Tunable emission from blue to white light in single-phase Na$_{0.34}$Ca$_{(0.66-x-y)}$Al$_{1.66}$Si$_{2.34}$O$_8$: $x$Eu$^{2+}$,$y$Mn$^{2+}$ ($x = 0.07$) phosphor for white-light UV LEDs

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Abstract: A series of single-phased emission-tunable Na$_{0.34}$Ca$_{0.66}$Al$_{1.66}$Si$_{2.34}$O$_8$:Eu$^{2+}$,Mn$^{2+}$ phosphors were successfully synthesized by a wet-chemical synthesis method. Photoluminescence excitation (PLE) spectra indicate that the phosphor can be efficiently excited by UV radiation from 250 to 420 nm. Also, NCASO:Eu$^{2+}$,Mn$^{2+}$ phosphor exhibit a broad blue emission band at 440 nm and an orange emission band at 570 nm, which originate from Eu$^{2+}$ and Mn$^{2+}$ ions, respectively. Therefore, overall emission color can be tuned from blue to white by increasing the concentration of Mn$^{2+}$ ions in the host lattice utilizing energy transfer from Eu$^{2+}$ to Mn$^{2+}$ ions. This energy transfer phenomenon was demonstrated to be a resonant type through dipole-dipole interaction determined with the help of PL spectra, decay time measurement, and energy transfer efficiency of the phosphor. These results indicate that NCASO:Eu$^{2+}$,Mn$^{2+}$ can be a promising single-phased white-emitting phosphor for white-light UV LEDs.

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References and links

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1. Introduction
In recent years, white light-emitting-diode (LED) technology has attracted much attention in lighting industry due to the advantages of white-LEDs including low power consumption,
reliability, long lifetime, safety, and environmentally friendly characteristics [1, 2]. The most dominant way to produce commercial white light-emitting diodes (WLEDs) is a combination of a blue emitting InGaN chip with a yellow emitting Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12}:Ce\textsuperscript{3+} (YAG:Ce\textsuperscript{3+}) phosphor. However, that combination shows several disadvantages including high correlated color temperature (CCT~7750 K) and low color-rendering index (CRI~70-80) because of a lack of sufficient red emission [3–5]. Therefore, as an alternative, a combination of UV LED with red, green and blue emitting phosphors has been developed to improve the CRI, color stability and to tune CCT value [6, 7]. However, the luminescence efficiency is low in this system because the blue emission is reabsorbed by green and red phosphors [8]. Therefore, a single composition white-emitting phosphor which can be effectively excited by UV light ought to receive much attention to enhance the luminous efficiency. More importantly, a single-phase white light emitting phosphor with UV-LED chip system show better performances in stability, color reproducibility, and fabrication process than those of white LEDs with multiple emitting components phosphor system [9, 10]. The method of co-doping sensitizer and activator into one host lattice is one way to create a single-phase white-light-emitting phosphor using the principle of energy transfer from sensitizer to activator, such as Eu\textsuperscript{2+} and Mn\textsuperscript{2+} co-doping system, which has been introduced and demonstrated in several previous works. The examples are follows, Ca\textsubscript{6-x-y}Mg\textsubscript{x}Si\textsubscript{2}O\textsubscript{8}:Eu\textsuperscript{2+},Mn\textsuperscript{2+}, Ca\textsubscript{1}Al\textsubscript{1}Si\textsubscript{2}O\textsubscript{8}:Eu\textsuperscript{2+},Mn\textsuperscript{2+}, Ca\textsubscript{4}Gd\textsubscript{2}(PO\textsubscript{4})\textsubscript{3}: Eu\textsuperscript{2+},Mn\textsuperscript{2+}, BaMg\textsubscript{2}Si\textsubscript{2}O\textsubscript{8}:Eu\textsuperscript{2+},Mn\textsuperscript{2+}, SrMg\textsubscript{3}O\textsubscript{3}:Eu\textsuperscript{2+},Mn\textsuperscript{2+}, Ca\textsubscript{2}Gd\textsubscript{2}(SiO\textsubscript{4})\textsubscript{3}O\textsubscript{7}:Ce\textsuperscript{3+},Mn\textsuperscript{2+}, Ba\textsubscript{2}Ca(BO\textsubscript{3})\textsubscript{2}:Ce\textsuperscript{3+},Mn\textsuperscript{2+}, Sr\textsubscript{3}B\textsubscript{2}O\textsubscript{6}:Ce\textsuperscript{3+},Eu\textsuperscript{2+} phosphors [11–18].

