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An Intense Green/Yellow Dual-Chromatic Calcium Chlorosilicate Phosphor Ca$_3$SiO$_4$Cl$_2$:Eu$^{2+}$–Mn$^{2+}$ for Yellow and White LED

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A series of intense green/yellow phosphors Ca$_3$SiO$_4$Cl$_2$:Eu$^{2+}$,Mn$^{2+}$ was synthesized by a high-temperature solid-state reaction. Their luminescent properties were characterized by means of powder diffuse reflection, photoluminescence excitation and emission spectra, and lifetime and temperature-dependent emission spectra in the temperature range of 10–450 K. The phosphors Ca$_3$SiO$_4$Cl$_2$:Eu$^{2+}$,Mn$^{2+}$ show intense broad absorption bands between 250 and 450 nm, matching well with the near-ultraviolet (380–420 nm) emission band of InGaN-based chips, and exhibit two dominating bands situated at 512 and 570 nm, ascribed to the allowed 5d $\rightarrow$ 4f transition of the Eu$^{2+}$ ion and the $^4T_{1g}(G)$ $\rightarrow$ $^2A_{1g}(S)$ transition of the Mn$^{2+}$ ion, respectively. The lifetime of the Eu$^{2+}$ ion decreases with increasing the concentration of the Mn$^{2+}$ ion, strongly supporting an efficient energy transfer from Eu$^{2+}$ to Mn$^{2+}$. By combining with near-ultraviolet (~395 nm) InGaN chips, intense yellow light-emitting diodes (LEDs) with a much lower ultraviolet light leakage were successfully fabricated based on the Ca$_3$SiO$_4$Cl$_2$:Eu$^{2+}$,Mn$^{2+}$ phosphor, and intense white LEDs were made based on a blend of blue chlorophosphate phosphor and the green/yellow phosphor Ca$_3$SiO$_4$Cl$_2$:Eu$^{2+}$,Mn$^{2+}$. The color coordinate, correlated color temperature $T_c$, general color-rendering index $R_g$, and luminous efficiency of the fabricated white LEDs are (0.3281, 0.3071), 6065 K, 84.5, and 11 lm/W, respectively.

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It is well known that the invention of white light-emitting diodes (LEDs) has brought another revolution to the illumination of this century to supersede conventional incandescent or fluorescent lamps because of their excellent properties such as high brightness, reliability, lower power consumption, and long life.1,2 At present, there are several ways to make the white LEDs.3,4 One significant scheme is phosphor-converted white LED (pc-wLED) that is further classified into two approaches: blue (440–470 nm) and a near-ultraviolet (n-UV) (390–410 nm) InGaN chip combined with down-converting phosphors. For the blue InGaN chip, the commonly used down-converting phosphor is yellow YAG:Ce$^{3+}$. However, such white LEDs encounter a low color-rendering index ($R_g < 80$) due to the scarcity of red emission. Besides, the white LED based on the blue InGaN chip encounters a low color reproducibility in the mass manufacture scale. The n-UV LED is considered more stable and efficient with a higher output.5 In addition, the n-UV LED generally emits at a wavelength shorter than 400 nm, which has little effect on the chromaticity coordinate of pc-wLED, which is generally determined by the visible radiation distribution of phosphor between 380–420 nm.6 Thus, the n-UV pc-wLEDs are expected to have a great application potential in the field of solid-state lighting.

