Na_{0.60}Ca_{0.40}Sc_{0.60}Mg_{0.40}Si_{2}O_{6}:Eu^{2+},Mn^{2+}: Tunable full-color-emitting solid-solution phosphor and its energy transfer property

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Novel Na_{0.60}Ca_{0.40}Sc_{0.60}Mg_{0.40}Si_{2}O_{6}:Eu^{2+},Mn^{2+} (NCSMS:Eu^{2+},Mn^{2+}) phosphors have been prepared, and the structural phase is derived from the solid-solution composition in \( (\text{Na}_x \cdot \text{Ca}_z)\cdot\text{Sc}_1\cdot\text{Mg}_y\cdot\text{Si}_z\cdot\text{O}_{12} \) \((x = 0.4, y = 0.6)\). The as-prepared phosphor shows full-color white emission with a three-band profile, including the 5d–4f transition of Eu^{2+} in different emission centers (447 and 533 nm) and the d–d transition of Mn^{2+} (654 nm). Energy transfer (ET) from Eu^{2+} to Mn^{2+} in this system is also discussed. A white LED lamp was fabricated by using the composition-optimized phosphor, and the result verified that the phosphor is a promising candidate for w-LEDs application.

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1. Introduction

Nowadays, phosphor-converted white light emitting-diodes (pc–LEDs) have drew more attentions, rather than polymer light emitting diodes (p-LEDs), organic light emitting diodes (o-LEDs) or compact fluorescent lighting (CFL) [1,2]. It is well known that the pc-LEDs can be employed by using a blue InGaN LED chip and a yellow phosphor (represented by Y_{3}O_{12}:Ce^{3+}) to realize white light [3,4]. However, this kind of phosphor plays the key roles in the present study and many reports describe the development of the RGB phosphors for near-ultraviolet (NUV) LEDs chip. Herein, it is very important to develop a single-phased full-color phosphor for the fabrication of w-LEDs. Most single-phased white light phosphor can be obtained through co-doping a sensitizer and an activator such as Eu^{2+} and Mn^{2+} into the same host, such as Na[Sc(Sr,Ba)PO_{4}:Eu^{2+},Mn^{2+} [5], Sr_{3}Y_{0.5}O_{2} (PO_{4})_{1.5}(SiO_{2})_{1.5}:Eu^{2+},Mn^{2+} [6] and KCaY[PO_{4}]_{2}:Eu^{2+},Mn^{2+} [7]. However, it will be more interesting that full-color emission in the single host system would be realized by designing the activator ions entering different crystallographic sites in one single host.

In our recent work [8], we have reported the color-tunable clinopyroxene solid-solution phosphors with the composition of \( (\text{Na}_1 \cdot \text{Ca}_x)(\text{Sc}_1 \cdot \text{Mg}_y)\cdot\text{Si}_z\cdot\text{O}_{12}:\text{Eu}^{2+} \). The \( (\text{Na}_1 \cdot \text{Ca}_x)(\text{Sc}_1 \cdot \text{Mg}_y)\cdot\text{Si}_z\cdot\text{O}_{12} \) belongs to clinopyroxene-type compound similar to the end members of CaMgSi_{2}O_{6} and NaScSi_{2}O_{6} possessing the general formula \( \{\text{M}_2\}\{\text{M}_1\}\text{T}_2\text{O}_6 \). As for \( \{\text{M}_2\}\{\text{M}_1\}\text{T}_2\text{O}_6 \), one cationic site is labeled as M2 which is defined as being 8-fold coordinated occupied by Na/Ca, and the other is labeled as M1 which is the 6-fold coordinated occupied by Mg/Sc. The charge balance in this solid-solution compound is maintained with a coupled Na^{+}–Ca^{2+} and Sc^{3+}–Mg^{2+} substitution. Therefore, the present studied Na_{0.60}Ca_{0.40}Sc_{0.60}Mg_{0.40}Si_{2}O_{6}:Eu^{2+},Mn^{2+} (NCSMS:Eu^{2+},Mn^{2+}) phosphors belongs to the same iso-structural compounds as CaMgSi_{2}O_{6} and NaScSi_{2}O_{6}.