In this work, we prepared a novel single-phased emission-tunable Na\textsubscript{0.34}Ca\textsubscript{0.66}Al\textsubscript{1.66}Si\textsubscript{2.34}O\textsubscript{8}:Eu\textsuperscript{2+},Mn\textsuperscript{2+} (NCASO:Eu\textsuperscript{2+},Mn\textsuperscript{2+}) phosphor suitable for UV-pumped white-emitting LED applications. Photoluminescence excitation (PLE) of NCASO:Eu\textsuperscript{2+},Mn\textsuperscript{2+} phosphor ranging from 250 to 420 nm fits well for the UV-LED application. Photoluminescence (PL) spectrum shows that the phosphor covers the full range of visible region which can create warm white emission resulted from the energy transfer from Eu\textsuperscript{2+} to Mn\textsuperscript{2+} ions. Furthermore, we have also investigated its luminescence properties as well as the energy transfer mechanism which was confirmed by observing the change in the luminescence spectra, energy transfer efficiency, and by decay profile analysis.

2. Experimental

2.1. Synthesis

Powder samples Na\textsubscript{0.34}Ca\textsubscript{0.66-x-y}Al\textsubscript{1.66}Si\textsubscript{2.34}O\textsubscript{8}:xEu\textsuperscript{2+},yMn\textsuperscript{2+} (x = 0.07, y = Mn dopant concentration) were synthesized by a wet chemical synthesis method based on hydrolysis of tetraethylorthosilicate (TEOS) [19]. As raw materials, sodium nitrate (NaNO\textsubscript{3} ≥ 99.99%, Aldrich), europium (III) chloride hexahydrate (EuCl\textsubscript{3}·6H\textsubscript{2}O ≥ 99.99%, Aldrich), calcium nitrate nonahydrate (Ca(NO\textsubscript{3})\textsubscript{2}·9H\textsubscript{2}O ≥ 99.99%, Aldrich), aluminum nitrate nonahydrate (Al(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O ≥ 98%, Aldrich), Manganese (II) chloride tetrahydrate (MnCl\textsubscript{2}·4H\textsubscript{2}O ≥ 98%, Aldrich), tetraethyl orthosilicate (TEOS, 99.999%, Aldrich) were used. All materials except for TEOS were dissolved in deionized water, and then the TEOS was dissolved in ethanol. These two solutions were thoroughly mixed together. The mixture was dehydrated in an oven at 120°C for about 24 h until the solvent was completely dried. The dried powders were fired at 1400°C in a reducing atmosphere of a mixture of H\textsubscript{2} (5%) and N\textsubscript{2} (95%) for 3 h.

2.2. Characterizations

The luminescent properties and quantum efficiency of NCASO:Eu\textsuperscript{2+},Mn\textsuperscript{2+} phosphors were analyzed by using a F-7000 Hitachi fluorescence spectrophotometer PL system equipped with a xenon lamp (500 W) as an excitation source. X-ray diffraction (XRD) data was obtained over a range of 15° ≤ 2θ ≤ 60° at step of 3°/min with Cu-K\textalpha radiation using a diffractometer (D/MAX-RB(12KW), RIGAKU, Japan). Decay characteristics are probed by a Fluorescence...
Lifetime Spectrometer (FL920, Edinburgh Instruments, Wales) which is operated based upon time correlated single photon counting scheme.

3. Result and discussion

3.1 Phase identification of NCASO:0.07Eu\textsuperscript{2+},yMn\textsuperscript{2+} phosphor

![XRD patterns of NCASO:0.07Eu\textsuperscript{2+},yMn\textsuperscript{2+} phosphors.]

