Luminescence and Energy Transfer of Eu- and Mn-Coactivated $CaAl_2Si_2O_8$ as a Potential Phosphor for White-Light UVLED

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A series of Eu^{2+}- and Mn^{2+}-coactivated $CaAl_2Si_2O_8$ phosphors have been synthesized at 1400 °C under a reduced atmosphere and their luminescence properties have been investigated as a function of activator and coactivator concentrations. We have discovered that energy transfers from Eu^{2+} to Mn^{2+} by directly observing significant overlap of the excitation spectrum of Mn^{2+} and the emission spectrum of Eu^{2+} as well as the systematic relative decline and growth of emission bands of Eu^{2+} and Mn^{2+}, respectively. The critical distance and average separation of Eu^{2+} and Mn^{2+} have also been calculated. By utilizing the principle of energy transfer, we have also demonstrated that with appropriate tuning of activator content $CaAl_2Si_2O_8$:Eu^{2+},Mn^{2+} phosphors exhibit great potential to act as a phosphor for white-light ultraviolet light-emitting diodes (UVLEDs).

1. Introduction

It has been well-known that Eu^{2+} may act as an efficient sensitizer that transfers energy to Mn^{2+} in several host lattices.[1,2] For instance, Caldino et al. described the $Eu^{2+}\rightarrow Mn^{2+}$ energy transfer process in $CaCl_2$:Eu^{2+},Mn^{2+} single crystals under photoexcitation. The authors suggested that the Eu^{2+} to Mn^{2+} energy transfer process observed in $CaCl_2$:Eu,Mn can be rationalized by the formation of small complexes of Eu−Mn in the lattice.[1] Similar energy transfer was also observed by Barry in the $BaMg_2Si_2O_7$:Eu^{2+},Mn^{2+} phosphor.[3] Recently, Yao et al. reported the luminescence and decay behaviors of $BaMg_2Si_2O_7$:Eu^{2+},Mn^{2+} as a function of dopant concentrations and confirmed the presence of $Eu^{2+}\rightarrow Mn^{2+}$ energy transfer.[4]

Rubio et al.[5] proposed an ionic radius criterion to predict paring between two impurity dopant ions in alkali halide host matrice, which may provide a reasonable basis for selecting appropriate impurity dopant ions for developing efficient phosphor materials. Furthermore, the $Eu^{2+}\rightarrow Mn^{2+}$ energy transfer mechanism in KBr:Eu^{2+},Mn^{2+} phosphor was described by Mendez et al.[6] who proposed the possible formation of small Eu^{2+}−Mn^{2+} clusters in the KBr lattice. Mendez et al. also indicated that the $Eu^{2+}\rightarrow Mn^{2+}$ energy transfer can be explained by assuming that a dipole−quadrupole or exchange (superexchange) interaction mechanism is active in the Eu^{2+}−Mn^{2+} cluster formation.[6]

Very recently, Kim et al. reported that $Ba_3MgSi_2O_8$:Eu,Mn can be used as a phosphor for fabrication of a warm white-light emitting diode.[7] They concluded that with optimal excitation wavelength at 375 nm $Ba_3MgSi_2O_8$:Eu,Mn was observed to show three emission bands centered at 442 nm (from Eu^{2+} and with decay time of 0.32 μsec), 505 nm (from Eu^{2+} and with decay time of 0.64 μsec), and 620 nm (from Mn^{2+} and with a decay time of 750 μsec)[7], respectively.

Despite the above-mentioned research on the luminescent properties and energy transfer of Eu and Mn-codoped materials, to the best of our knowledge, there have been no investigations regarding the luminescence in $CaAl_2Si_2O_8$:Eu,Mn published, nor is the energy transfer between Eu^{2+} and Mn^{2+} in the host of $CaAl_2Si_2O_8$ reported in the literature. Anorthite ($CaAl_2Si_2O_8$) was reported to be crystallized in a triclinic crystal system with space group $I\bar{1}$ under ambient pressure by Angel in 1988.[8] In the crystal lattice, there are six crystallographically independent cation sites, namely, four Ca^{2+} sites, one Al^{3+} site, and one Si^{4+} site. One type of Ca^{2+} ion occupies an octahedral site with six oxygen atoms and the average Ca−O bond distance is 2.485 Å. Other Ca^{2+} ions occupy three kinds of polyhedral sites with seven coordinated oxygen atoms and their average bond distances are 2.508, 2.531, and 2.562 Å, respectively. Al and Si atoms both occupy tetrahedral sites with four coordinated oxygen atoms, and the average bond distances for Al−O and Si−O are 1.735 and 1.611 Å, respectively.[8]

Motivated by the above investigations and the attempt to develop phosphors excitable by ultraviolet radiation for the applications of white-light LED, we have investigated the

