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Luminescent Properties of Mn^{2+} Co-doped $Ca_8Mg(SiO_4)_4Cl_2:Eu^{2+}$ Phosphor and Its Application in White LEDs

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Since visible LEDs were first reported in the 1960s, they have been widely studied as a backlight for liquid crystal displays (LCD) and solid-state lighting.[1-2] In particular, the efficiency of white LED lighting is higher than that of the incandescent lamps, and is currently competitive with fluorescent lamps. LEDs are a type of diode with a P-N junction semiconductor.[3-5] The most common method for generating a white LED for solid state lighting is to combine a blue LED with a yellow phosphor, a technique developed by Nichia. The white LEDs were composed of blue LEDs emitting at 460 nm, and cerium doped yttrium aluminum garnet (YAG:Ce) phosphor has a yellow emission band.[6]

In the present work, we have synthesized a $Ca_8Mg(SiO_4)_4Cl_2$: Eu^{2+}, Mn^{2+} yellow phosphor. The Mn^{2+} co-doped $Ca_8Mg(SiO_4)_4Cl_2:Eu^{2+}$ phosphor is an efficient phosphor which emits yellow emission band (550 nm) through excitation under the ultraviolet and blue light. The photoluminescence excitation and emission spectra, and the temperature dependence of $Ca_8Mg(SiO_4)_4Cl_2$: Eu^{2+}, Mn^{2+} were measured. The optical properties of LEDs fabricated by combining UV chips (λ_{em}=405 nm) with $Ca_8Mg(SiO_4)_4Cl_2:Eu^{2+}$, Mn^{2+} phosphors were measured.

Experimental

$Ca_8Mg(SiO_4)_4Cl_2:Eu^{2+}$, Mn^{2+} phosphor was synthesized *via* a solid-state reaction method. The starting materials were CaO, $CaCl_2$, MgO, SiO_2, Eu_2O_3 and MnO with a purity of 99.9% (Aldrich). Initially, appropriate proportions of the raw materials were mixed in acetone and dried in an air oven at 80 °C. The mixed powder was fired at 900 °C, 1000 °C, 1100 °C and 1200 °C for 3h under a reduced atmosphere using 25% H_2/75% N_2 gas. The resultant samples were characterized by using a Rigaku (D/MAX-2200V) X-ray diffraction (XRD) system with Cu Kα radiation (Ni filter). Photoluminescence characteristics of the synthesized phosphor were measured by a spectrophotometer. White LEDs were manufactured by synthesized phosphor with epoxy on InGaN-based blue chips with 405 nm emission wavelength. The luminescent properties of the LEDs were investigated in a spectrascan PR650 with a 50 cm single-grating monochrometer under a forward bias of 20 mA.

Results and Discussion

The phosphor samples with Mn^{2+} co-doped $Ca_8Mg(SiO_4)_4Cl_2:Eu^{2+}$ were prepared using a solid-state method. The optimum conditions of the phosphors at various concentrations of Eu^{2+} and Mn^{2+}, flow of the gas, and the reaction temperature were determined by measuring their photoluminescence spectra.

The $Ca_8Mg(SiO_4)_4Cl_2:Eu^{2+}$, Mn^{2+} was fired at 900 °C, 1000 °C, 1100 °C and 1200 °C in 25% H_2/75% N_2 gas atmosphere, respectively. The XRD results are shown in Figure 1. The patterns demonstrate mixed phases with a major phase ($Ca_8Mg(SiO_4)_4Cl_2$) and a minor phase (Ca_2SiO_4) in the sample fired at 1000 °C. This change arose due to the reaction of calcium oxide with calcium chloride. The crystallinity and phase purity of $Ca_8Mg(SiO_4)_4Cl_2:Eu^{2+}$, Mn^{2+} were improved by decreasing the ratio of calcium oxide to calcium chloride mixed precursor and increasing the temperature of synthesis. The $Ca_8Mg(SiO_4)_4Cl_2$ phase (JCPDS card No. 49-1855) was clearly observed at 1100 °C when the mole ratio of calcium oxide compared to calcium chloride was under 150%.