Phase purity of all samples was analyzed by XRD analysis. Figure 1 illustrates the X-ray diffraction (XRD) patterns of NCASO:0.07Eu\textsuperscript{2+},yMn\textsuperscript{2+} phosphors with various Mn\textsuperscript{2+} doping concentration (y = 0, 0.05, 0.1, 0.2, 0.3). All of the profiles were found to match well with that reported in JCPDS file 86-1650 regardless of the content of dopants and this observation indicates that no impurity phase is present in the prepared samples. It clearly suggests that the activator and sensitizer have been incorporated in the lattice. The crystal structure of NCASO host, which is included in the plagioclase feldspars group, was reported in our previous report [20]. In the crystal structure of NCASO phosphor, Na\textsuperscript{+} and Ca\textsuperscript{2+} ions share the same sites. The Na\textsuperscript{+}/Ca\textsuperscript{2+} ions have four different coordination numbers (Na\textsuperscript{+}/Ca\textsuperscript{2+}-1, Na\textsuperscript{+}/Ca\textsuperscript{2+}-2, and Na\textsuperscript{+}/Ca\textsuperscript{2+}-4 are 8-coordinated; Na\textsuperscript{+}/Ca\textsuperscript{2+}-3 is 10-coordinated). Typically, effective radii (r) of cations change depending on the coordination number (CN) [21]. The ionic radii of Eu\textsuperscript{2+} ions (r = 1.25 Å when CN = 8, r = 1.35 Å when CN = 10) and those of Mn\textsuperscript{2+} ions (r = 0.96 Å when CN = 8) are similar to those of Na\textsuperscript{+} ions (r = 1.18 Å when CN = 8, 1.24 Å when CN = 9, 1.39 Å when CN = 12) and Ca\textsuperscript{2+} ions (r = 1.12 Å when CN = 8, 1.23 Å when CN = 10). Since both 4-coordinated Al\textsuperscript{3+} (r = 0.39 Å) and Si\textsuperscript{4+} (r = 0.26 Å) sites are too small for Eu\textsuperscript{2+} and Mn\textsuperscript{2+} ions to occupy, we have suggested that Eu\textsuperscript{2+} and Mn\textsuperscript{2+} ions are expected to occupy the Na\textsuperscript{+}/Ca\textsuperscript{2+} shared sites in the host lattice.

3.2 Photoluminescence properties

![PLE and PL spectra of NCASO:0.07Eu\textsuperscript{2+} phosphor.]

Fig. 1. XRD patterns of NCASO:0.07Eu\textsuperscript{2+},yMn\textsuperscript{2+} phosphors.

Fig. 2. PLE and PL spectra of NCASO:0.07Eu\textsuperscript{2+} phosphor.
PLE and PL spectra of NCASO:0.07Eu$^{2+}$ phosphor are presented in Fig. 2. PLE spectrum shows a broad band from 250 to 420 nm which corresponds to the $4f^7 \rightarrow 4f^65d^1$ transition of Eu$^{2+}$ ions. Under excitation at 365 nm, the NCASO:Eu$^{2+}$ phosphor produces broad band blue emission centered at around 440 nm which is attributed to the $4f^65d^1 \rightarrow 4f^7$ of the Eu$^{2+}$ ion. As represented in Fig. 3, PL spectrum of NCASO:Eu$^{2+}$ shows a very broad blue emission band peaking at around 440 nm, which is assigned to the typical $4f^65d^1 \rightarrow 4f^7$ transition of Eu$^{2+}$ ion and the PLE spectrum of NCASO:Mn$^{2+}$ consist of several bands centered at around 342, 405, 420, and 460 nm, corresponding to the transition of the Mn$^{2+}$ ion from the ground level $^6A_1(S)$ to $^4T_2(D)$, $^4A_1(G)$, $^4E(G)$, $^4T_1(G)$, and $^4T_1(G)$ levels, respectively [13]. We have observed a spectral overlap between the emission band of the Eu$^{2+}$ ions and the excitation band of the Mn$^{2+}$ ions at around 410 nm which implies that a part of energy transfers between Eu$^{2+}$ and Mn$^{2+}$ ions. Therefore, effective energy transfer from Eu to Mn ($E_{Eu\rightarrow Mn}$) was expected.