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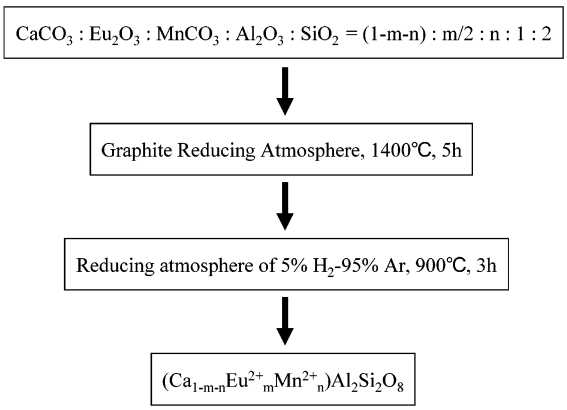

Figure 1. Flowchart diagram for the synthesis of $CaAl_2Si_2O_8$:Eu,Mn phosphors.

luminescence, energy transfer, and color chromaticity properties of $CaAl_2Si_2O_8$:Eu,Mn phosphor in the present work. We have also calculated the average separation between Eu^{2+} and Mn^{2+} ions (R_{Eu-Mn}) in the host lattice as well as the critical distance (R_c) between Eu^{2+} and Mn^{2+} ions for the occurrence of energy transfer based on the model proposed by Blasse.[9] Our investigation has demonstrated that $CaAl_2Si_2O_8$:Eu,Mn can emit white-light under ultraviolet excitation by systematically tuning the relative doping content of Eu^{2+} relative to that of Mn^{2+}.

2. Experimental Section

2.1 Materials and Synthesis. A series of polycrystalline $(Ca_{1-m-n}Eu_mMn_n)Al_2Si_2O_8$ (abbreviated as $CaAl_2Si_2O_8$:Eu,Mn) samples investigated in this work were prepared by solid-state reactions and the synthetic procedure is summarized in Figure 1. Briefly, the constituent oxides or carbonates $CaCO_3$ (99.99%), Eu_2O_3 (99.99%), $MnCO_3$ (99.99%), Al_2O_3 (99.99%), and SiO_2 (99.99%) (all from Aldrich Chemicals, Milwaukee, WI) were intimately mixed in the requisite proportions. The mixtures were first calcined and then sintered at 1400 °C for 5 h to avoid the inclusion of carbonate impurities. The obtained product was then reduced at 900 °C for 3 h under 5:95 H_2/Ar atmosphere. The $Y_3Al_5O_{12}$:Ce (Catalog NP-204) sample used as a blue-LED convertible phosphor to generate white light in the Commission International de I'Eclairage (CIE) chromaticity investigations was obtained from Nichia Corporation, Japan.

2.2 Characterizations. The phase purity of the as-prepared phosphor samples was checked by powder X-ray diffraction (XRD) analysis with a Bruker AXS D8 advanced automatic diffractometer with Cu Kα radiation operating at 40 kV and 20 mA. The XRD profiles were collected in the range of $10° < 2\theta < 80°$. The measurements of photoluminescence (PL) and photoluminescence excitation (PLE) spectra were performed by using a Spex Fluorolog-3 spectrofluorometer (Instruments S.A., NJ) equipped with a 450-W Xe light source and double excitation monochromators. The powder samples were compacted and excited under 45° incidence and emitted fluorescence was detected by a Hamamatsu Photonics R928 type photomultiplier perpendicular to the excitation beam. The spectral response of the measurement system is calibrated automatically on start up. To eliminate the second-order emission of the source radiation, a cutoff filter was used in the measurements.

The emission lifetime was measured by using a third harmonic (355 nm, pulse width ~10 ns) of Nd:YAG laser (Continuum NY60). The emission signal passing through a monochromator (ARC spectraPro 300i) was detected by a photomultiplier tube (Hamamatsu 1P28) and was averaged by a digital oscilloscope (LeCroy LT372).

The reflectance spectra of the samples were measured with a Hitachi 3010 double-beam UV−vis spectrometer (Hitachi Co., Tokyo, Japan) equipped with a ø60-mm integrating sphere whose inner face was coated with $BaSO_4$ or Spectralon and α-Al_2O_3 was used as a standard in the measurements. The Commission International de I'Eclairage (CIE) chromaticity coordinates for all samples were determined by a Laiko DT-100 color analyzer equipped with a CCD detector (Laiko Co., Tokyo, Japan).

3. Results and Discussion

Polycrystalline $CaAl_2Si_2O_8$:Eu,Mn phosphor samples used in this work have been synthesized at 1400 °C and then annealed under a reduced atmosphere of 5:95 H_2/Ar. Samples not annealed under reduced atmosphere were found to exhibit much weaker luminescence intensity, which may be attributed to the absence of Eu^{2+} and/or Mn^{2+}. The XRD patterns of $CaAl_2Si_2O_8$:Eu, Mn phases with different doping contents are shown in Figure 2 and all of the profiles were found to be in good agreement with that reported in JCPDS file 89-1462 regardless of the content of dopants and this observation indicates that no impurity phase is present.