As reported previously in our group [8,9], NaScSi_{2}O_{6}:Eu^{2+} has been regarded as a new yellow-emitting phosphor since Eu^{2+} ions enter the Na^+ sites, and the introduction of Mn^{2+} can show yellow-orange emission. NCMS:Eu^{2+} will give the comparable blue and yellow emission, and the white LEDs lamp has been fabricated by using this composition. However, it lacks the red emission for this composition and it will lead to the poor color-rendering index (CRI) value. We can expect that the single-phased NCM:Eu^{2+},Mn^{2+} phosphor can yield three major emission bands in full-color spectral region including the blue emission (477 nm) and yellow emission (533 nm) from the 5d–4f transitions of Eu^{2+} ions, and the broad red-emitting band from Mn^{2+} d–d transitions. The luminescent properties and energy transfer process between the Eu^{2+} and Mn^{2+} ions have been discussed in detail. A white LED device was also fabricated by combining the selected phosphor sample. All results indicate that this phosphor can be regarded as a promising candidate for NUV pumped w-LEDs.

2. Experimental section

Eu^{2+}/Mn^{2+} doped NCSMS phosphors were prepared via the sol-gel method. Eu_{2}O_{3} (>99.99%), Sc_{2}O_{3} and Mn(NO_{3})_{2} (A.R.) were dissolved in HNO_{3} to obtain the Eu(NO_{3})_{2}, Sc(NO_{3})_{3} and Mn(NO_{3})_{2}. Stoichiometric amounts of NaNO_{3}, Ca(NO_{3})_{2}.4H_{2}O, and Mg(NO_{3})_{2}.6H_{2}O were dissolved in ethanol under stirring. Eu(NO_{3})_{2}, Mn(NO_{3})_{2}, Sc(NO_{3})_{3} and Si(OH)_{4} (A.R.) were then added in the above solution. The resultant mixtures continued to be stirred at 80 °C for 30 min until homogeneous gels were formed. After being...
dried at 120 °C for 12 h in an oven, the gels were ground and pre- 
fired at 800 °C for 20 h in air, and then fully ground and sintered at 
1200 °C for 5 h in the CO reducing atmosphere. After that, the 
samples were furnace-cooled to room temperature, and ground again 
into powders. Thus, a series of NCSMS:Eu\(^{2+}\),Mn\(^{2+}\) phosphors were 
finally obtained. Room temperature photoluminescence excitation 
(PLE) and emission (PL) spectra were characterized on F-4600 fluo-
rescence spectrophotometer with a photomultiplier tube operating 
at 400 V, and a 150 W Xe lamp as the excitation source. The decay 
curves were recorded on a spectrophotometer (HORIBA, JOBIN 
YVON FL3-21), and the 370 nm pulse laser radiation (nano-LED) 
was used as the excitation source. The optical properties, including 
the electroluminescent spectrum, \( R_a \), \( \tau_c \), and CIE value of the fab-
ricated lamp, were measured by a HAAS-2000 (Everfine, China) light 
and radiation measuring instrument. The quantum efficiency (QE) 
was measured by an Absolute Photoluminescence Quantum Yield 
Measurement System (C9920-02, Hamamatsu-Photonics) with an 
integrating sphere at room temperature.