In addition, another evidence for the energy transfer in NCASO:Eu$^{2+},y$Mn$^{2+}$ is shown in Fig. 4. PLE spectra monitored at 440 nm and 570 nm of Eu$^{2+}$ and Mn$^{2+}$, respectively, appears very similar to each other. Moreover, the absence of characteristic Mn$^{2+}$ excitation band rules out direct excitation of Mn$^{2+}$ ions which indicates efficient energy transfer form Eu$^{2+}$ ions to Mn$^{2+}$ ions. The PLE spectrum shows a broad band ranged at 250-420 nm which means that the NCASO:Eu$^{2+},y$Mn$^{2+}$ phosphor has a potential for UV LED application. After co-doping Eu$^{2+}$ and Mn$^{2+}$ ion in NCASO host lattice, the sample exhibits two broad emission bands centered at around 440 and 570 nm under the 365 nm excitation which consist of a blue band and orange one originating from the $f-d$ transition of the Eu$^{2+}$ ion and the $^4T_1,^6A_1$ transition of the Mn$^{2+}$ ion, respectively. The emission spectrum nearly covers the entire visible region.
Thus, white-light can be obtained by combining the emission of Eu$^{2+}$ and Mn$^{2+}$ ions present in a single host lattice by simply adjusting the relative ratio of Eu$^{2+}$ and Mn$^{2+}$ activators via the principle of energy transfer.

![Image](NCASO: 0.07Eu$^{2+}$, yMn$^{2+}$ phosphors on Mn$^{2+}$ doping content (y)

In order to further investigate the energy transfer mechanism between the Eu$^{2+}$ and Mn$^{2+}$ ions on NCASO phosphor, a series of samples were synthesized and their luminescent properties are demonstrated. Figure 5 shows that the PL spectra of NCASO:0.07Eu$^{2+}$,yMn$^{2+}$ phosphors with different Mn$^{2+}$ contents ($y = 0, 0.03, 0.07, 0.10, 0.15, 0.20, 0.30$) under 365 nm excitation. The PL emission intensity of Eu$^{2+}$ at around 440 nm was found to decrease with increasing of Mn$^{2+}$ content due to the enhancement of the energy transfer from Eu$^{2+}$ to Mn$^{2+}$ ions. On the other hand, the emission intensity of Mn$^{2+}$ at 570 nm reaches a maximum when $y = 0.20$ and decreases on account of the Mn$^{2+}$-Mn$^{2+}$ internal concentration quenching [22]. This result further supports the energy transfer process from Eu$^{2+}$ to Mn$^{2+}$ ions.

![Image](Fig. 5. PL spectra for NCASO:0.07Eu$^{2+}$, yMn$^{2+}$ phosphors on Mn$^{2+}$ doping content (y)

![Image](Fig. 6. Decay curves of Eu$^{2+}$ emission for NCASO:0.07Eu$^{2+}$, yMn$^{2+}$ monitored at 440nm.

Table 1. Decay times of NCASO: 0.07Eu$^{2+}$, yMn$^{2+}$ phosphors excited at 375 nm with emission monitored at 440nm.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$t_1$ (μs)</th>
<th>$A_1$</th>
<th>$t_2$ (μs)</th>
<th>$A_2$</th>
<th>$t$ (μs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$y = 0$</td>
<td>0.364</td>
<td>4048.1</td>
<td>0.734</td>
<td>3606.9</td>
<td>0.637</td>
</tr>
<tr>
<td>$y = 0.05$</td>
<td>0.295</td>
<td>4412.3</td>
<td>0.682</td>
<td>5168.4</td>
<td>0.578</td>
</tr>
<tr>
<td>$y = 0.10$</td>
<td>0.264</td>
<td>4933.1</td>
<td>0.662</td>
<td>4455.1</td>
<td>0.540</td>
</tr>
<tr>
<td>$y = 0.15$</td>
<td>0.223</td>
<td>5149.7</td>
<td>0.619</td>
<td>3963.9</td>
<td>0.492</td>
</tr>
<tr>
<td>$y = 0.20$</td>
<td>0.202</td>
<td>5287.3</td>
<td>0.594</td>
<td>3798.8</td>
<td>0.468</td>
</tr>
<tr>
<td>$y = 0.30$</td>
<td>0.173</td>
<td>5397.6</td>
<td>0.564</td>
<td>3369.1</td>
<td>0.435</td>
</tr>
</tbody>
</table>
The decay curves of NCASO:0.07Eu$^{2+}$,yMn$^{2+}$ phosphor samples excited at 375 nm and monitored at 440 nm are shown in Fig. 6. The corresponding luminescence decay curves can be fitted by a second-order exponential decay mode by following equation [23, 24]:

$$I = A_1 \exp(-t / \tau_1) + A_2 \exp(-t / \tau_2)$$

(1)

where $I$ is the luminescence intensity; $A_1$ and $A_2$ are constant; $t$ is the time, and $\tau_1$ and $\tau_2$ are decay time for exponential components. Using this parameters, the average decay time ($\tau$) can be obtained by the formula given in the following [25];

$$\tau = (A_1 \tau_1^2 + A_2 \tau_2^2) / (A_1 \tau_1 + A_2 \tau_2)$$

(2)

