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Near UV and blue-based LED fabricated with $Ca_8Zn(SiO_4)_4Cl_2:Eu^{2+}$ as green-emitting phosphor

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ABSTRACT

Green-emitting phosphor $Ca_8Zn(SiO_4)_4Cl_2:Eu^{2+}$ has been prepared by the solid state reaction method and there luminescence properties are investigated. The excitation spectrum of $Ca_8Zn(SiO_4)_4Cl_2:Eu^{2+}$ shows an intense excitation band in the blue centered at 450 nm and emits with a maximum at 505 nm. The concentration quenching mechanism is studied and verified to be the energy transfer among the nearest-neighbor ions. Upon 450 nm excitation, the emission intensity of $Ca_8Zn(SiO_4)_4Cl_2:Eu^{2+}$ is much stronger than the green emitting $Ca_3SO_4Cl_2:Eu^{2+}$ phosphor and even higher than YAG:Ce^{3+}. This excitation spectrum range matches UV and blue light-emitting diodes (LEDS) chips very well, suggesting $Ca_8Zn(SiO_4)_4Cl_2:Eu^{2+}$ could be a promising green emitting phosphor candidate for LED devices.

1. Introduction

The light-emitting diodes (LEDS)-based white light sources have received increasing interest in recent years for their promising applications such as automotive displays, and solid-state lighting due to lower energy consumption, good reliability, long lifetime and environmental protection [1,2]. The first commercially available white light emitting diodes (LEDs) based on phosphors was produced in 1996, which combines a blue light emitting (In,Ga)N with a yellow YAG:Ce phosphor [3]. However, this type of white light has poor color rendering because of the color deficiency in the red and blue–green region. To solve this problem, green and red phosphors in combination with a blue LED and red, green, and blue phosphors with a UV LED have been suggested as alternatives [4,5]. Besides, the UV or blue LEDs are expected to replace the conventional green LEDs in the field of traffic, for example, Zhang et al. reported near-UV LED-pumped green LEDs that were considered stable and efficient for potential applications for traffic signals [6]. Thus, for excellent color rendering index and high down-converting efficiency, both applications need efficient green phosphors that should have the excitation wavelength matching with the emission wavelength of the blue LEDs (λ_{em} = 440–470 nm) or the UV LEDs (λ_{em} = 350–410 nm).

Recently, Eu^{2+}-activated chlorosilicates have attracted more attention due to their high luminescent efficiency, low synthesis temperature, and high physical chemistry stability. Especially, Eu^{2+} activated $Ca_3SiO_4Cl_2$ and $Ca_8Mg(SiO_4)_4Cl_2$ emitting a bluish green band just peaking at around 505 nm are expected to be fairly suitable for near-UV and blue LED excitation [7–10]. Synthesis methods have been investigated to further improve the luminescent intensity of these phosphors for UV excitation [11–13].

In our previously reported, we have synthesized an intense green emitting $Ca_8Zn(SiO_4)_4Cl_2:Eu^{2+}$ phosphor by doping Zn in $Ca_3SiO_4Cl_2:Eu^{2+}$ and $Ca_8Zn(SiO_4)_4Cl_2:Eu^{2+}$ was confirmed well suited for UV and blue light excitation [14]. In this paper, Luminescent properties of $Ca_8Zn(SiO_4)_4Cl_2:Eu^{2+}$ and the effect of the Eu^{2+} concentration on the emission intensity are investigated in detail. We especially focus on the comparison of $Ca_8Zn(SiO_4)_4Cl_2$ with chlorosilicate phosphors and YAG:Ce^{3+} in terms of PLE and PL spectra, and the green LEDs are fabricated by coating the synthesized phosphors on a UV and blue LED chip to verify the real application capability.