The emission spectra (λ_{ex} = 450 nm) of phosphor $Ca_8Mg(SiO_4)_4Cl_2:Eu^{2+}$, Mn^{2+} are shown in Figure 2. When the Mn^{2+} ion is not present, the emission spectra show broadband characteristics with a green band emission at 512 nm and a blue band emission at 428 nm. These two bands are due to the Eu^{2+} ions occupying a different crystal site. The 428nm and 512nm emission bands are attributed to the $4f^7(^8S_{7/2})$-$4f^65d$ transition of a Eu^{2+} ion substituted by a Ca^{2+} (I) and a Ca^{2+} (II) site. Eu^{2+} ions in $Ca_8Mg(SiO_4)_4Cl_2:Eu^{2+}$, Mn^{2+} phosphors have optimal con-

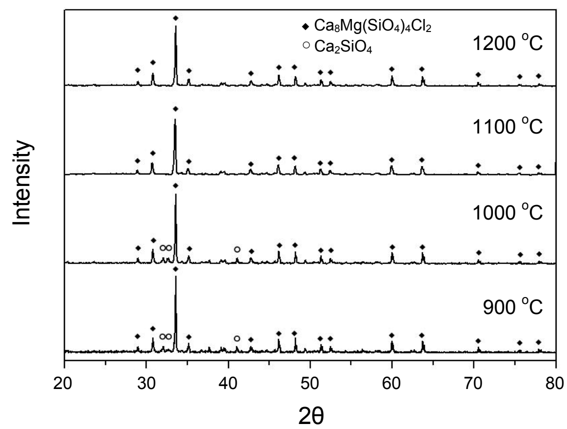

Figure 1. XRD patterns of the $Ca_8Mg(SiO_4)_4Cl_2:Eu^{2+}$, Mn^{2+} phosphors heat-treated at different temperatures ((a) 900 °C, (b) 1000 °C, (c) 1100 °C, (d) 1200 °C).

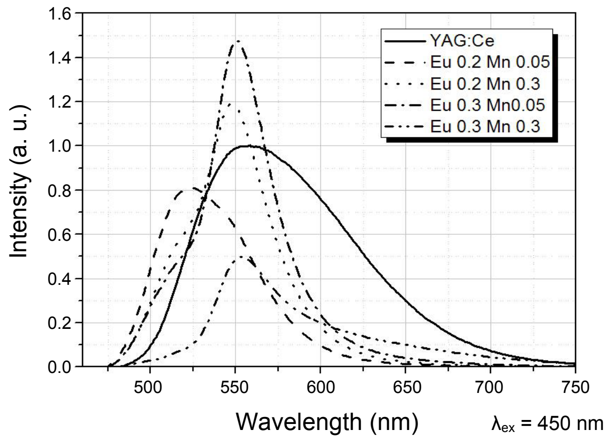

Figure 2. The emission spectra of the $Ca_8Mg(SiO_4)_4Cl_2$:Eu^{2+}, Mn^{2+} phosphors.

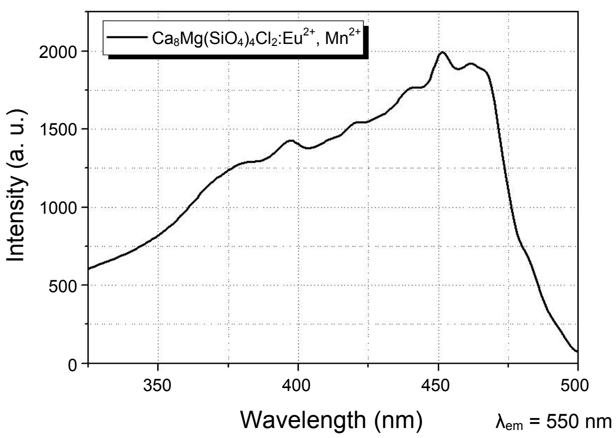

Figure 3. The excitation spectra of the $Ca_8Mg(SiO_4)_4Cl_2$:Eu^{2+}, Mn^{2+} phosphors.