Nowadays, many phosphors have been investigated including orthosilicates, aluminates, sulfides, molybdates, and oxynitrides/nitrides. However, they often have some serious drawbacks, for example, low down-converting efficiency, poor chemical stability, and poor high-temperature stability, or harsh synthesis conditions (such as $> 1700^\circ$C high temperature or about a few MPa high pressure).7–11 Recently, Eu$^{2+}$-activated chlorosilicates have attracted more attention due to their high luminescence efficiency, low synthesis temperature, and high physical chemistry stability.12–14 In 2005, Liu et al. reported a single green-emitting phosphor based on Ca$_3$SiO$_4$Cl$_2$:Eu$^{2+}$ with a low-temperature phase and fabricated a white LED with a low color-rendering index of 73, due to the scarcity of blue and green content in the white emission.15 In this paper, a series of intense dual-chromatic green/yellow emitting phosphors, Ca$_3$SiO$_4$Cl$_2$:Eu$^{2+}$,Mn$^{2+}$, was reported. The highly efficient energy transfer between Eu$^{2+}$ and Mn$^{2+}$ ions was systematically investigated. More importantly, intense yellow LEDs with a low UV leakage and high down-converting efficiency, and white LEDs with a high color-rendering index and high luminous efficiency were successfully fabricated based on Ca$_3$SiO$_4$Cl$_2$:Eu$^{2+}$,Mn$^{2+}$. The synthesis of Ca$_3$SiO$_4$Cl$_2$:Eu$^{2+}$–Mn$^{2+}$.— Powder samples were synthesized via a solid-state reaction at high temperature. The raw materials were Eu$_2$O$_3$ (99.9%), analytical regent grade CaCO$_3$, CaCl$_2$, SiO$_2$, and MnCO$_3$. The mixtures of corresponding raw materials by a molar ratio of CaCO$_3$:SiO$_2$:CaCl$_2$:Eu$_2$O$_3$:MnCO$_3$ = 2:1:1:1 and a small amount of Eu$_2$O$_3$ and MnCO$_3$ were thoroughly ground with an agate mortar and pestle. They were then put into a corundum crucible and subsequently kept at 1123 K for 4 h in a reducing atmosphere (25% H$_2$, 75% N$_2$). Finally, as-synthesized samples were slowly cooled to room temperature inside the tube furnace in a nitrogen atmosphere. Y$_2$O$_3$:Eu$^{3+}$O$_{0.6}$Ce was prepared by a solid-state reaction according to Ref. 16.

Characterization of Ca$_3$SiO$_4$Cl$_2$:Eu$^{2+}$–Mn$^{2+}$.— Powder X-ray diffraction (XRD) was performed on a Rigaku D/max-IB X-ray diffractometer with Cu Kα$_1$ ($\lambda = 1.5405$ Å) radiation. The diffuse reflection spectra of as-synthesized samples were measured on a Cary 5000 UV-Vis-NIR spectrophotometer (Varian Inc.) equipped with a double-out-of-plane Littrow monochromator, using BaSO$_4$ as a standard reference in the measurements. The photoluminescence (PL) excitation and emission spectra were measured on a Fluorolog-3 spectrophotofluorometer (Jobin Yvon Inc./Specx) equipped with a 450 W Xe lamp, double-excitation monochromators, and single-emission monochromator. The room-temperature lifetime measurement and temperature-dependent emission properties of as-synthesized samples in the temperature range of 10–450 K were determined on an FL9200-combined time resolved and steady-state fluorescence spectrometer (Edinburgh Instruments) equipped with the closed-cycle helium cryostats (Advance Inc.).
Results and Discussion

Photoluminescence properties of Ca$_3$(SiO$_4$)Cl$_2$:Eu$^{2+}$—Mn$^{2+}$—The body colors of the as-synthesized samples doped with Eu$^{2+}$ or Eu$^{2+}$—Mn$^{2+}$ ions were white, green, and yellow. It was reported that Ca$_3$(SiO$_4$)Cl$_2$ had a monoclinic crystal structure with the space group of P2$_1$/c, which is composed of layers of calcium chloride and dicalcium silicate. Figure 1 shows the XRD patterns of Ca$_3$(SiO$_4$)Cl$_2$:Eu$^{2+}$, Mn$^{2+}$. It can be concluded that the as-synthesized samples are generally of a single phase that is consistent with the low-temperature phase Ca$_3$(SiO$_4$)Cl$_2$ (JCPDS 24–0032). The substitution of europium and manganese ions does not induce any significant phase change.

Figure 2 shows the powder diffuse reflection spectra of the host, Eu$^{2+}$ singly doped, and Eu$^{2+}$ and Mn$^{2+}$ codoped samples. It is obvious that the host Ca$_3$(SiO$_4$)Cl$_2$ shows a platform of high reflection in the wavelength range of 350–800 nm and then starts to decrease dramatically from 350 to 200 nm, due to the host absorption. From curve 1, the low-energy edge of the host absorption can be estimated at around 5.4 eV. When the Eu$^{2+}$ ion is singly doped into the host, two broad bands appear between 250 and 500 nm, which are derived from the 4f–5d electronic dipole allowed transitions of Eu$^{2+}$ ion from the lowest excited 5d level to the 4f ground state, and its full width at half maximum is about 2440 cm$^{-1}$. Monitoring the green emission at 509 nm, there are several broad bands around 275, 323, 368, and 454 nm. The fine structure of the excitation spectra of Eu$^{2+}$ ion indicates that the site occupied by the Eu$^{2+}$ ion has a lower symmetry. The redshift of the Eu$^{2+}$ ion expressed by the depression value of the lowest excited 5d level in the present host when compared to the free gaseous ion is calculated to be 14,350 cm$^{-1}$. The Stokes shift is about 2380 cm$^{-1}$. These results are in general agreement with those reported by Liu and Wannemaker.