Refinements of the XRD patterns for $(Ca_{1-m-n}Eu_mMn_n)Al_2Si_2O_8$ samples with different doping contents of Mn^{2+} indicated that the refined lattice parameters do not show significant change considering the standard deviations. Therefore, based on the effective ionic radii (r) of cations with different coordination number (CN) reported by Shannon,[11] we have proposed that Eu^{2+} and Mn^{2+} ions are expected to and, in fact, occupy the Ca^{2+} sites preferably, because the ionic radii of Eu^{2+} ($r = 1.17$ Å when $CN = 6$ and $r = 1.20$ Å when $CN = 7$) and Mn^{2+} ($r = 0.83$ Å when $CN = 6$ and $r = 0.90$ Å when $CN = 7$) are close to that of Ca^{2+} ($r = 1.00$ Å when $CN = 6$, $r = 1.06$ Å when $CN = 7$).[11] Since both four-coordinated Al^{3+} ($r = 0.39$ Å) and Si^{4+} ($r = 0.26$ Å) sites are too small for Mn^{2+} to occupy, we thereby conclude that Mn^{2+} ($r = 0.66$ Å when $CN = 4$) tends to prefer the Ca^{2+} sites due to size consideration.

The PL and PLE spectra for the purely Eu^{2+}-activated $CaAl_2Si_2O_8$ are shown in Figure 3a. An intense broad band centered at 425 nm and attributed to the typical $4f^65d^1(t_{2g}) \rightarrow 4f^7(^8S_{7/2})$ transition of Eu^{2+} was observed at ambient temperature. Furthermore, the PL and PLE for purely Mn^{2+}-activated $CaAl_2Si_2O_8$ are represented in Figure 3b. The d−d transitions of Mn^{2+} are forbidden in spin and parity, so their excitation transitions are difficult to pump and emission intensity is very weak. The broad emission band centered at 568 nm is attributed to the spin-forbidden $^4T_1(^4G) \rightarrow {}^6A_1(^6S)$ transition of Mn^{2+}. The excitation spectrum consists of several bands centering at 340, 355, 403, 418, and 469 nm,

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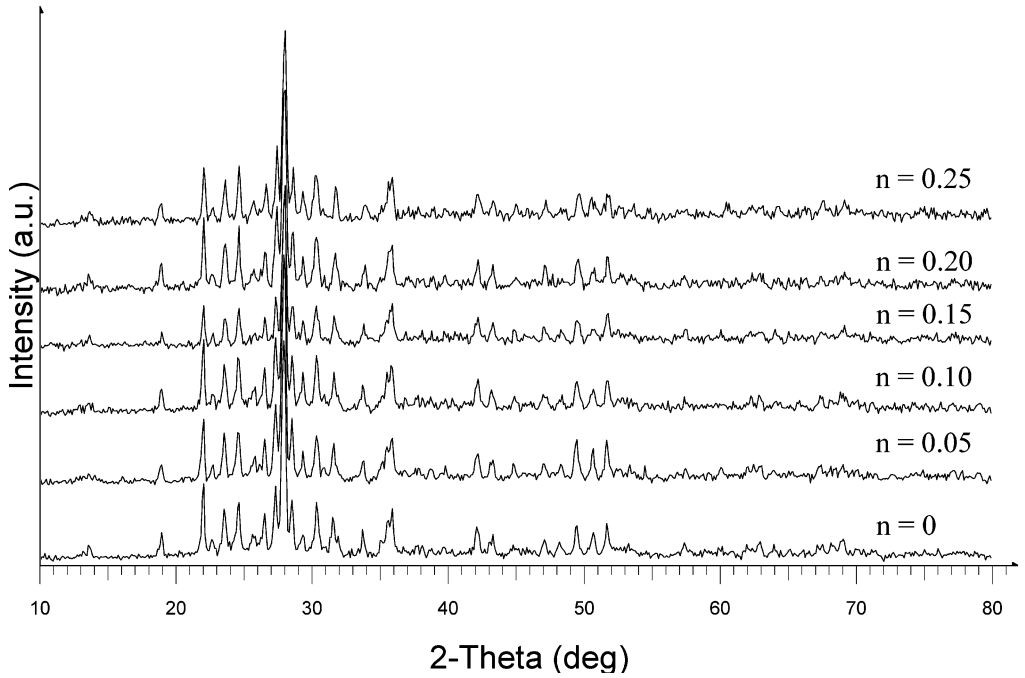

Figure 2. Dependence of XRD profiles for $(Ca_{0.99-n}Eu_{0.01}Mn_n)Al_2Si_2O_8$ phosphors on Mn^{2+} doping content (n).

