generated with combination of tunable yellow green-to-orange red emitting phosphor $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+},\text{Mn}^{2+}$ (CMSO:Eu,Mn) and violet-blue (380–420 nm) radiation source. We have also proven that a warm white light can be achieved by increasing the contents of Mn^{2+} .

The silicate compound of $\text{Ca}_2\text{MgSi}_2\text{O}_7$ with akermanite structure was reported to crystallize in the tetragonal crystal system with the space group $P-42_1m$ and the lattice parameters $a=7.8338(6)\text{Å}$ and $c=5.0082(5)\text{Å}$.⁷ Three crystallographically independent cation sites, namely, one Ca^{2+} , one Mg^{2+} , and one Si^{4+} exist in the crystal lattice. The Ca^{2+} ion is coordinated by eight oxygen atoms with an average Ca–O distance of 2.573 Å, and both Mg^{2+} and Si^{4+} cations were reported to occupy in the tetrahedral sites with an average M–O distance of 1.916 Å ($M=\text{Mg}$) and 1.624 Å ($M=\text{Si}$), respectively.⁷ In view of the effective ionic radii of cations with different coordination numbers,⁸ we have predicted that

Eu^{2+} and Mn^{2+} prefer to occupy the Ca^{2+} and Mg^{2+} sites, respectively, because the ionic radii of Eu^{2+} (1.25 Å) and Mn^{2+} (0.66 Å) are compatible with those of Ca^{2+} (1.12 Å) and Mg^{2+} (0.57 Å). Nevertheless, the Si^{4+} site (0.26 Å) is too small for the substitution of Eu^{2+} and Mn^{2+} to take place.

High temperature solid-state reactions were employed to synthesize CMSO:Eu,Mn. Powders of high-purity (all in 99.99%, Aldrich Chemical Co., WI, USA) CaCO_3 , MgO , SiO_2 , MnCO_3 , and Eu_2O_3 were weighed in stoichiometric proportions, thoroughly ground and mixed in an agate mortar, pressed into pellets, and calcined at 1300 °C for 8 h in an inner alumina crucible that was contained in a covered outer alumina crucible filled with graphite powder. Afterwards, the product was reduced further at 900 °C for 3 h under an atmosphere of 5% $\text{H}_2/95\%$ Ar. The phase purity of all the samples was characterized and evaluated by powder x-ray diffraction (XRD) analysis by using a Bruker AXS D8 advanced automatic diffractometer with $\text{Cu } K_\alpha$ radiation operated at 40 kV and 20 mA. Figure 1 shows the XRD profile for the optimized composition $(\text{Ca}_{0.996}\text{Eu}_{0.004})_2(\text{Mg}_{0.65}\text{Mn}_{0.35})\text{Si}_2\text{O}_7$, which agrees very well with that reported in Ref. 9, indicating that both of the host

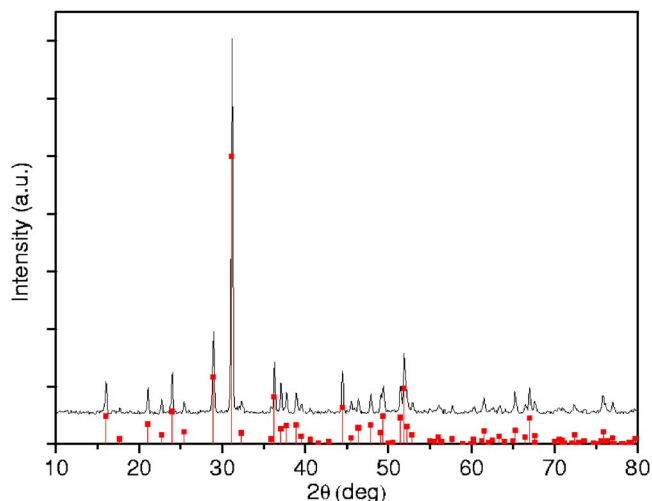


FIG. 1. (Color online) XRD profile of $(\text{Ca}_{0.996}\text{Eu}_{0.004})_2(\text{Mg}_{0.65}\text{Mn}_{0.35})\text{Si}_2\text{O}_7$ showing good agreement with that reported in Ref. 9.