For $x = 0.06–0.18$, the Ca$_3$(SiO$_4$)Cl$_2$:0.09Eu$^{2+}$,xMn$^{2+}$ samples show an additional strong yellow broadband emission around 568 nm besides the green one. The new yellow emission band is considered to be associated with the Mn$^{2+}$ ion. For this purpose, the sample Ca$_3$(SiO$_4$)Cl$_2$:0.09Mn$^{2+}$ was also synthesized and optically investigated. It shows a much lower optical property of the Mn$^{2+}$ ion. For clarity, the emission slit was set at 5 nm for Ca$_3$(SiO$_4$)Cl$_2$:Mn but at 1 nm for Ca$_3$(SiO$_4$)Cl$_2$:Eu:Mn when the signals were recorded. Figure 4 shows several broad bands and peaks in the wavelength range of 300–500 nm, due to the transitions of the Mn$^{2+}$ ion from the ground state 6A$_1$(g) to the crystal field components of the excited 2E$_g$(4T$^2$g), 4T$^2$g(4T$^2$g), 4E_g(4T$^2$g), and 4T$^1$g(4T$^1$g) levels. Under excitation at 419 nm, one broad emission band is predominant around 570 nm, assigned to the transition of the Mn$^{2+}$
ion from the lowest excited level of $^4T_{1g}$ to the ground state $^5A_{1g}$ ($S$). Consequently, a new yellow emission band in Eu$^{2+}$, Mn$^{2+}$ codoped samples is derived from the Mn$^{2+}$ ion. The Mn$^{2+}$ ion in solid compounds is usually characterized by green or orange–red emissions. The emission color is strongly dependent on the coordination environment of the Mn$^{2+}$ ion in the host lattice, such as the strength of the ligand field and coordination number (CN). The stronger the ligand field, the longer the emission peak will be.\(^\text{19}\) The CN also has a huge effect on the emission color: the Mn$^{2+}$ ion emits green light when it is tetrahedrally coordinated (CN = 4) in the lattice, whereas it emits orange–red light in an octahedral coordination (CN = 6).\(^\text{20}\) For example, the Mn$^{2+}$ ion substitutes the cation site with tetrahedral symmetry in Zn$_3$SiO$_4$ and emits intense green light around 520 nm, whereas it occupies the Zn site with octahedral coordination in Zn$_3$(PO$_4$)$_2$ and emits red light at 616 nm.\(^\text{17,21}\) In the present case, the broad emission band around 568 nm indicates that the Mn$^{2+}$ ion occupies an octahedral site.

Monitoring the yellow emission at 568 nm, the Mn$^{2+}$ ion shows the same excitation features as the Eu$^{2+}$ ion, as shown in curves 2 and 3 of Fig. 3. Here, the 3d–3d forbidden transition bands of the Mn$^{2+}$ ion with low oscillator strength are so weak as to be hidden behind the 4f–5d allowed transition band of the Eu$^{2+}$ ion with a high oscillator strength. The effect of the Mn$^{2+}$ ion concentration was also studied. As shown in Fig. 3, the yellow emission intensity enhances, whereas the green one decreases gradually when the concentration of the Mn$^{2+}$ ion increases. These results support the efficient energy transfer from Eu$^{2+}$ to Mn$^{2+}$ ions.\(^\text{22,23}\) The emission intensity of the Mn$^{2+}$ ion attains the maximum at $x = 0.12$ and then starts to decrease due to the concentration quenching of the Mn$^{2+}$ ion.

The PL decay curves of Eu$^{2+}$ in Ca$_3$(SiO$_4$)Cl$_2$:0.09Eu$^{2+}$,xMn$^{2+}$ ($x = 0, 0.06, 0.09, 0.12, 0.15, 0.18$) were measured and are presented in Fig. 5 and 6. All the decay curves can be well fitted by the double-exponential equation given by

