Eu²⁺⁺?-Activated Ca₈Zn?(SiO₄)₄Cl₂: An Intense Green Emitting Phosphor for Blue Light Emitting Diodes

Wei Lü, Zhendong Hao, Xia Zhang, Yongfu Liu, Yongshi Luo, Xingyuan Liu, Xiaojun Wang and Jiahua Zhang

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We report intense green luminescence upon blue light excitation in Eu\(^{2+}\)-activated Ca\(_8\)Zn(SiO\(_4\))\(_4\)Cl\(_2\) prepared by high temperature solid-state reaction with nominal composition of (2 - \(x\))CaO - \(x\)ZnO - SiO\(_2\)-CaCl\(_2\) (0 \(\leq x \leq 1\)). It is observed that the material phase gradually converts from Ca\(_3\)SiO\(_4\)Cl\(_2\):Eu\(^{2+}\) to Ca\(_8\)Zn(SiO\(_4\))\(_4\)Cl\(_2\):Eu\(^{2+}\) followed by improved luminescent properties with increasing \(x\). The two phosphors both emit with a maximum at 505 nm. Significantly, Ca\(_8\)Zn(SiO\(_4\))\(_4\)Cl\(_2\):Eu\(^{2+}\) shows a more intense excitation band in the blue centered at 450 nm. Upon 450 nm excitation, the integrated emission intensity of Ca\(_8\)Zn(SiO\(_4\))\(_4\)Cl\(_2\):Eu\(^{2+}\) is 1.3 times stronger than Ca\(_3\)SiO\(_4\)Cl\(_2\):Eu\(^{2+}\) and nearly the same as Ca\(_3\)Sc\(_2\)Si\(_2\)O\(_6\):Ce\(^{3+}\) phosphors. Attempts to understand the origins of the intense luminescence are presented on the basis of diffuse reflection spectra and fluorescence decays of Ca\(_8\)Zn(SiO\(_4\))\(_4\)Cl\(_2\):Eu\(^{2+}\) in comparison with related phosphors. The present results suggest that Ca\(_8\)Zn(SiO\(_4\))\(_4\)Cl\(_2\):Eu\(^{2+}\) could be a promising green emitting phosphor for excitation by blue light emitting diodes.

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phors totally change into the single cubic Ca$_8$Zn(Si$_4$O$_4$)$_2$Cl$_2$ phase. In this work, the CaCl$_2$ and ZnO mole ratio in the firing process of a Ca$_8$Zn(Si$_4$O$_4$)$_2$Cl$_2$ phosphor is higher than the normal stoichiometric ratio. It is understandable that Cl and Zn could be evaporated in the form of CaCl$_2$ and metallic Zn during firing under the reducing atmosphere. That is why excess CaCl$_2$ and ZnO are added in the reactant as preparation of chlorosilicates and sorosilicate phases of Ca$_8$Zn$_x$SiO$_4$Cl$_2$. Kang reported that the increase of the mole ratio of Cl/Ca is beneficial to crystallinity and phase purity, resulting in the enhancement luminescence intensity of Ca$_8$Mg(Si$_4$O$_4$)$_2$Cl$_2$:Eu$^{2+}$. Consequently, the nonstoichiometry is just supposed to form purity phases of Ca$_8$Zn$_x$(Si$_4$O$_4$)$_2$Cl$_2$ in our present work.