2. Experimental

The $Ca_{8-x}Zn(SiO_4)_4Cl_2:xEu^{2+}$ (CZSC:xEu^{2+}) phosphors were synthesized by a high-temperature solid-state reaction. The starting materials, $CaCO_3$, $CaCl_2$, SiO_2 and ZnO of reagent grade, were mixed together with a mole ratio of $CaCO_3$, ZnO, SiO_2, and $CaCl_2$ = 1:1:1:1. A small amount of high-purity Eu_2O_3 was added into the mixture. The well-mixed reactants were placed in a crucible closed with a lid. The reactants were calcined at 900 °C in 10% H_2/90% N_2 for 4 h. The excess of $CaCl_2$ and ZnO was added in the reactant when synthesized phosphors [14]. The synthesis procedure of samples $Ca_3SiO_4Cl_2$(CSC) are similar to that described previously [7].

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Powder X-ray diffraction (XRD) data were collected using Cu Kα radiation (λ = 1.54056 Å) on a Bruker D8 Advance diffractometer equipped with a linear position-sensitive detector (PSD-50 m, M. Braun), operating at 40 kV and 40 mA with a step size of 0.02° (2θ) in the range of 10–70°. Field emission scanning electron microscopy (FE-SEM) images were taken on S-4800 (Hitachi Company) electron microscopes. The measurements of photoluminescence (PL) and photoluminescence excitation (PLE) spectra were performed by using a Hitachi F4500 spectrometer equipped with a 150 W xenon lamp under a working voltage of 700 V. The phosphors, $Ca_3SiO_4Cl_2$(CSC), Ba_2SiO_4 and YAG, were synthesized as references. We determined the Eu^{2+} concentrations at 2% which the PL intensities reach their maxima under 450 nm light excitation for $Ca_3SiO_4Cl_2$. These appropriate samples were used to obtain the following experimental results.

3. Results and discussion

Fig. 1 shows the XRD patterns of Eu^{2+} doped CZSC. The CZSC:0.12Eu^{2+} sample is in general agreement with the standard data of PDF Card No. 39-1421. Some weak impurity peaks are also observable, that are assigned to $Ca_3SiO_4Cl_2$ phase and marked with circle symbols. The intensity of impurity phases is too small that the effect on luminescence of CZSC:Eu^{2+} could be neglected.

The diffuse reflectance, PL and PLE spectra of CZSC:Eu^{2+} are depicted in Fig. 2. A strong absorption in the region from 300 to 480 nm is observed, which is derived from the 4f–5d electronic dipole allowed transitions of the Eu^{2+} ion. Upon 315 nm excitation, CZSC:0.12Eu^{2+} shows a strong green emission band with a peak at 505 nm and a weak blue band peaking around 425 nm. This result is similar to the $Ca_8Mg(SiO_4)_4Cl_2$:Eu^{2+} reported by Zhang and Liu [10]. According to the crystal structure given in Refs. [15,16], $Ca_8Zn(SiO_4)_4Cl_2$ crystallizes in a cubic system with the space group of P21/c and has three crystallographically independent cation sites in a unit cell, namely, one eight-coordinated Ca^{2+} site, one six-coordinated Ca^{2+} sites and one four-coordinated Zn^{2+} sites. The blue emission band at around 425 nm can be assigned to the Eu^{2+} ions occupying six-coordinated Ca^{2+} sites, and the green emission band at around 505 nm is assigned to Eu^{2+} ions occupying eight-coordinated Ca^{2+} site. With different excitation wavelengths of 315, 400, and 450 nm, there are little changes in the green emission except the emission intensity. As shown in Fig. 2, the very broad excitation spectrum for 505 nm emission has several excitation bands peaking around 253, 320, 400, and 450 nm, indicating CZSC:Eu^{2+} can be used as a promising phosphor with an green component applied to white LED technology, due to its strong luminescence and excellent profile of the PLE spectra.