3. Results and discussion

As we reported previously, Na\(_{0.5555}\)Ca\(_{0.4145}\)Sc\(_{0.60}\)Mg\(_{0.4273}\)Si\(_2\)O\(_6\) host 
belongs to the same iso-structural compounds as CaMgSi\(_2\)O\(_6\) and 
NaScSi\(_2\)O\(_6\). The exact composition was determined by Rietveld 
refinement and the composition is: (Na \(_{0.5555}\)Ca\(_{0.4145}\)Sc\(_{0.60}\)Mg\(_{0.4273}\)Si\(_2\)O\(_6\)) \(_{176}\) [8]. Figure 1a 
displays the PL and PLE spectra of the Eu\(^{2+}\) singly doped NCSMS:0.05Eu\(^{2+}\) phosphor. Under the excita-
tion of 365 nm, the PL spectrum presented a broad band from 400 
and 700 nm, peaked around 447 and 533 nm, which is ascribed to 
the electric dipole allowed transition of the Eu\(^{2+}\) ions from the 
lowest level of the 5d excited state to the 4f ground state. This spectral 
result also demonstrate that Eu\(^{2+}\) ions are accommodated at the 
Na/Ca sites randomly in the NCSMS host, and the Eu\(^{2+}\) emission 
center in Na\(^{+}\) environment leads to spectrum with maximum in 
yellow region, and Ca\(^{2+}\) environment produce blue emission, which 
is similar as the report of yellow-emitting NaScSi\(_2\)O\(_6\):Eu\(^{2+}\) and blue 
emitting CaMgSi\(_2\)O\(_6\):Eu\(^{2+}\). Monitored by the emission at 533 
and 447 nm, the PLE spectrum exhibits a broad band in the range from 
220 to 430 nm, which corresponds to the transitions between the 
ground state 4f\(^{7}\) and the crystal-field split 4f\(^{5}\)d\(^{5}\) configuration of 
Eu\(^{2+}\) ions and well matches the application for w-LEDs with near 
ultraviolet light [10].

As can be seen in Figure 1b, when monitored by the emission at 
654 and 579 nm, the PLE spectrum of NCSMS:0.10Mn\(^{2+}\) includes 
several distinct peaks centered at 362, 410 and 536 nm, which is 
good agreement with the transitions of the Mn\(^{2+}\) ions from the ground 
level \( ^{4}A_{1}(S) \) to \( ^{4}T_{2}(D) \), \( ^{4}A_{1}(G) \), \( ^{4}E(G) \) and \( ^{4}T_{1}(G) \) excited 
levels, respectively [11]. Since Mn\(^{2+}\) ions can occupy two different 
crystallographic sites, Sc\(^{3+}\) and Mg\(^{2+}\) sites, in the NCSMS host, it 
will lead to different crystal field environment for the Mn\(^{2+}\) d–d 
transitions. Therefore, as shown in Figure 1b, the PL spectrum in-
cludes two broad emission bands centered at 579 and 654 nm, 
which are both ascribed to the spin-forbidden \( ^{4}T_{1}(G) \)\( ^{4}A_{1}(S) \) trans-
ition of the Mn\(^{2+}\) ions [12].

On the basis of the comparison of the PLE and PL spectra in 
Figure 1a and b, it is found that there is a spectral overlap between 
the PL of Eu\(^{2+}\) and PLE of Mn\(^{2+}\). Then, the energy transfer from Eu\(^{2+}\) 
Tn Mn\(^{2+}\) ions is expected in the NCSMS:Eu\(^{2+}\),Mn\(^{2+}\) system [13]. In 
order to confirm the phenomenon, Figure 1c illustrates the PLE 
and PL spectra NCSMS:0.05Eu\(^{2+}\),0.10Mn\(^{2+}\) phosphors. It is observed 
that the shapes of PLE spectra are similar except for the intensity 
by using different monitoring wavelength. And the PL spectra of 
the co-doped sample are made up of the emission bands of the Eu\(^{2+}\) ions Mn\(^{2+}\) ions. Therefore, we can observe full-color white 
emission with three major emission bands in visible spectral re-
region, the blue emission (477 nm) and yellow emission (533 nm) 
arise from the 5d–4f transitions of Eu\(^{2+}\) ions, the broad red-emit-
ting band (653 nm) originates from Mn\(^{2+}\) d–d transitions.

In order to further optimize the white-light-emitting perfor-
mance of the phosphors, a series of samples with different Eu\(^{2+}\)/ 
Mn\(^{2+}\) concentrations were synthesized. Figure 2 gives the PL spec-
tra of the NCSMS:0.05Eu\(^{2+}\),xMn\(^{2+}\) phosphors with different Mn\(^{2+}\) 
amounts upon the excitation of 365 nm. One can see that the inten-
sity of the Eu\(^{2+}\) emission decreases monotonically with increasing 
Mn\(^{2+}\) content. In contrast, the emission intensity of the Mn\(^{2+}\) emis-
sion reaches a maximum at \( x = 0.07\) and then begins to decrease 
with further increasing concentration because of the concentration 
quenching effect. The observed variations in the emission intensity 
of the Eu\(^{2+}\) and Mn\(^{2+}\) ions strongly indicate the energy transfer 
from Eu\(^{2+}\) to Mn\(^{2+}\). Meanwhile, by co-doped Eu\(^{2+}\) and Mn\(^{2+}\) ions, 
a tunable warm-white-light phosphor system was eventually 
obtained.