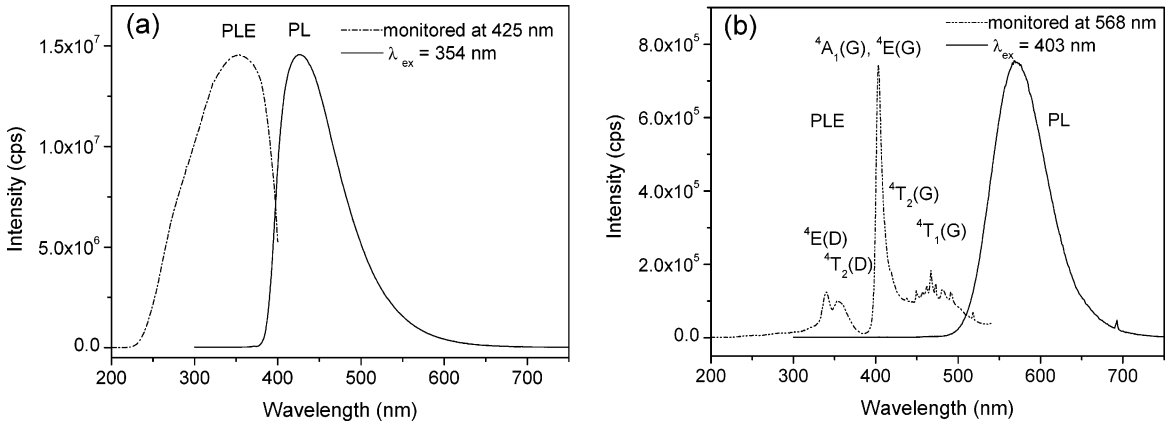

Figure 3. PLE and PL spectra for phosphors with compositions of $CaAl_2Si_2O_8$:$0.01Eu^{2+}$ (a) and $CaAl_2Si_2O_8$:$0.25Mn^{2+}$ (b).

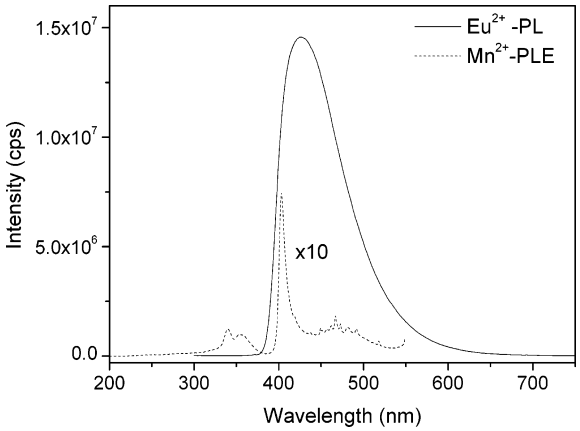

Figure 4. Spectral overlap between the PL spectrum of $(Ca_{0.99}Eu_{0.01})Al_2Si_2O_8$ (solid line) and PLE spectrum of $(Ca_{0.75}Mn_{0.25})Al_2Si_2O_8$ (dashed line).

corresponding to the transitions from $^6A_1(^6S)$ to $^4E(^4D)$, $^4T_2(^4D)$, $[^4A_1(^4G)$, $^4E(^4G)]$, $^4T_2(^4G)$, and $^4T_1(^4G)$ levels, respectively.

As shown in Figure 3a and b and Figure 4, the comparison of the PL and PLE spectra for $CaAl_2Si_2O_8$:Eu and $CaAl_2Si_2O_8$:Mn phosphors reveals a significant spectral overlap between the emission band of Eu^{2+} centered at 425 nm and the Mn^{2+} excitation transitions of $^6A_1(^6S)\rightarrow{}^4T_1(^4G)$, $^4T_2(^4G)$, $[^4A_1(^4G)$, $^4E(^4G)]$. Therefore, the effective resonance-type energy transfer from Eu^{2+} to Mn^{2+} is expected. This type of energy transfer is quite common and has been observed in several Eu^{2+}- and Mn^{2+}-coactivated phosphors such as $CaCl_2$:Eu,Mn,[2] KBr:Eu,Mn,[6] $BaMg_2Si_2O_7$:Eu,Mn,[4] and $Ba_3MgSi_2O_8$:Eu,Mn,[7] respectively.

Figure 5 shows the PLE and PL spectra for six Eu^{2+} and Mn^{2+}-coactivated $(Ca_{0.99-n}Eu_{0.01}Mn_n)Al_2Si_2O_8$ phosphors with different dopant contents n of 0, 0.05, 0.10, 0.15, 0.20, and 0.25, respectively. The PLE spectra monitored at 425 nm (Eu^{2+} emission) show an optimal excitation band centered at 354 nm, which consists of unresolved bands due to the 4f5d multiplets of the Eu^{2+} excited state. Interestingly and reasonably, the PL intensity of Mn^{2+} activator (or energy acceptor) was observed to increase, whereas that of Eu^{2+} sensitizer (or energy donor) is simultaneously found to decrease monotonically with increasing Mn^{2+} dopant content. The dependence of the relative emission intensity of Eu^{2+} on different Mn^{2+} dopant content (n) is represented in Figure