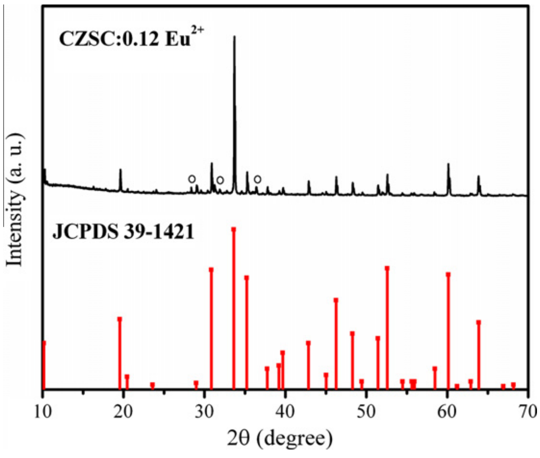

Fig. 1. XRD patterns of Eu^{2+} doped CZSC. ○ represents phase of $Ca_3SO_4Cl_2$.

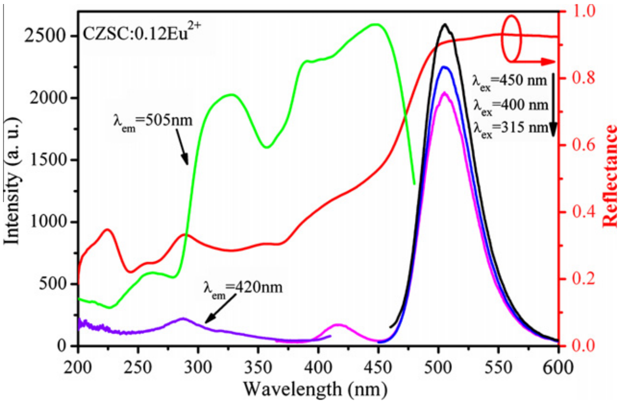

Fig. 2. The diffuse reflection, PL and PLE spectra of the CZSC:Eu^{2+} phosphor.

The effect of the Eu^{2+} concentration x on the emission intensity of Eu^{2+}-doped CZSC is shown in Fig. 3. The emission intensity under 450 nm excitation increases with increasing Eu^{2+} concentration, maximizing at about $x = 0.12$. Concentration quenching occurs, when the Eu^{2+} concentration is beyond 0.12. Concentration quenching is mainly caused by the nonradiative energy transfer among Eu^{2+}, which usually occurs as a result of an exchange interaction, radiation reabsorption or a multipole–multipole interaction [16]. Since the fluorescent mechanism of Eu^{2+} in CZSC phosphor is the 4f–5d allowed electric-dipole transition, the process of energy transfer should be controlled by electric multipole–multipole interaction [17]. According to the report of Van Uitert, the emission intensity (I) per activator ion follows the equation [18,19]

$$\frac{I}{x} = K\left[1 + \beta(x)\frac{Q}{3}\right]^{-1} \tag{1}$$

where x is the activator concentration, I/x is the emission intensity (I) per activator concentration (x), and K and β are constants for the same excitation condition for a given host crystal. According to (1), $Q = 3$ for energy transfer among the nearest-neighbor ions, while $Q = 6$, 8 and 10 for dipole–dipole (d–d), dipole–quadrupole (d–q), and quadrupole–quadrupole (q–q) interactions [18,20]. To get a Q value for the emission center, the dependence of log (I/x) on log (x) is plotted, as shown in Fig. 4. It can be seen that the dependence of log (I/x) on log (x) is linear and the slope is −0.985. The value of Q can be calculated to be 2.96, which is approximately equal to 3. It

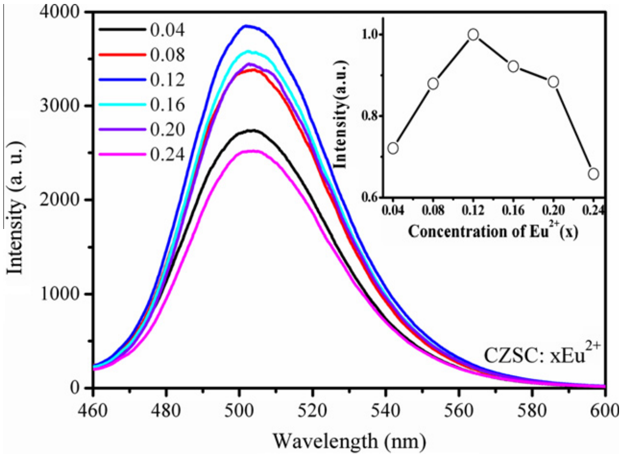

Fig. 3. The PL spectra of the CZSC:xEu^{2+} phosphors system for various Eu^{2+} concentrations. The inset represents the Eu^{2+} emission intensities as a function of Eu^{2+} concentration (x) (λ_{ex} = 450 nm).