$$I(t) = I_0 + Ae^{-t/\tau_1} + Be^{-t/\tau_2}$$

where $I_0$ and $I$ are the luminescence intensities at time 0; $t$, $A$, and $B$ are constants; $\tau_1$ and $\tau_2$ are the lifetimes for the exponential components, respectively.\(^\text{5}\) For Ca$_3$(SiO$_4$)Cl$_2$:0.09Eu$^{2+}$, the lifetimes are determined to be 2.6 and 9.2 $\mu$s. These results indicate that there are two lattice sites occupied by Eu$^{2+}$ ions, which is also supported by the emission spectra of Ca$_3$(SiO$_4$)Cl$_2$:Eu$^{2+}$. As shown in Fig. 3, the Ca$_3$(SiO$_4$)Cl$_2$:Eu$^{2+}$ phosphor shows an asymmetrical emission band at 508 nm, tailing toward 600 nm, suggesting that two strongly overlapping emission bands exist. The lifetime of the Eu$^{2+}$ ion is usually in the range of 0.2–2 $\mu$s.\(^\text{24,25}\) However, it is beyond the normal range in a few host compounds. For example, in BaSi$_2$O$_5$:Eu$^{2+}$ and Ba$_2$Mg(BO$_3$)$_2$:Eu$^{2+}$ host lattices, relatively long decay times are 3.3 and 12.6 $\mu$s, respectively.\(^\text{27}\) Poort et al. state that such an anomalous lifetime is due to a larger delocalization in the excited state where the wave function overlap between the electron and the hole will be largely reduced, resulting in a longer lifetime. In our case, the Eu$^{2+}$ ions may also experience a similar condition. When Mn$^{2+}$ ions are doped into Ca$_3$(SiO$_4$)Cl$_2$:0.09Eu$^{2+}$, the decay lifetimes for Eu$^{2+}$ ion are found to generally decrease with increasing the Mn$^{2+}$ ion concentration, as shown in Fig. 6. For Ca$_3$(SiO$_4$)Cl$_2$:0.09Eu$^{2+}$,0.18Mn$^{2+}$, the decay lifetimes for the Eu$^{2+}$ ion are 1.8 and 6.8 $\mu$s. These results are reasonable for the 5d–4f allowed transition of Eu$^{2+}$ ions of less than microseconds.\(^\text{27}\) The trend in lifetime for the Eu$^{2+}$ ion in the absence and presence of the Mn$^{2+}$ ion provides strong evidence for energy transfer from Eu$^{2+}$ to Mn$^{2+}$.

The energy transfer efficiency ($\eta_{ET}$) from Eu$^{2+}$ to Mn$^{2+}$ was evaluated based on the following expression:\(^\text{8}\)

\[ \eta_{ET} = \frac{T_2 - T_1}{T_2} \]

where $T_1$ and $T_2$ are the lifetimes for the Eu$^{2+}$ ion in Ca$_3$(SiO$_4$)Cl$_2$:0.09Eu$^{2+}$,xMn$^{2+}$ ($x = 0$ and 0.18).

**Figure 4.** The excitation and emission spectra of Ca$_3$(SiO$_4$)Cl$_2$:0.09Mn$^{2+}$.

**Figure 5.** The decay curves of Eu$^{2+}$ ion in Ca$_3$(SiO$_4$)Cl$_2$:0.09Eu$^{2+}$,xMn$^{2+}$ ($x = 0$ and 0.18).

**Figure 6.** Dependence of the lifetime of Eu$^{2+}$ ion on Ca$_3$(SiO$_4$)Cl$_2$:0.09Eu$^{2+}$,xMn$^{2+}$ on Mn$^{2+}$ content $x$. (Downloaded on 2014-12-04 to IP 129.72.129.237 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).)
where $\eta_T$ is energy transfer efficiency, $I_0$ and $I_d$ are the corresponding intensities of the donor Eu$^{2+}$ ion in the absence and presence of the acceptor Mn$^{2+}$. As Fig. 7 shows, the energy transfer efficiency $\eta_T$ is found to increase gradually with increasing Mn$^{2+}$ dopant content and finally saturate, which is similar to Ce$^{3+} \rightarrow$ Eu$^{2+}$ in Ba$_2$ZnS$_3$.