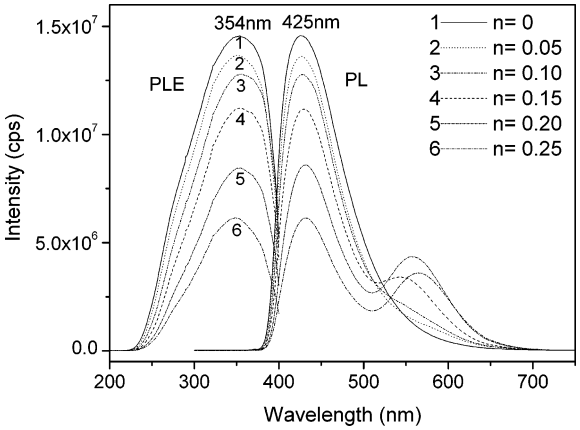

Figure 5. PLE and PL spectra for $(Ca_{0.99-n}Eu_{0.01}Mn_n)Al_2Si_2O_8$ phosphors (PLE monitored at 425 nm and PL excited at 354 nm).

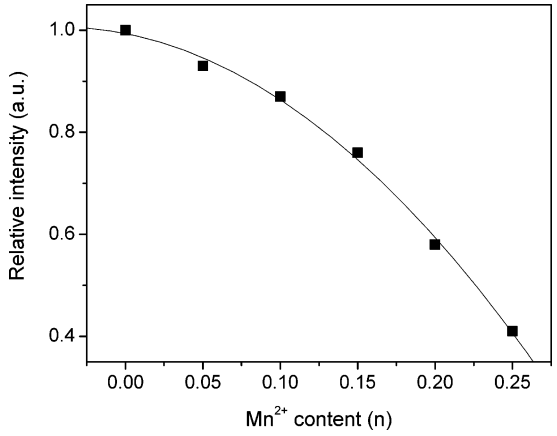

Figure 6. Dependence of the relative emission intensity of Eu^{2+} in $(Ca_{0.99-n}Eu^{2+}_{0.01}Mn^{2+}_n)$ $Al_2Si_2O_8$ on Mn^{2+} content *n*.

6. The PL intensity of Eu^{2+} emission band was found to decrease monotonically with increasing doped Mn^{2+} concentration. Similar observations reported by Yamashita et al.[12] and Ruelle et al.[13] is attributed to the formation of paired Mn^{2+} centers with faster decay than single Mn^{2+} centers.

The PL decay curves of Eu^{2+} in $(Ca_{0.99-n}Eu^{2+}_{0.01}Mn^{2+}_n)$-$Al_2Si_2O_8$ were measured and are represented in Figure 7. As described by Blasse and Grabmaier,[14] it is well established that the decay behavior of Eu^{2+} can be expressed by

$$I = I_0 \exp(-t/\tau) \tag{1}$$

, where I and I_0 are the luminescence intensities at time t and 0, and τ is the luminescence lifetime. On the basis of eq 1 and decay curves, the lifetime values were determined to be 0.73, 0.66, 0.57, 0.43, and 0.34 μs for $(Ca_{0.99-n}Eu_{0.01}Mn_n)$-$Al_2Si_2O_8$ with $n = 0$, 0.10, 0.15, 0.20, and 0.25, respectively. The decay lifetime for Eu^{2+} was found to decrease with increasing Mn^{2+} dopant content, which is strong evidence for the energy transfer from Eu^{2+} to Mn^{2+}, as reported by Ruelle et al.[13] and Jiao et al.,[15] respectively.

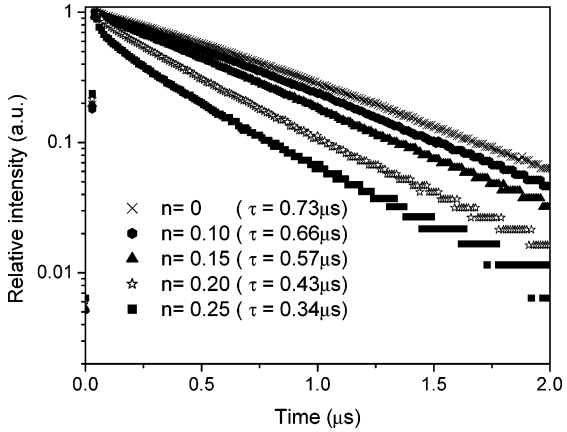

Figure 7. Photoluminescence decay curve of Eu^{2+} in $(Ca_{0.99-n}Eu^{2+}_{0.01}Mn^{2+}_n)$-$Al_2Si_2O_8$ (excited at 355 nm, monitored at 425 nm).

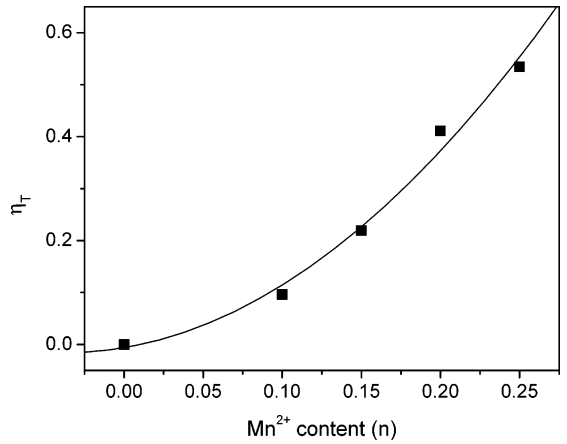

Figure 8. Dependence of the energy transfer efficiency η_T in $(Ca_{0.99-n}Eu^{2+}_{0.01}Mn^{2+}_n)Al_2$ Si_2O_8 on Mn^{2+} content *n*.