The value of $\tau_1$, $\tau_2$, $A_1$, and $A_2$ are analyzed and summarized in Table 1. The average decay times were determined to be 0.637, 0.578, 0.540, 0.492, 0.468, and 0.435 $\mu$s for NCASO:0.07Eu$^{2+}$,yMn$^{2+}$ with $y = 0$, 0.05, 0.10, 0.15, 0.20, and 0.30, respectively. The results show that the average decay time for the Eu$^{2+}$ ions decreases with increase in the Mn$^{2+}$ doping content $y$, which is a strong evidence for the energy transfer from Eu$^{2+}$ to Mn$^{2+}$ ions in the NCASO:0.07Eu$^{2+}$,yMn$^{2+}$ phosphor.

Fig. 7. Dependence of the energy transfer efficiency $\eta_T$ on the Mn$^{2+}$ content ($y$)

Generally, energy transfer efficiency ($\eta_T$) can be described by using the following formula [26];

$$\eta_T = 1 - \frac{I_S}{I_{SO}}$$

(3)

where $I_{SO}$ is the luminescence intensities of the Eu$^{2+}$ of the samples in the absence of the Mn$^{2+}$ ions and $I_S$ is the luminescence intensities of the Eu$^{2+}$ ions in the presence of the Mn$^{2+}$ ions. The dependance of the energy transfer efficiency ($\eta_T$) as a function of Mn$^{2+}$ content is displayed in Fig. 7. It is shown that the energy transfer efficiency ($\eta_T$) of NCASO:0.07Eu$^{2+}$,yMn$^{2+}$ phosphor increase gradually with increasing the Mn$^{2+}$ doping concentration. Thus, we confirm that the energy transfer process from Eu$^{2+}$ to Mn$^{2+}$ ions is efficient in NCASO host.

According to Dexter and Schulman, the concentration quenching of luminescence occurs due to the energy transfer from one activator to another until the energy is consumed in the lattice [27]. The critical distance $R_{Eu-Mn}$ for energy transfer from Eu$^{2+}$ to Mn$^{2+}$ ions was suggested by Blasse [28]. The critical distance can be expressed according to the following equation:

$$R_{Eu-Mn} = \frac{2(3V)}{4\pi x N}$$

(4)
where $V$ is the volume of the unit cell; $x$ is the critical concentration; and $N$ is the number of available cation site for dopant in the unit cell. For the NCASO host, $N = 8$ and $V = 1345.28$ Å$^3$ [20]. The critical concentration is 0.13 at which the luminescence intensity of Eu$^{2+}$ becomes only half of that of the sample with no Mn$^{2+}$ included (when the energy transfer efficiency is 0.5). From the above equation, the critical distance $R_{\text{Eu-Mn}}$ was calculated to be about 13.52 Å. There are two types of energy transfer: one is exchange interaction and the other is multi-polar interaction [29, 30]. In the case of the exchange interaction, the critical distance between the sensitizer and activator should be shorter than 3-4 Å [31]. However, the calculated critical distance for NCASO:Eu$^{2+}$,Mn$^{2+}$ phosphor is much longer than 3-4 Å so that the energy transfer between the Eu$^{2+}$ and Mn$^{2+}$ ion in NCASO phosphor is probably the electric multi-polar interaction type.

![Fig. 8. Dependence of $I_0/I$ of Eu$^{2+}$ on (a) $C_6^{\text{EuMn}}$, (b) $C_8^{\text{EuMn}}$, and (c) $C_{10}^{\text{EuMn}}$.](image)