The excitation and emission spectra suggest that the phosphors Ca$_3$SiO$_4$Cl$_2$:0.09Eu$^{2+}$,xMn$^{2+}$ are a series of efficient dual-chromatic emitting phosphors with broad absorption bands, matching well with the widely used near-UV LED chips (380–420 nm). Figure 8 shows the CIE 1931 chromaticity diagram of the phosphors Ca$_3$SiO$_4$Cl$_2$:0.09Eu$^{2+}$,xMn$^{2+}$. The UV excitation light is selected at 395 nm, which is the same as the electroluminescent emission peak of the commercial InGaN chip used in the present case under direct current $I_F = 20$ mA. The emission light of the Eu$^{2+}$ singly doped phosphor with the color coordination of (0.191,0.572) is situated in the green area. For Ca$_3$SiO$_4$Cl$_2$:0.09Eu$^{2+}$,0.18Mn$^{2+}$, the color coordination is (0.447,0.501) in the yellow region. Along the line between the two end points, the emission color is tunable in the visible region from green to yellow by controlling the concentration of the Mn$^{2+}$ ions. Therefore, the series Ca$_3$SiO$_4$Cl$_2$:Eu$^{2+}$,Mn$^{2+}$ are promising candidates for color tunable phosphors of the n-UV pc-wLEDs.

The temperature dependence of the emission characteristics of Ca$_3$(SiO$_4$)Cl$_2$:Eu$^{2+}$,Mn$^{2+}$ was investigated in the temperature range of 10–450 K, as shown in Fig. 9 and 10. The intensities of both the green and yellow emissions decrease with increasing temperature. The emission intensity of the Eu$^{2+}$ ion is thermally quenched at a lower temperature than that of Mn$^{2+}$ ion: the quenching temperature, at which the initial PL intensity at 10 K is halved, is 250 K for the Eu$^{2+}$ ion and above 450 K for the Mn$^{2+}$ ion. The decrease in emission intensity with increasing temperature is due to the temperature dependence of the electron–phonon interaction in both the ground state and excited states of the luminescence center.29 This nonradi-
In our case, the Eu\(^{2+}\) ion shows an asymmetrical emission band and green and yellow emission of Ca\(_3\) due to different thermal quenching behaviors and the blueshift of the emission band at 514 nm is dominant, and in Ba\(_2\)SiO\(_4\)Eu\(^{2+}\), the peak positions of Eu\(^{2+}\) ion at 450 K are 565 and 554 nm. The same phenomenon was also observed in M\(_2\)SiO\(_4\)Eu\(^{2+}\) (M = Ca and Ba) where there are two different sites, M(I) and M(II). \(^{31}\) In Ca\(_3\)SiO\(_4\)Eu\(^{2+}\), the single asymmetrical emission at 514 nm is dominant, and in Ba\(_2\)SiO\(_4\)Eu\(^{2+}\), the single asymmetrical emission at 507 nm dominates. Both of them exhibit an unusual blueshift with increasing temperature. To account for this phenomenon, the authors proposed that a thermally active phonon-assisted tunneling from the excited states of the low-energy emission band [M(2)] to the excited states of the high-energy emission band [M(1)] in the configuration coordinate diagram occurred. In our case, the Eu\(^{2+}\) ion shows an asymmetrical emission band and two lifetimes as shown in Fig. 3, 5, and 6. As discussed above, these results indicate that there are two distinct lattice sites, Eu\(_I\) and Eu\(_{II}\), in Ca\(_3\)SiO\(_4\)Cl\(_2\). Therefore, a similar tunneling process may also occur between the excited states of Eu\(_I\) and Eu\(_{II}\) as the temperature increases.

The color stability of phosphor against temperature is a significant factor for a high-power LED device, the joint temperature of which is generally around 420 K. Figure 8 also shows the CIE 1931 chromaticity diagram of Ca\(_3\)(SiO\(_4\))Cl\(_2\):0.09Eu\(^{3+}\),0.12Mn\(^{2+}\) with the PL emission spectra of Ca\(_3\)SiO\(_4\)Cl\(_2\):Eu\(^{2+}\),Mn\(^{2+}\) under \(\lambda_{ex} = 365\) nm. In our case, the white LED shows a much lower UV light intensity, indicating this Ca\(_3\)SiO\(_4\)Cl\(_2\):Eu\(^{2+}\),Mn\(^{2+}\) phosphor has a high UV absorption efficiency and high down-converting efficiency. It is essential for the white LEDs fabricated with the near-UV chip and phosphors to prevent the UV light from leaking out because the UV light is harmful to human eyes and degrades the packing resins. The color coordinate of the as-fabricated LED is (0.4348, 0.4985) as shown in Fig. 8 after \(\lambda_{ex} = 365\) nm. Liu et al. reported the white LED based on the n-UV (\(\lambda_{em} = 402\) nm) InGaN chip and a monochromatic emitting phosphor Ca\(_3\)SiO\(_4\)Cl\(_2\):Eu\(^{3+}\),Mn\(^{2+}\) with the high-temperature phase. The white light of such a w-LED is located at the edge of the white circle near the blue chlorophosphate and green/yellow chlorosilicate phosphors. As shown in Fig. 13, the emission bands are located at about 397, 454, 510, and 570 nm, derived from the n-UV LED and the commercial blue and UV LED chips. It is estimated that the integrated emission intensity of Ca\(_3\)SiO\(_4\)Cl\(_2\):Eu,Mn reaches 96% of home-prepared YAG:Ce (\(\lambda_{em} = 450\) nm). These results indicate that Ca\(_3\)SiO\(_4\)Cl\(_2\):Eu,Mn is ideal for 365 or 400 nm UV LED applications. Because of the scarcity of the 365 nm UV chip, the 400 nm UV chip was chosen to fabricate the phosphor converted white LED.