We are also interested in investigating the energy transfer efficiency (η_T) of $Eu^{2+} \rightarrow Mn^{2+}$ and a simple operational definition as suggested by Paulose et al.,[16] η_T can be expressed by

$$\eta_T = 1 - \frac{\tau_S}{\tau_{S0}} \tag{2}$$

where τ_{S0} is the intrinsic decay lifetime of the sensitizer (Eu^{2+}) and τ_S is the decay lifetime of the sensitizer (Eu^{2+}) in the presence of the activator (Mn^{2+}). The energy transfer efficiency for $Eu^{2+} \rightarrow Mn^{2+}$ in $(Ca_{0.99-n}Eu^{2+}_{0.01}Mn^{2+}_n)Al_2Si_2O_8$ was calculated and is illustrated in Figure 8. With increasing Mn^{2+} dopant content, the energy transfer efficiency η_T was found to increase gradually.

According to Dexter and Schulman, concentration quenching is in many cases due to energy transfer from one activator to another until an energy sink in the lattice is reached.[17] As suggested by Blasse,[9] the average separation R_{Eu-Mn} can be expressed by

$$R_{Eu-Mn} = 2\left[\frac{3V}{4\pi xN}\right]^{1/3} \tag{3}$$

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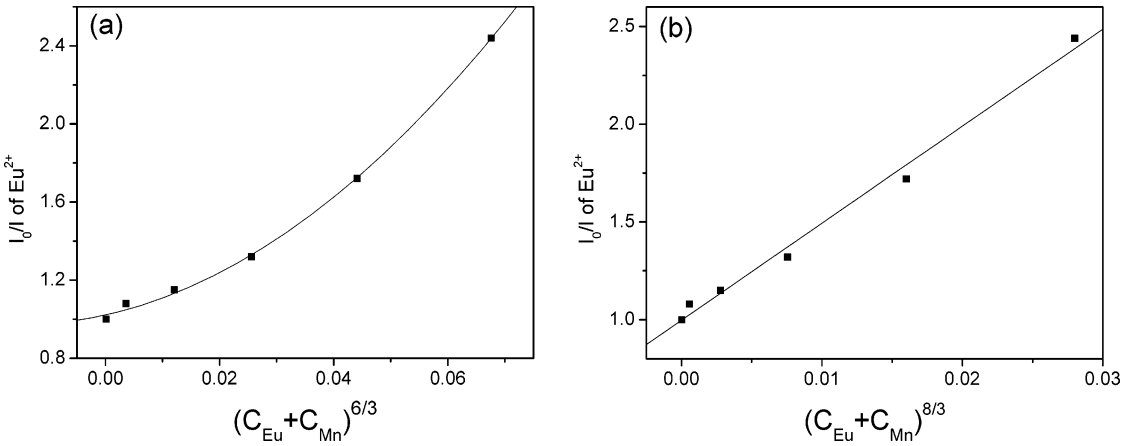

Figure 9. Dependence of I_{S0}/I_S of Eu^{2+} on (a) $C^{6/3}$ and (b) $C^{8/3}$.

where N is the number of Z ions in the unit cell, and V is the volume of the unit cell. For $CaAl_2Si_2O_8$ host, $N = 8$ and $V = 1337.8$ Å^3 .[8] x is the total concentration of Eu^{2+} and Mn^{2+}. Thus, R_{Eu-Mn} (in Å) is determined to be 17.5, 14.3, 12.6, 11.5, and 10.7 for $n = 0.05$, 0.10, 0.15, 0.20, and 0.25, respectively, in $(Ca_{0.99-n}Eu_{0.01}Mn_n)Al_2Si_2O_8$. The critical concentration x_c, at which the luminescence intensity of Eu^{2+} is half that in the sample in the absence of Mn^{2+}, is 0.24. Therefore, the critical distance (R_c) of energy transfer was calculated to be about 11.0 Å. We have also observed that the radiative emission from Eu^{2+} prevails when $R_{Eu-Mn} > R_c$ and energy transfer from Eu^{2+} to Mn^{2+} dominates when $R_{Eu-Mn} < R_c$.