On the basis of Dexter’s energy transfer formula for exchange interaction and the Reisfeld’s approximation, the following relation can be described [27, 32]:

$$\frac{\eta_0}{\eta} \propto C^n$$

(5)

where $\eta_0$ and $\eta$ are the luminescence quantum efficiency of Eu$^{2+}$ without and with Mn$^{2+}$; $C$ is the sum of the content of Eu$^{2+}$ and Mn$^{2+}$; $n = 6, 8, 10$ correspond to dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions, respectively. The value of $\eta_0/\eta$ can be approximately calculated by the ratio of relative luminescence intensities [27, 28, 32]:

$$\frac{I_0}{I} \propto C^n$$

(6)

where $I_0$ is intrinsic luminescence intensity of Eu$^{2+}$ and $I$ is the luminescence intensity of Eu$^{2+}$ with the presence of Mn$^{2+}$. The results of $I_0/I-C^n$ plots are illustrated in Fig. 8 and a linear relationship was found when $n = 6$. This clearly implies that the energy transfer mechanism from the Eu$^{2+}$ to Mn$^{2+}$ ions in NCASO:Eu$^{2+}$,Mn$^{2+}$ phosphor is an electric dipole-dipole interaction.
Fig. 9. PL spectra of NCASO:0.07Eu²⁺,0.20Mn²⁺ phosphor excited at 365 nm with different temperatures. The inset shows the normalized PL intensity as a function of temperatures.

For high power LED applications, thermal stability of phosphor is one of the important parameter. Temperature-dependent emission spectra of NCASO:0.07Eu²⁺,0.20Mn²⁺ phosphor under 365 nm excitation are indicated in Fig. 9. The inset displays the thermal quenching of Eu²⁺ and Mn²⁺ emission intensity in NCASO and that of commercial BaMgAl₁₀O₁₇:Eu²⁺ phosphor (KEMK63/F-P1, Phosphor Technology Ltd). It can be seen that normalized PL peak intensity of Eu²⁺ and Mn²⁺ ions decreased to 74% and 79% of the initial value at 100 °C, respectively (integrated intensity of NCASO: 0.07Eu²⁺,0.20Mn²⁺ phosphor decreased to 76%). Above 100 °C, the thermal quenching of NCASO:0.07Eu²⁺,0.20Mn²⁺ phosphor is much significant. Also, compared to BaMgAl₁₀O₁₇:Eu²⁺ phosphor, NCASO:0.07Eu²⁺,0.20Mn²⁺ phosphor shows lower thermal stability. These thermal quenching phenomena can be explained by the help of configurational coordinate diagram. With increasing temperature, electron-phonon interaction is enhanced. Through phonon interaction, the excited luminescent center is thermally activated and subsequently released through cross-over between the excited state and ground state. As a result, the emission intensity decreases due to enhanced population density of phonon [33].

To better understand the thermal quenching phenomena, the thermal quenching data were fitted using the Arrhenius equation [34],

$$\ln\left(\frac{I}{I_0}\right) = \ln A - \frac{E_a}{k_B T}$$  \hspace{1cm} (7)

where $I_0$ and $I(T)$ are the luminescence intensity of NCASO:0.07Eu²⁺,0.20Mn²⁺ (by integrating the area of each spectrum) at room temperature and a given temperature, respectively, $A$ is constant, $E_a$ is the activation energy for thermal quenching, and $k_B$ is Boltzmann’s constant (8.617 x 10⁻⁵ eV K⁻¹). From the equation, we have obtained $E_a$ of NCASO:0.07Eu²⁺,0.20Mn²⁺ to be 0.066 eV.
Fig. 10. CIE chromaticity diagram for NCASO:Eu$^{2+}$,yMn$^{2+}$ phosphors (point A to H) excited at 365nm and the ideal white point (0.33, 0.33) depending on the different y value.

Table 2. Comparison of the CIE chromaticity coordinates ($x$, $y$), IQE and EQE for NCASO:0.07Eu$^{2+}$,0.30Mn$^{2+}$ phosphors excited at 365nm