PL and PLE properties of CZSC(x):0.02Eu$^{2+}$.—The PL and PLE spectra of CZSC(x):0.02Eu$^{2+}$ (0 ≤ x ≤ 1.1) are shown in Fig. 2, where each spectrum is normalized at the maximum of the spectral intensity. The PL spectra present a green emission band peaking at 505 nm due to Eu$^{2+}$ 4f$^5$d$^-1$4f$^7$ transition, of which the position and the shape stay unchanged for various Zn contents x. In contrast to the PL, the spectral distribution of PLE exhibits a remarkable enhancement in the blue spectral range of 370–470 nm with increasing x. Especially for x ≈ 0.7, the PLE peak position changes from the original at 325 nm to the final at 450 nm. In view of the phase change with x shown in XRD, the enhanced PLE band in the blue spectral region for x ≈ 0.7 is attributed to the characteristic of the Ca$_8$Zn(Si$_4$O$_4$)$_2$Cl$_2$:Eu$^{2+}$. It should be noted that the PL spectrum of Ca$_8$Zn(Si$_4$O$_4$)$_2$Cl$_2$:Eu$^{2+}$ is very similar with that of Ca$_8$Mg(Si$_4$O$_4$)$_2$Cl$_2$:Eu$^{2+}$ and Ca$_3$SiO$_4$Cl$_2$:Eu$^{2+}$ as previously reported by Zhang and Baginskys. and there are two Ca$^{2+}$ sites for Eu$^{2+}$ in Ca$_8$Zn(Si$_4$O$_4$)$_2$Cl$_2$:Eu$^{2+}$ just as in Ca$_8$Mg(Si$_4$O$_4$)$_2$Cl$_2$:Eu$^{2+}$. Figure 2 indicates that a 450 nm light can only excite one site with a PL band at 505 nm that is assigned to Eu(I) on an eight-coordinated Ca$^{2+}$ site with strong crystal field. If a shorter wavelength, for instance, 365 nm light is applied, both sites can be excited, resulting in an additional weak PL band at 425 nm that is assigned to Eu(I) on a six-coordinated Ca$^{2+}$ site with weak crystal field. In addition, a very small amount of Eu$^{3+}$ ions exist in Ca$_8$Zn(Si$_4$O$_4$)$_2$Cl$_2$:Eu$^{3+}$ prepared in this work because the very weak emission lines due to $^5$D$_0$ → $^7$F$_{J}$ transitions (peaked at 578, 593, and 612 nm, respectively) of Eu$^{3+}$ is detected even under 254 nm excitation into their efficient charge transfer bands. When the $^5$D$_0$ → $^7$F$_{J}$ transition of Eu$^{3+}$ was subjected to a detailed high-resolution emission spectral investigation, another relatively weak emission line at 575 nm was observed, indicating that the Eu$^{3+}$ ions were situated at two distinct sites. According to the crystal structure given in Ref. 13 and 22, the site ratio of Ca(II) against Ca(I) is 3:1. We therefore infer that most of the Eu$^{3+}$ ions enter Ca(II) sites, leading to the dominant emission line at 578 nm. As a result, we conclude that the contribution to the luminescence of the present phosphors is only made by Eu$^{2+}$(II) ions upon near UV and blue excitation.

Figure 3 depicts the comparison of PL intensities in CZSC(x=0.9):yEu$^{2+}$ and CZSC(x=0):yEu$^{2+}$ for different Eu$^{2+}$ concentrations (y = 0.02, 0.03, 0.04, 0.05, and 0.06) under 450 nm excitation. Clearly, considerable enhancements of PL are demonstrated in
The typical diffuse reflection spectra of some CZSC/H2O849 = 0.9 in CZSC reflection spectra are measured for various samples. Figure 4 depicts the two factors results in luminescent enhancement, the diffuse reflection spectra are measured for various samples. The absorptivity and the samples CZSC/H2O849 are determined by two factors: the absorptivity and internal quantum efficiency. In Eu2+ doped hosts, there are obvious absorptions in the range of 250–500 nm, which are derived from the 4f 7–4f65d electronic dipole allowed transitions of Eu2+. Using reflection spectra, we may estimate absorptivity at the excitation wavelength of 450 nm. Subsequently, we plot the integral PL intensities versus absorptivities for various samples as shown in Fig. 5, where each dot represents one sample. One can find the PL intensities go linearly with absorptivity (ηab), indicating that the different samples have the identical internal quantum efficiency because PL intensity is proportional to ηab/ηab. Therefore, the enhancement of the PL intensities in Ca3Zn(SiO4)Cl2:Eu2+ is attributed to the increase of absorption strength of 4f7–4f55d transitions of Eu2+. One can also see that the point for the Ca3Sc2Si3O12:Ce3+ is close to the straight line shown in Fig. 5, suggesting that the internal quantum efficiency of our samples is nearly the same as CSS:Ce3+. Figure 6 represents the PL decay curves of CZSC(x):0.02Eu2+ (x = 0, 0.3, and 1.1) excited by a 355 nm pulsed laser. The lifetimes are determined to be 1.64, 1.08, and 0.77 μs, respectively. The fluorescence lifetimes of Eu2+ reduce with increasing x, as plotted in the inset. Because the phosphor is mixed by two phases of Ca3SiO4Cl2 and Ca3Zn(SiO4)Cl2, the longest lifetime of 1.64 μs for Zn free phosphor is attributed to the Ca3SiO4Cl2 phase. Accordingly, the shortest lifetime of 0.77 μs for x = 1.1 belonging to the Ca3Zn(SiO4)Cl2 phase. Thus, the mixed phases exhibit an intermediate lifetime depending on the components in proportion of the two phases. The decay curves can be expressed by a double-exponential equation

$$I(t) = A e^{-\frac{t}{\tau_1}} + B e^{-\frac{t}{\tau_2}}$$  \[1\]

where A and B are representative of the relative amount of Ca3SiO4Cl2 and Ca3Zn(SiO4)Cl2 phases, with A + B = 1. The fluorescence decay curves for various x are well fitted by using Eq. 3 with variable A and B pair values. As an example, the decay pattern for x = 0.3 with a good fitting is shown in Fig. 6.