ditions at 0.05 mol. Moreover, with the gradual addition of Mn^{2+} ions, the emission peak appeared at 550 nm with an increase in emission peak intensity. When the Mn^{2+} concentration increased, the emission intensities of the 428 and 512 nm bands decreased with a significant increase of the 550 nm band. The 550 nm emission band occurred as a result of the transtion from $^4T_1$ to $^6A_1$ of Mn^{2+} ions substituted in the Ca^{2+} (I, II) site.

The excitation spectra of the Mn^{2+} co-doped $Ca_8Mg_1(SiO_4)_4Cl_2$: Eu^{2+} phosphor are shown in Figure 3. The prepared phosphors were fired at different temperatures. The $Ca_8Mg(SiO_4)_4Cl_2$:Eu^{2+}, Mn^{2+} phosphor showed a broad excitation wavelength ranging from 300 nm to 500 nm. As can be seen from the figure, $Ca_8Mg(SiO_4)_4Cl_2$:Eu^{2+}, Mn^{2+} can be applied as a yellow phosphor for UV white LED with an emission spectrum.

The $Ca_8Mg_1(SiO_4)_4Cl_2$: Eu^{2+}, Mn^{2+} phosphor was mixed with transparent epoxy and accumulated on an InGaN-based LED

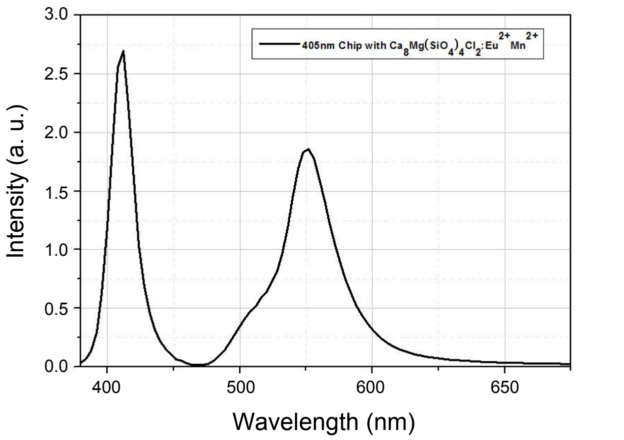

Figure 4. The emission spectra of phosphor on a InGaN-based UV LED under a 20 mA drive current.

chip. The emission spectra of the InGaN (405 nm)-based $Ca_8Mg_1(SiO_4)_4Cl_2$: Eu^{2+}, Mn^{2+} phosphor are shown in Figure 4. In the case of the InGaN-based $Ca_8Mg_1(SiO_4)_4Cl_2$: Eu^{2+}, Mn^{2+} LED, there are two distinct emission bands from the InGaN-based LED chip and this phosphor. The manufactured white LED in this study shows the CIE chromaticity (CIE x = 0.33, CIE y = 0.33) and the color temperature of 5950K. These results suggest that $Ca_8Mg(SiO_4)_4Cl_2$: Eu^{2+}, Mn^{2+} phosphors are suitable for general illumination.

Conclusion

In the present work, Mn^{2+} co-doped $Ca_8Mg(SiO_4)_4Cl_2$: Eu^{2+} phosphors were synthesized by a solid-state method, and their optical properties were investigated. $Ca_8Mg(SiO_4)_4Cl_2$: Eu^{2+}, Mn^{2+} phosphors have good photoluminescence properties for pc-LED due to a broad excitation band in the near-UV range. In addition, integrating the fabricated white LED InGaN-base chip (405 nm) with a $Ca_8Mg(SiO_4)_4Cl_2$: Eu^{2+}, Mn^{2+} phosphor shows white light. The $Ca_8Mg(SiO_4)_4Cl_2$:Eu^{2+}, Mn^2 is a good phosphor candidate for creating white light in pc white LEDs.

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