<table>
<thead>
<tr>
<th>Point No. in chromaticity diagram</th>
<th>Sample composition</th>
<th>($x$, $y$)</th>
<th>IQE</th>
<th>EQE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$y = 0$</td>
<td>(0.183, 0.148)</td>
<td>89%</td>
<td>68%</td>
</tr>
<tr>
<td>2</td>
<td>$y = 0.03$</td>
<td>(0.201, 0.173)</td>
<td>77%</td>
<td>64%</td>
</tr>
<tr>
<td>3</td>
<td>$y = 0.05$</td>
<td>(0.212, 0.186)</td>
<td>76%</td>
<td>63%</td>
</tr>
<tr>
<td>4</td>
<td>$y = 0.07$</td>
<td>(0.229, 0.209)</td>
<td>74%</td>
<td>61%</td>
</tr>
<tr>
<td>5</td>
<td>$y = 0.10$</td>
<td>(0.245, 0.228)</td>
<td>69%</td>
<td>57%</td>
</tr>
<tr>
<td>6</td>
<td>$y = 0.15$</td>
<td>(0.287, 0.276)</td>
<td>63%</td>
<td>53%</td>
</tr>
<tr>
<td>7</td>
<td>$y = 0.20$</td>
<td>(0.302, 0.293)</td>
<td>62%</td>
<td>53%</td>
</tr>
<tr>
<td>8</td>
<td>$y = 0.30$</td>
<td>(0.333, 0.317)</td>
<td>57%</td>
<td>46%</td>
</tr>
</tbody>
</table>

Table 2 reports the Commission Internationale de L'Eclairage (CIE) chromaticity coordinates, Internal Quantum Efficiency (IQE), and External Quantum Efficiency (EQE) of NCASO:Eu$^{2+}$,yMn$^{2+}$ phosphors excited at 365nm, which were calculated based on the corresponding PL spectrum. Figure 10 represents the data in the CIE chromaticity diagram. The result shows that the emission color can be gradually modulated from blue to white by increasing the Mn$^{2+}$ concentration from 0 to 0.30. In other words, it is possible to obtain both blue emission from the Eu$^{2+}$ ions and the orange emission from the Mn$^{2+}$ ions in a single host based on the energy transfer mechanism under 365nm excitation. In particular, the sample composition of NCASO:0.07Eu$^{2+}$,0.30Mn$^{2+}$ with CIE coordinates of (0.333, 0.317) shows the warm white light with correlated color temperatures of 5469 K and is very close to ideal white point (0.333, 0.333). Thus, we can simply control the color of the phosphor and make the white light with a preferred CCT value through changing the Mn$^{2+}$ doping concentration so as to meet the requirements of practical lighting application.

In addition, the quantum efficiency (QE) of a phosphor is an important parameter for LED application. In order to determine the absolute quantum efficiency of photo conversion for phosphor, the internal quantum efficiencies (IQE, $\eta_i$) and external quantum efficiencies (EQE, $\eta_o$) were calculated by using the following equations [35]:

$$\eta_o = \frac{\int \lambda P(\lambda)d\lambda}{\int \lambda E(\lambda)d\lambda}$$

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where $E(\lambda)/h\nu$, $R(\lambda)/h\nu$, and $P(\lambda)/h\nu$ are the number of photons in the spectrum of excitation, reflectance, and emission of the phosphor, respectively. The reflection spectrum of spectralon diffusive white standards is used for calibration (the reflectivity is nearly 100% in the range of 200-900 nm). Under 365 nm excitation, IQE and EQE of NCASO:Eu$^{2+}$,Mn$^{2+}$ phosphors are displayed in Table 2. The IQE and EQE of NCASO:Eu$^{2+}$,Mn$^{2+}$ phosphor decrease from 89% to 57% and from 68% to 46%, respectively for an increase in $y$ content from 0 to 0.3. The tendency shows that the QE decreases with increase of Mn$^{2+}$ content. The overall QEs can be enhanced through further optimization of the experimental condition and composition of phosphors.

4. Conclusion

In summary, we have successfully synthesized a new single-phased emission-tunable NCASO:Eu$^{2+}$,Mn$^{2+}$ phosphor. The phase formation of NCASO:Eu$^{2+}$,Mn$^{2+}$ was identified by the XRD analysis. Under 365 nm excitation, the emission color can be easily tuned from blue to white by simply adjusting the Mn$^{2+}$ content in the host lattice due to energy transfer from Eu$^{2+}$ to Mn$^{2+}$ ions. An efficient energy transfer was inferred from the changes in relative intensity of blue and orange emission from Eu$^{2+}$ and Mn$^{2+}$ respectively and was identified as electric dipole-dipole mechanism. Finally, a warm-white-light emission with CIE coordinates of (0.333, 0.317) and CCT of 5469 K was realized in NCASO:0.07Eu$^{2+}$,0.30Mn$^{2+}$ phosphor under 365 nm excitation. Thus, the obtained phosphor has been proven to be potentially useful as a single-phased white-emitting phosphor for UV-LEDs.

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