Generally, the energy transfer from a sensitizer to an activator 
in a phosphor system may take place via exchange interaction 
and electric multipolar interaction [9,14]. If energy transfer results 
from the exchange interaction, the critical distance between sensi-
tizer and activator should be shorter than 4 Å. In our 
NCSMS:0.05Eu\(^{2+}\),xMn\(^{2+}\) system, the critical distance \( R_c \) for energy
transfer from the Eu$^{2+}$ to Mn$^{2+}$ ions can be estimated according to critical concentration using the following equation [15,16]:

$$R_c \approx 2 \left( \frac{3V}{4\pi x_cN} \right)^{\frac{1}{3}}$$

(1)

where $x_c$ is the critical concentration (the total concentration of sensitizer ions of Eu$^{2+}$ and activator ions of Mn$^{2+}$) at which the quenching occurs; $N$ is the number of cations in the unit cell and $V$ is the volume of the unit cell. In our case, the crystallographic parameters are $V = 449.57$ Å$^3$, $N = 1$, and $x_c = 0.12$ denotes the sum of Eu$^{2+}$ concentration of 0.05 and the critical Mn$^{2+}$ concentration of 0.07. The critical distance $R_c$ is determined to be 19.3 Å, showing energy transfer mechanism in this system is governed by multipolar interaction.

According to Dexter's formula of multipolar interaction, the following relation can be obtained [17]:

$$\frac{I_{so}}{I_s} \propto C^{n/3}$$

(2)

where $I_{so}$ and $I_s$ are the luminescence intensities of the sensitizer Eu$^{2+}$ with and without activator Mn$^{2+}$ present, and $C$ is the Mn$^{2+}$ ion concentration. The plots of $(I_{so}/I_s)$ versus $C^{n/3}$ with $n = 6$, 8, and 10 correspond to dipole–dipole ($d$–$d$), dipole–quadrupole ($d$–$q$), and quadrupole–quadrupole ($q$–$q$) interactions, respectively. The relationships between $(I_{so}/I_s)$ and $C^{n/3}$ are illustrated in Figure 3, and a linear behavior was observed only when $n = 6$. This clearly indicates that the energy transfer from Eu$^{2+}$ to Mn$^{2+}$ follows a non-radiative dipole–dipole interaction.

Figure 4a and b give the fluorescence decay curves of Eu$^{2+}$ emission in NCSMS:0.05Eu$^{2+}$,xMn$^{2+}$ ($x = 0.00, 0.04, 0.10, 0.20, 0.30$) phosphors by monitoring the emission wavelength at 447 nm and 533 nm. It is found that all the decay curves can be well fitted based on the following non-exponential Eq. (3) [18]:

$$\tau = \int_{t_0}^{t} \frac{I(t)dt}{I_0} = \tau_0$$

(3)

where $I(t)$ stands for the intensity at time $t$. The decay lifetimes at 447 nm are determined to be 194.98, 161.27, 141.56, 109.06, and 103.04 ns, and 394.99, 329.65, 248.77, 107.26, and 100.54 ns for 533 nm with different Mn$^{2+}$ doped concentrations, respectively. Obviously, the decay times are decreases monotonically as the Mn$^{2+}$ concentration increases, which strongly demonstrated the energy transfer from Eu$^{2+}$ to Mn$^{2+}$. As also shown in the insets, the energy transfer efficiency $\eta_T$ from the Eu$^{2+}$ to Mn$^{2+}$ ions can be calculated by the following expression [6]:

$$\eta_T = 1 - \frac{\tau_s}{\tau_0}$$

(4)

where $\tau_0$ and $\tau_s$ are the corresponding lifetimes of Eu$^{2+}$ in the absence and the presence of the acceptor Mn$^{2+}$. The value of energy transfer efficiency $\eta_T$ were calculated according to Eq. (4) and given in the insets of Figure 4. The energy transfer efficiency increases with the increase of Mn$^{2+}$ content clearly. And once the doping concentration of Mn$^{2+}$ is 0.30, the value of $\eta_T$ is estimated to be as high as 75.8% and 74.6% at 477 nm and 533 nm.