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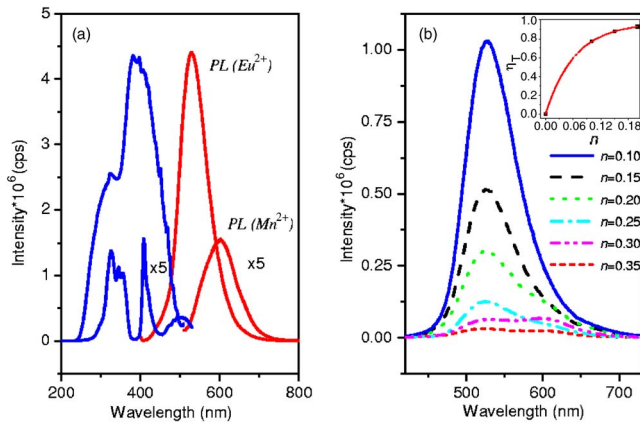


FIG. 2. (Color online) (a) PLE (blue line) and PL (red line) spectra for $(\text{Ca}_{0.996}\text{Eu}_{0.004})_2\text{MgSi}_2\text{O}_7$ (PLE monitored at 528 nm and PL excited at 381 nm) and $\text{Ca}_2(\text{Mg}_{0.65}\text{Mn}_{0.35})\text{Si}_2\text{O}_7$ (PLE monitored at 602 nm and PL excited at 408 nm). (b) PL spectra for $(\text{Ca}_{0.996}\text{Eu}_{0.004})_2(\text{Mg}_{1-n}\text{Mn}_n)\text{Si}_2\text{O}_7$ phosphors (excited at 381 nm) and dependence of the energy transfer efficiency η_T on Mn^{2+} content n .

structure and single-phased composition are retained even at high codoping level of Eu^{2+} and Mn^{2+} .

The measurements of photoluminescence (PL) and photoluminescence excitation (PLE) spectra for CMSO:Eu,Mn phosphors were performed by using a Spex Fluorolog-3 spectrofluorometer (Instruments S.A., NJ, USA) equipped with a 450 W Xe light source and double excitation monochromators, and the details have been described in our previous work.⁵ Figure 2(a) depicts the PLE and PL spectra of Eu^{2+} - and Mn^{2+} -doped $\text{Ca}_2\text{MgSi}_2\text{O}_7$, respectively. In solely Eu^{2+} -activated system, the PL spectrum shows a broad green emission band centered at 528 nm attributed to the typical $4f^65d^1(t_{2g}) \rightarrow 4f^7(^8S_{7/2})$ transition of Eu^{2+} , and the absorptions observed in the PLE spectrum situate between the UV and blue region consisting of unresolved bands due to the $4f5d$ multiplets of the Eu^{2+} excited state. However, in the solely Mn^{2+} -doped system, the PL spectrum exhibits a broad red emission around at 602 nm which is ascribed to the spin-forbidden $^4T_1(^4G) \rightarrow ^6A_1(^6S)$ transition of Mn^{2+} and the PLE spectrum contains several bands centering at 325, 350, 408, 425, and 500 nm, corresponding to the transitions of Mn^{2+} from $^6A_1(^6S)$ to $^4E(^4D)$, $^4T_2(^4D)$, $[^4A_1(^4G)$, $^4E(^4G)]$, $^4T_2(^4G)$, and $^4T_1(^4G)$ energy levels, respectively.

As also shown in Fig. 2(a), based on the observed significant overlap between the excitation spectrum of Mn^{2+} and emission spectrum of Eu^{2+} , the effective resonance-type energy transfer is expected to take place from Eu^{2+} to Mn^{2+} . The PL spectra obtained by excitation at 381 nm for $(\text{Ca}_{0.996}\text{Eu}_{0.004})_2(\text{Mg}_{1-n}\text{Mn}_n)\text{Si}_2\text{O}_7$ with varied Mn^{2+} dopant contents are presented in Fig. 2(b) and it can be visualized clearly that the intensity of Eu^{2+} sensitizer was found to decrease remarkably and simultaneously as the contents of Mn^{2+} increased gradually. The observed energy transfer efficiency (η_T) from Eu^{2+} to Mn^{2+} has been discussed by Paulose *et al.*¹⁰ and can be expressed by

$$\eta_T = 1 - \frac{I_S}{I_{S0}}, \quad (1)$$

where I_{S0} and I_S are the luminescence intensity of the sensitizer (Eu^{2+}) with and without activator (Mn^{2+}) present. The η_T from Eu^{2+} to Mn^{2+} in $(\text{Ca}_{0.996}\text{Eu}_{0.004})_2(\text{Mg}_{1-n}\text{Mn}_n)\text{Si}_2\text{O}_7$