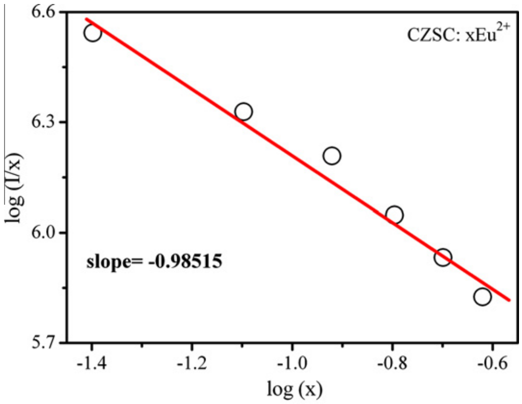

Fig. 4. The dependence of log (I/x) on log (x) in CZSC:xEu^{2+} phosphors (λ_{ex} = 450 nm).

means that the quenching is directly proportional to the ion concentration, which indicates that the concentration quenching is caused by the energy transfer among the nearest-neighbor ions in the CZSC:Eu^{2+} phosphor system.

With the purpose of a green emitting phosphor for LED devices, the scanning electron microscope image and the temperature-dependent emission intensity of CZSC:0.12Eu^{2+} sample is shown in Figs. 5 and 6. The phosphor powders are uniform and the phosphor crystals show irregular shapes with the dimension of 1–5 μm, which may ensure that CZSC:0.12Eu^{2+} phosphor powders would be dispersed well in the solvent and form phosphor film coated onto the surface of a GaN chip when fabricating LEDs. A comparison between the thermal quenching properties of CZSC:0.12Eu^{2+} and Ba_2SiO_4:Eu^{2+} (Fig. 6, inset) shows that the thermal quenching of CZSC:0.12Eu^{2+} is as good as Ba_2SiO_4:Eu^{2+}. These results also indicate the CZSC:0.12Eu^{2+} could be a promising phosphor for LED applications.

The PLE and PL spectra of CZSC:0.12Eu^{2+} are presented in Fig. 7 with that of CSC:0.02Eu^{2+} and YAG:0.06Ce^{3+} phosphors for comparison. The PL peak intensity of CZSC:0.12Eu^{2+} can be 1.9 times higher than the green emitting phosphor $Ca_3SO_4Cl_2$:Eu^{2+} and even higher than YAG:Ce^{3+} under the same excitation condition at 450 nm. According to the above discussion, the CZSC:Eu^{2+} phosphor could be a green phosphor candidate for creating white light in phosphor converted LEDs. Fig. 6b and c presents the blue and UV pumped green pcLED using CZSC:0.12Eu^{2+} phosphor under the forward-bias currents of 20 mA. The UV and blue light is down-converted into an intensive green light around 505 nm, which is exactly close to the ideal wavelength for green traffic lights and as a component of white LED.

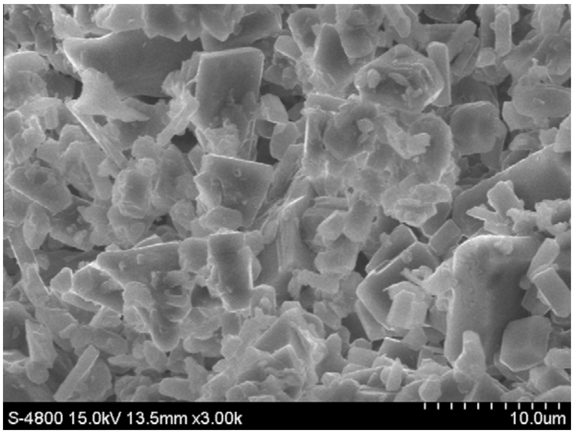

Fig. 5. SEM image of the CZSC:0.12Eu^{2+} phosphor power.