**Yellow and white LED application of Ca\(_3\)SiO\(_4\)Cl\(_2\):Eu\(^{2+}\),Mn\(^{2+}\)**

Figure 12 shows the intense yellow LED fabricated with the Ca\(_3\)SiO\(_4\)Cl\(_2\):Eu\(^{2+}\),Mn\(^{2+}\) under \(\lambda_{ex} = 20\) mA. It is obvious that there are three emission bands: the weak sharp band at 395 nm, the dominant band at 570 nm, and the intense shoulder around 510 nm, respectively. The UV emission is due to the electroluminescence of the UV GaN chip. The green and yellow emissions are consistent with the PL emission spectra of Ca\(_3\)SiO\(_4\)Cl\(_2\):Eu\(^{2+}\),Mn\(^{2+}\) as shown in Fig. 3. The fabricated LED shows a much lower UV light intensity, indicating this Ca\(_3\)SiO\(_4\)Cl\(_2\):Eu\(^{2+}\),Mn\(^{2+}\) phosphor has a high UV absorption efficiency and high down-converting efficiency. It is essential for the white LEDs fabricated with the near-UV chip and phosphors to prevent the UV light from leaking out because the UV light is harmful to human eyes and degrades the packing resins. The color coordinate of the as-fabricated LED is (0.4348, 0.4985) as shown in Fig. 8 after \(\lambda_{ex} = 365\) nm. Liu et al. reported the white LED based on the n-UV (\(\lambda_{em} = 402\) nm) InGaN chip and a monochromatic emitting phosphor Ca\(_3\)SiO\(_4\)Cl\(_2\):Eu\(^{3+}\),Mn\(^{2+}\) with the high-temperature phase. The white light of such a w-LED is located at the edge of the white circle near the blue chlorophosphate and green/yellow chlorosilicate phosphors. As shown in Fig. 13, the emission bands are located at about 397, 454, 510, and 570 nm, derived from the n-UV LED and the blue and green/yellow phosphors, respectively. The color coordinate and correlated-color temperature \(T_c\) of the two-phosphor white LED are about (0.3281, 0.3071) and 6065 K, respectively. The luminous efficiency (\(\eta_L\)) and the color-rendering index \(R_c\) are 11 lm/W and 84.5, respectively.
84.5, higher than those ($\eta_0 = 3.8, 6,$ or 9 lm/W; $R_a = 68, 85,$ or 78) fabricated with a UV chip and strontium silicate or calcium pyrophosphates phosphor. The two-phosphor white LED based on a UV chip also shows a higher $R_a$ than the commercial white LED ($R_a = 75$) based on the blue chip and yellow YAG:Ce phosphor.

**Conclusion**

In summary, a series of intense yellow phosphors, Ca$_3$SiO$_4$Cl$_2$:Eu$^{2+}$,Mn$^{2+}$, is reported. They exhibit the efficient broad absorption band, intense green to yellow tunable emission, high efficient energy transfer between Eu$^{2+}$ and Mn$^{2+}$, and good color stability with increasing temperature. The yellow LED based on Ca$_3$SiO$_4$Cl$_2$:Eu$^{2+}$,Mn$^{2+}$ shows the intense yellow light and much lower UV light leakage. The white LED based on the UV chip, blue phosphor, and Ca$_3$SiO$_4$Cl$_2$:Eu$^{2+}$,Mn$^{2+}$ produces good white light ([0.3281, 0.3071), 6065 K, 84.5, and 11 lm/W]. These results indicate that Ca$_3$SiO$_4$Cl$_2$:Eu$^{2+}$,Mn$^{2+}$ is a promising phosphor applicable to near-UV LEDs for solid-state lighting.

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