In fact, the lifetime τ is dominated by the radiative transition rate WR and the nonradiative decay rate WNR, which can be written as τ = 1/(WR + WNR). Generally, the nonradiative rate increases with raising temperature. In Fig. 7, the fluorescence lifetimes almost stayed unchanged against temperatures for the samples CZSC(x):0.02Eu2+ (x = 0, 0.3, and 0.9). This indicates that the nonradiative decay rate is much less than the radiative decay rate, leading to high internal quantum efficiency based on the relationship

$$\eta_{in} = \frac{W_R}{W_R + W_{NR}}$$

Comparison of luminescent properties of Ca3Zn(SiO4)Cl2(CZSC):Eu2+ with Ca3Mg(SiO4)Cl2(CMSC): Eu2+ and Ca3Sc2Si3O12(CSS):Ce3+ green-emitting phosphors.— In Eu2+-doped alkaline-earth chlorosilicate phosphors, only Ca3Mg(SiO4)Cl2:Eu2+ can be compared with commercial phosphors in terms of PL intensity as an LED phosphor. In 2007, Shimomura et al. developed Ca3Sc2Si3O12:Ce3+ as a green-emitting color converter for white LED. It was pointed out that both CMSC:Eu2+ and CSS:Ce3+ are higher than the reference YAG in PL peak intensity under 450 nm excitation.7,21 With the purpose of a green emitting phosphor for LED devices, the PLE and PL spectra of CZSC:0.05Eu2+ are presented in Fig. 8a with that of CMSC:0.1Eu2+ and CSS:0.06Ce3+ phosphors for comparison. The

Figure 4. (Color online) Powder diffuse reflection spectra of Ca3SiO4Cl2 and the samples CZSC(x):yEu2+.

Figure 5. (Color online) The integrated PL intensities vs absorptivities of 450 nm excitation light in CZSC(x):yEu2+ series samples and Ca3Sc2Si3O12:Ce3+ (CSS) phosphor.

Figure 6. (Color online) The fluorescence decay curves of CZSC(x):0.02Eu2+ (x = 0, 0.3, and 1.1) excited by 355 nm pulsed laser. The inset is the dependence of the fluorescence lifetimes on Zn concentration (x). The red lines are the fitting results using Eq. 1.
PL integrated intensity of CZSC:0.05Eu2+ for the CZSC:0.05Eu2+ sample is much higher than CMSC:0.1Eu2+, which notice that the intensity of the PLE band in the range of 400–450 nm for ZnCa8Zn4SiO4Cl2:Eu2+ shows an emission band peaked at 505 nm with a more intense excitation band in blue centered at 450 nm than CaMgSiO4Cl2:Eu2+ and CaSiO4Cl2:Eu2+. The PL integrated intensity under blue excitation at 450 nm of CaZn(SiO3)Cl2:Eu2+ can be 1.3 times stronger than that of CaMg(SiO3)Cl2:Eu2+ and nearly the same as that of a CaSc2SiO4Cl2:Ce3+ phosphor. The enhanced PL intensity in CaZn(SiO3)Cl2:Eu2+ is attributed to the enhanced absorption in the blue region. The broad excitation band and strong emission indicate that CaZn(SiO3)Cl2:Eu2+ could be a good phosphor candidate for blue LED pumped green traffic light LED lights and white LEDs.

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**References**


**Figure 7.** (Color online) Temperature dependence of fluorescence lifetimes in CZSC(0.02Eu2+)
(x = 0, 0.3, and 0.9) in the temperature range of 10–300 K.

**Figure 8.** (Color online) (a) PL and PLE spectra of green-emitting CZSC:0.05Eu2+, CMSC:0.1Eu2+, and CSS:0.06Ce3+ phosphors under 450 nm excitation. (b) The blue-pumped green LED with the blends of CZSC:0.05Eu2+ phosphors under the forward-bias currents of 20 mA.