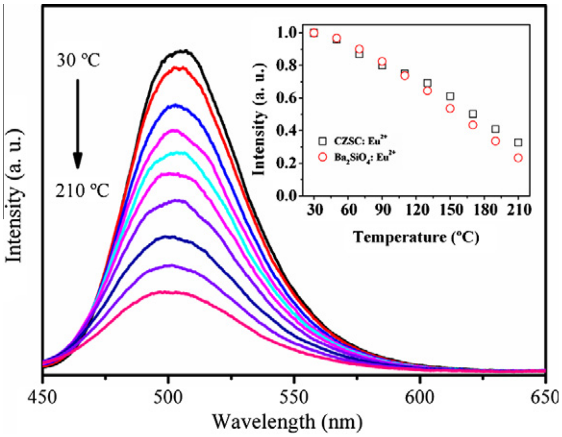

Fig. 6. The temperature-dependent emission intensity of the CZSC:0.12Eu^{2+} sample. Inset: normalized PL intensity as a function of temperature. For comparison, thermal quenching data of Ba_2SiO_4:Eu^{2+} excited at 400 nm is also measured as a reference.

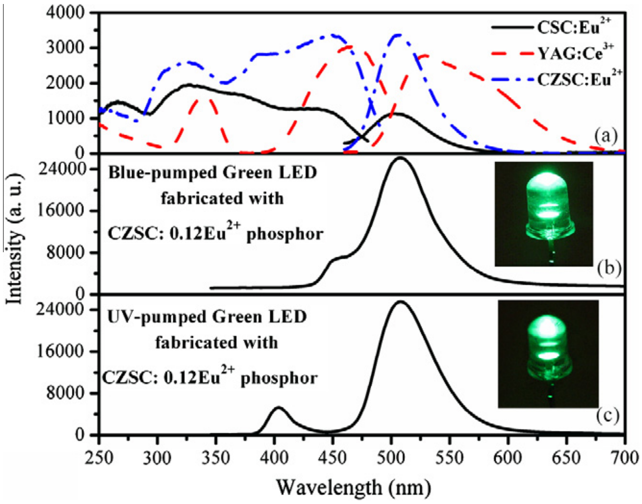

Fig. 7. (a) The PLE and PL spectra of CZSC:0.12Eu^{2+}, CSC:0.02Eu^{2+} and YAG:0.06Ce^{3+} phosphors. (b) The blue-pumped green LED with the blends of CZSC:0.12Eu^{2+} phosphors under the forward-bias currents of 20 mA. (c) The UV-pumped green LED with the blends of CZSC:0.12Eu^{2+} phosphors under the forward-bias currents of 20 mA.

4. Conclusion

In summary, we have prepared green emitting $Ca_8Zn(SiO_4)_4Cl_2$:Eu^{2+} phosphors by high temperature solid state reaction method. It shows an emission band peaking at 505 nm with a more intense excitation band in the blue centered at 450 nm. The luminescent intensity reaches the maximum when the concentration of Eu^{2+} is 12%, and the result of theoretical calculation suggests that the energy transfer among the nearest-neighbor ions plays a major role in the mechanism of concentration quenching of Eu^{2+}. The PL peak intensity under blue excitation at 450 nm of $Ca_8Zn(SiO_4)_4Cl_2$:Eu^{2+} is much stronger than the green emitting phosphor $Ca_3SO_4Cl_2$:Eu^{2+} and even higher than YAG:Ce^{3+} phosphor. The fabricated pcLED using blue and UV LED with the phosphors show a bright green luminescence, implying that $Ca_8Zn(SiO_4)_4Cl_2$:Eu^{2+} may be serve as a potential green emitting phosphor candidate for LED devices.

Acknowledgments

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