Figure 5 depicts the CIE chromaticity diagram of the selected NCSMS:0.05Eu$^{2+}$,xMn$^{2+}$ phosphors under excitation at 365 nm. Interestingly, in the NCSMS:0.05Eu$^{2+}$,xMn$^{2+}$ system, as the value of $x$ increases from 0 to 0.30, the chromaticity coordinates can be easily modulated from (0.248, 0.324) to (0.419, 0.333). Thus, we can nicely find a white-emitting phosphor in the system. The absolute quantum efficiencies of the selected compositions of NCSMS:0.05Eu$^{2+}$ and NCSMS:0.05Eu$^{2+}$,0.04Mn$^{2+}$ are measured to be 11.5% and 14.5%, respectively. However, we should notice that the quantum efficiencies can be controlled by the phosphor particle size, size distribution, morphology and crystalline defects through optimization of the processing conditions and chemical composition. Furthermore, combining with a NUV 370-nm chip, the white-emitting NCSMS:0.05Eu$^{2+}$,0.04Mn$^{2+}$ phosphor can be selected to fabricate a white LED lamp. As given in the inset of Figure 5, the electroluminescent spectrum displays three emission.

Figure 3. Dependence of $I_{so}/I_s$ of Eu$^{2+}$ on $C_{\text{Mn}^{2+}}$: (a), $C_{\text{Mn}^{2+}}$: (b), and $C_{\text{Mn}^{2+}}$: (c).
bands at 370, 477, 533, and 654 nm, which are corresponding to the emission of the NUV chip (370 nm), Eu$^{2+}$ emission (477 and 533 nm), and Mn$^{2+}$ emission (654 nm), respectively. Furthermore, the white-light LED lamp gave a color rendering index $R_a=88.13$, correlated color temperature $T_c$ of 6580 K and CIE color coordinates of (0.308, 0.351). These results indicate that the finally prepared composition-optimized NCSMS:0.05Eu$^{2+}$,0.04Mn$^{2+}$ phosphor may have promising applications for white-light NUV LEDs.

4. Conclusion

In summary, a novel white-emitting NCSMS:Eu$^{2+}$,Mn$^{2+}$ phosphors were synthesized and compositional-optimized studied. Under excitation at 365 nm, the color-tunable phosphors can exhibit broad-bands emission peaking at 447, 533 and 654 nm. The significant spectral overlap and monotonic decrease decay times indicate efficient energy transfer from Eu$^{2+}$ to Mn$^{2+}$ in the system, the energy transfer efficiency $\eta_T$ was estimated to be 75.8% and 74.6% at 477 and 533 nm when the doping concentration of Mn$^{2+}$ is 0.30 mol. The mechanism of energy transfer was proved to be dipole–dipole interactions. A warm w-LED device has been obtained by combining the white-emitting NCSMS:0.05Eu$^{2+}$,0.04Mn$^{2+}$ phosphor with a NUV 370-nm chip, with the CIE color coordinates of (0.308, 0.351), a high color rendering index $R_a$ of 88.13 and a correlated color temperature $T_c$ of 6580 K. On basis of the interesting tunable emission properties, the color-tunable NCSMS:Eu$^{2+}$,Mn$^{2+}$ phosphors have great potential prospects for white light emitting diodes application.

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References


Figure 5. CIE chromaticity diagram of the selected NCSMS:0.05Eu$^{2+}$,0.04Mn$^{2+}$ phosphors under excitation at 365 nm. The inset shows the EL spectrum of white LED lamps fabricated using a NUV 370-nm chip combined with a white-emitting NCSMS:0.05Eu$^{2+}$,0.04Mn$^{2+}$ phosphor driven by a current of 25 mA.