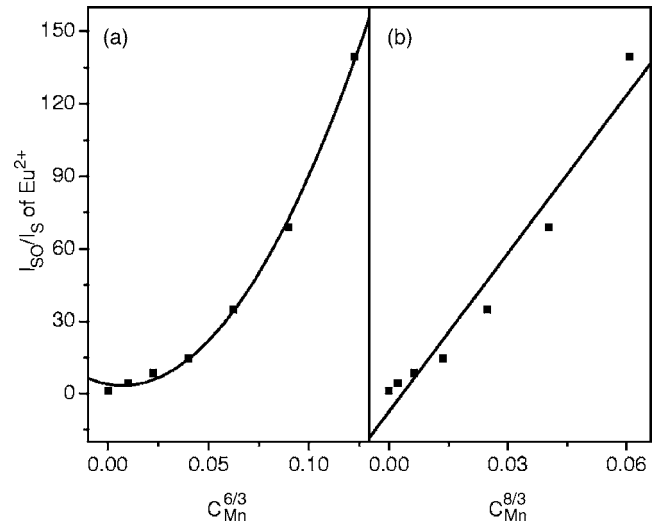


FIG. 3. Dependence of I_{S0}/I_S of Eu^{2+} on (a) $C^{6/3}$ and (b) $C^{8/3}$.

was calculated as a function of n and is represented in the inset of Fig. 2(b). With increasing Mn^{2+} dopant content, the η_T was found out to increase and reach the saturation when n is above 0.2.

Based on Dexter's energy transfer formula of multipolar interaction and Reisfeld's approximation, the following relation can be obtained:¹¹

$$\frac{\eta_0}{\eta} \propto C^{n/3}, \quad (2)$$

where η_0 and η are the luminescence quantum efficiency of Eu^{2+} in the absence and presence of Mn^{2+} , respectively; the values of 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+} ; and $n=6, 8,$ and 10 correspond to dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions, respectively. The $I_{S0}/I_S-C^{n/3}$ plots are further illustrated in Figs. 3(a) and 3(b), and the linear relation was observed only when $n=8$, implying that $\text{ET}_{\text{Eu} \rightarrow \text{Mn}}$ is the dipole-quadrupole mechanism, which is similar to those previously investigated and observed in our group.^{5,6}

The critical distance (R_c) of $\text{ET}_{\text{Eu} \rightarrow \text{Mn}}$ for the dipole-quadrupole mechanism can be calculated by using the following simplified equation for dipole-quadrupole mechanism:⁵

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

where Q_A is the absorption coefficient of Mn^{2+} that is equal to $4.8 \times 10^{-16} f_d$ given by Blasse;¹² $f_d=10^{-7}$ and $f_q=10^{-10}$ are the oscillator strengths of the activator (Mn^{2+}) dipole and quadrupole electric transitions, respectively; λ_s (in \AA) and E (in eV) are the emission wavelength and emission energy of Eu^{2+} ; and $\int F_S(E) F_A(E) dE$ expresses 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 1.79 eV^{-1} . Therefore, the R_c for $\text{ET}_{\text{Eu} \rightarrow \text{Mn}}$ in CMSO:Eu,Mn was reckoned to be 11.97 \AA , which is longer than 11.4 and 10.8 \AA reported for $\text{SrZn}_2(\text{PO}_4)_2:\text{Eu,Mn}$ (Ref. 6) and $\text{CaSi}_2\text{Al}_2\text{O}_8:\text{Eu,Mn}$,⁵ respectively.

The diffuse reflectance spectra of selected samples doped with different amounts of Mn^{2+} and the pristine

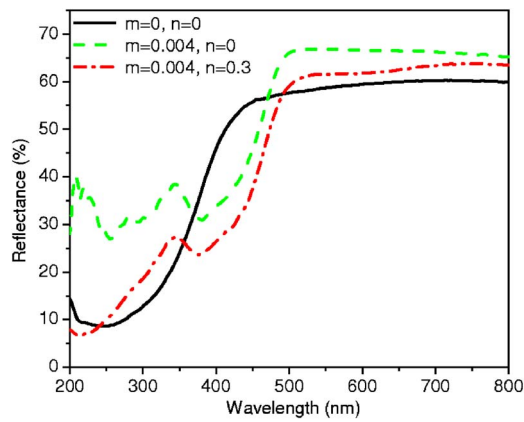


FIG. 4. (Color online) Diffuse reflectance spectra for undoped $\text{Ca}_2\text{MgSi}_2\text{O}_7$, $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{mEu}^{2+}$, and $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{mEu}^{2+} \text{ nMn}^{2+}$

$\text{Ca}_2\text{MgSi}_2\text{O}_7$ are depicted in Fig. 4. The $\text{Ca}_2\text{MgSi}_2\text{O}_7$ host shows an absorption edge only in the UV spectral region. However, the strong absorption in the near-UV to visible spectral region (370–450 nm) was clearly observed not only for $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ but also for Eu^{2+} - and Mn^{2+} -codoped systems, and the results were found to be consistent with the PLE spectra shown in Fig. 2(a).