On the basis of Dexter's energy transfer formula of multipolar interaction and Reisfeld's approximation the following relation can be obtained[15,18,19]

$$\frac{\eta_0}{\eta} \propto C^{n/3} \tag{4}$$

where η_0 and η are, respectively, the luminescence quantum efficiency of Eu^{2+} in the absence and presence of Mn^{2+}; C is the sum of the content of Eu^{2+} and Mn^{2+}; $n = 6$, 8, and 10, corresponding to dipole−dipole, dipole−quadrupole, and quadrupole−quadrupole interactions, respectively. The value η_0/η is approximately calculated by the ratio of related luminescence intensities as[15,17]

$$\frac{I_{S0}}{I_S} \propto C^{n/3} \tag{5}$$

, where I_{S0} is the intrinsic luminescence intensity of Eu^{2+} and I_S is the luminescence intensity of Eu^{2+} in the presence of the Mn^{2+}. The $I_{S0}/I_S - C^{n/3}$ plot is represented in Figure 9a and b, and only when $n = 8$ does it show linear relation. This clearly indicates that the energy transfer from Eu^{2+} to Mn^{2+} is the dipole−quadrupole mechanism.

For dipole−quadrupole mechanism, the transfer probability is given by Dexter[9,20] as

$$P^{DQ}_{Eu-Mn} = 0.63 \times 10^{28} \frac{f_q \lambda_S{}^2 Q_A}{\tau_{S0} f_d R_{Eu-Mn}{}^8 E_S{}^4} \int F_S(E) F_A(E) dE \tag{6}$$

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 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 the Eu^{2+} emission $F_S(E)$ and Mn^{2+} excitation $F_A(E)$, and it is estimated at about 2.39 eV^{-1}.

The critical distance (R_c) of energy transfer from Eu^{2+} to Mn^{2+} is defined as the distance for which the probability of transfer equals the probability of radiative emission of Eu^{2+}, i.e., the distance for which $P_{Eu-Mn}\tau_{S0} = 1$. Therefore, R_c can be found from eq 6

$$R_c{}^8 = 0.63 \times 10^{28} \frac{f_q \lambda_S{}^2 Q_A}{f_d E_S{}^4} \int F_S(E) F_A(E) dE \tag{7}$$

In this system, the critical distance of energy transfer was calculated to be about 10.8 Å. This result is in good agreement with that obtained using the concentration quenching method.

As we know, the PLE spectrum is comparable to an absorption spectrum, the single excitation band centered at ca. 354 nm in the PLE spectra can be reasonable referred to one absorption process. To investigate the energy absorption of the aluminosilicate phosphors, diffuse reflectance spectra for parent and doped $CaAl_2Si_2O_8$ phosphors were measured and are shown in Figure 10. As indicated in Figure 10, for parent $CaAl_2Si_2O_8$ an increase of reflectance from 275 to 345 nm was noted. The middle points at ca. 311 nm may be used to estimate the approximate band gap of host material $CaAl_2Si_2O_8$. Furthermore, the reflectance spectra for $(Ca_{0.99-n}Eu_{0.01}Mn_n)Al_2Si_2O_8$ phases with $n = 0$, 0.10, 0.15, 0.20, and 0.25 show extreme resemblance with a decrease of reflectance at 375 nm. On the other hand, reflectance spectra for $(Ca_{0.75}Mn_{0.25})Al_2Si_2O_8$ phase exhibit two slight changes at 275 and 380 nm, respectively, which may be attributed to the energy absorption feature of the host material.

In an attempt to investigate the chromaticity of the phosphors as a function of dopant contents, we have prepared

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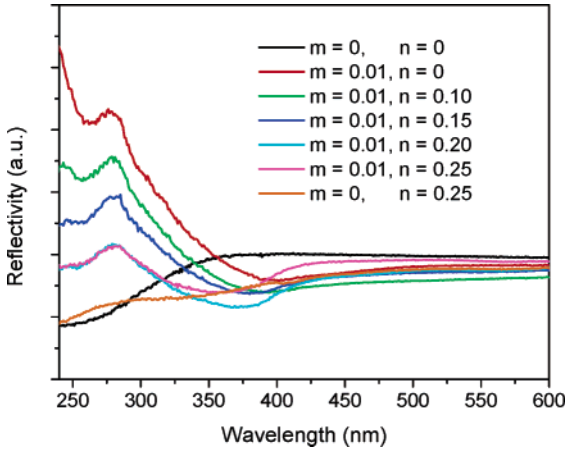

Figure 10. Reflectance spectra for Eu^{2+}- and Mn^{2+}-activated and Eu^{2+}/Mn^{2+}-coactivated $CaAl_2Si_2O_8$ phosphors.