Figure 5 portrays the Commission International de l'Eclairage (CIE) chromaticity coordinates for $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu},\text{Mn}$ phosphors with various dopant concentrations. The chromaticity coordinates (x, y) of $(\text{Ca}_{1-m}\text{Eu}_m)_2(\text{Mg}_{1-n}\text{Mn}_n)\text{Si}_2\text{O}_7$ vary from (0.36, 0.55) (point G) through (0.45, 0.44) and finally to (0.57, 0.36) (point R) corresponding to solely Eu^{2+} -doped, Eu^{2+} - and Mn^{2+} -coactivated, and solely Mn^{2+} -doped systems, respectively. As shown in Fig. 5, points on the line GR represents the change of hue from yellow-green to orange-red and this variation is also summarized in Table I. We have observed that white light can be generated by exciting $(\text{Ca}_{1-m}\text{Eu}_m)_2(\text{Mg}_{1-n}\text{Mn}_n)\text{Si}_2\text{O}_7$ phosphors under 381 nm ra-

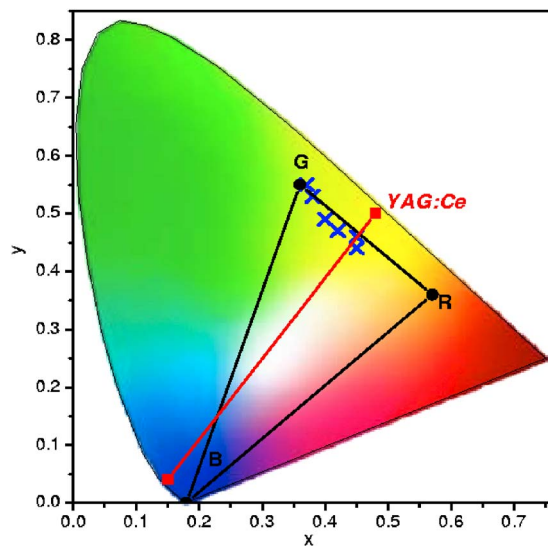


FIG. 5. (Color online) CIE chromaticity diagram for $(\text{Ca}_{1-m}\text{Eu}_m)_2(\text{Mg}_{1-n}\text{Mn}_n)\text{Si}_2\text{O}_7$ phosphors with different Mn^{2+} dopant contents represented as line GR ($m=0.004$ excited at 381 nm; $m=0$ excited at 408 nm) and simulated white light generated with YAG:Ce [excited at 467 nm with chromaticity coordinates at (0.15, 0.04)].

TABLE I. Variation of CIE chromaticity coordinates from yellowish-green ($n=0$) to orange-red ($m=0$) as a function of n for $(\text{Ca}_{1-m}\text{Eu}_m)_2(\text{Mg}_{1-n}\text{Mn}_n)\text{Si}_2\text{O}_7$.

λ_{ex} (nm)	$(\text{Ca}_{1-m}\text{Eu}_m)_2(\text{Mg}_{1-n}\text{Mn}_n)\text{Si}_2\text{O}_7$		(x, y)
381	$m=0.004$	$n=0$	(0.36, 0.55)
381	$m=0.004$	$n=0.10$	(0.37, 0.55)
381	$m=0.004$	$n=0.15$	(0.38, 0.53)
381	$m=0.004$	$n=0.20$	(0.40, 0.49)
381	$m=0.004$	$n=0.25$	(0.42, 0.47)
381	$m=0.004$	$n=0.30$	(0.45, 0.46)
381	$m=0.004$	$n=0.35$	(0.45, 0.44)
408	$m=0$	$n=0.25$	(0.57, 0.36)
Simulated white light with			
467	YAG:Ce		(0.31, 0.27)

diation source with chromaticity coordinates at (0.18, 0.00) (point B). Comparing the white light produced by our emission-tunable phosphors and violet-blue light source with that from commercial YAG:Ce and blue LED chip, our system shows exceptionally flexible hues with increasing Mn^{2+} content than those of the commodity because the approaching RGB primary area can be effectively established in our system. The above observations hint enormously promising application of $\text{CMSO}:\text{Eu},\text{Mn}$ as a single-phased white-emitting phosphor under violet-blue irradiation.

In conclusion, the white light with varied hues and color temperature has been obtained by combination of wavelength-tunable yellowish green-to-orange red-emitting $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu},\text{Mn}$ phosphors and the violet-blue (381–420 nm) radiation source. The energy transfer from Eu^{2+} to Mn^{2+} in $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu},\text{Mn}$ phosphors has been demonstrated to be a resonant type via a dipole-quadrupole mechanism. Therefore, the $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu},\text{Mn}$ phosphors can play an important role in a potential single-phased white-emitting phosphor for violet-blue emitting LEDs by utilizing the principle of energy transfer and properly designed activator contents.

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