Table 1. Comparison of CIE Chromaticity Coordinates for $(Ca_{0.99-n}Eu_{0.01}Mn_n)Al_2Si_2O_8$ (λ_{ex}= 354 nm) and Simulated White Light Using Commercial $Y_3Al_5O_{12}$:Ce Phosphors (λ_{ex}= 467 nm)

sample	(*x*, *y*)
$n = 0$	(0.17, 0.11)
$n = 0.05$	(0.18, 0.12)
$n = 0.10$	(0.20, 0.14)
$n = 0.15$	(0.24, 0.21)
$n = 0.20$	(0.30, 0.29)
$n = 0.25$	(0.33, 0.31)
simulated white light with $Y_3Al_5O_{12}$:Ce	(0.31, 0.27)

a series of $(Ca_{0.99-n}Eu_{0.01}Mn_n)Al_2Si_2O_8$ phosphors with n = 0, 0.05, 0.10, 0.15, 0.20, and 0.25, respectively. Table 1 summarizes the comparison of CIE chromaticity coordinates for $(Ca_{0.99-n}Eu_{0.01}Mn_n)Al_2Si_2O_8$ as a function of Mn^{2+} content (λ_{ex}= 354 nm), simulated white-light using commercial $Y_3Al_5O_{12}$:Ce phosphors (λ_{ex}= 467 nm), and $Y_3Al_5O_{12}$:Ce itself. The chromaticity coordinates for $(Ca_{0.99-n}Eu_{0.01}Mn_n)$-$Al_2Si_2O_8$ are represented as series A in Figure 11. We have observed that the (*x*,*y*) coordinates vary systematically from (0.17, 0.11) to (0.33, 0.31), and corresponding hue of the samples varied gradually from blue, aqua, and eventually to white, as we vary the dopant contents of Mn^{2+} from n = 0 to 0.25, as indicated in the chromaticity diagram. Furthermore, to evaluate the potential of our tunable aluminosilicates as white-emitting phosphors, we have investigated and compared the chromaticity characteristics of the simulated white light generated from commercial YAG:Ce (Nichia Co., Japan) that was excited with monochromatic blue light of 467 nm with coordinates of (0.15, 0.04). As represented as series B in Figure 11, the experimentally determined chromaticity coordinates were found to be (0.48, 0.50) for YAG:Ce and (0.31, 0.27) for the simulated white light, the color saturation of which was found to be inferior to that generated from our phosphor. In practice, with increasing the amount of electrical current, the hue of a white-light LED changes from yellow to white and to blue. Therefore, the white-light LED of YAG:Ce excited by blue-light chip tends

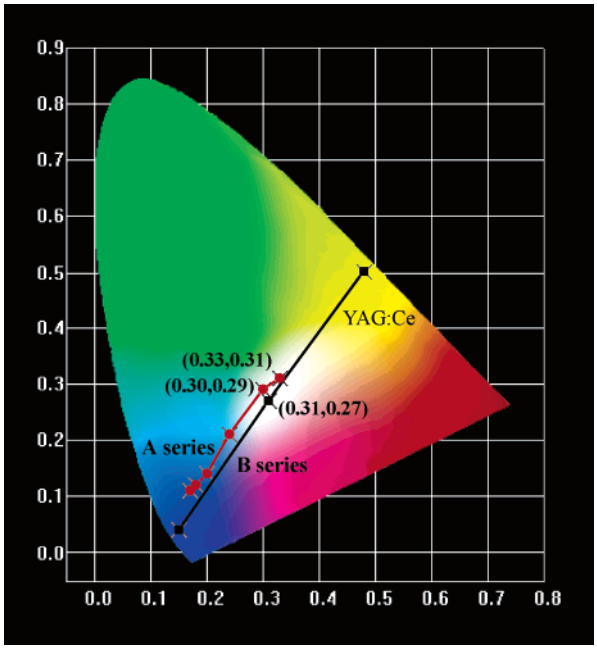

Figure 11. CIE chromaticity diagram for $(Ca_{0.99-n}Eu_{0.01}Mn_n)Al_2Si_2O_8$ phosphors with different Mn^{2+} dopant contents (λ_{ex} = 354 nm) (series A) and simulated white light generated with YAG:Ce (Nichia Co.) (λ_{ex} = 467 nm) (series B).

to produce color aberration when the LED chip is degrading. In contrast, our $CaAl_2Si_2O_8$:Eu^{2+},Mn^{2+} phosphors excited with ultraviolet light will not have that problem because the excited light is invisible. The above observations hint the promising application of $(Ca_{0.99-n}Eu_{0.01}Mn_n)Al_2Si_2O_8$ phases as a white-emitting phosphor for ultraviolet LEDs.

4. Conclusions

In summary, we have synthesized and investigated the luminescent properties of $CaAl_2Si_2O_8$ phosphors coactivated with Eu^{2+} and Mn^{2+} under photoexcitation. The spectroscopic data indicate that the $Eu^{2+}\rightarrow Mn^{2+}$ energy transfer process takes place in the host matrix of $CaAl_2Si_2O_8$. The energy transfer from Eu^{2+} to Mn^{2+} has found to occur via a dipole−quadrupole mechanism. The critical energy transfer distance has also been calculated by the concentration quenching and spectral overlap methods. The results obtained from the two approaches are in good agreement. Furthermore, we have also demonstrated that the $(Ca_{0.99-n}Eu_{0.01}Mn_n)Al_2Si_2O_8$ can be systematically tuned to generate white light under ultraviolet radiation and it has been shown to exhibit the potential to act as a white-emitting phosphor for ultraviolet LEDs.

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