

Synthesis and Luminescence Properties of CaS:Eu²⁺, Si⁴⁺, Ga³⁺ for a White LED

Sung-Il Oh, Yong-Kwang Jeong, and Jun-Gill Kang*

Department of Chemistry, Chungnam National University, Daejeon 305-764, Korea. *E-mail: jgkang@cnu.ac.kr

Received October 8, 2008, Accepted December 29, 2008

The luminescence intensity of calcium sulfide codoped with Eu²⁺, Si⁴⁺ and Ga³⁺ was investigated as a function of the dopant concentration. An enhancement of the red luminescence resulted from the incorporation of Si⁴⁺ and Ga³⁺ into CaS:Eu²⁺. The non-codoped CaS:Eu²⁺ converted only 3.0% of the absorbed blue light into luminescence. As the Si⁴⁺ and Ga³⁺ were embedded into the host lattice, the luminescence intensity increased and reached a maximum of Q = 10.0% at optimized concentrations of the codopants in CaS. Optimized CaS:Eu²⁺, Si⁴⁺, Ga³⁺ phosphors were fabricated with blue GaN LED and the chromaticity index of the phosphor-formulated GaN LED was investigated as a function of the wt% of the optimized phosphor.

Key Words: CaS:Eu²⁺ phosphor, Incorporation of Si⁴⁺ and Ga³⁺, Luminescence, LED

Introduction

The combination of a blue gallium nitride (GaN) light-emitting-diode (LED) and a yellow YAG:Ce³⁺ ((Y_{1-x}Gd_x)₃(Al_{1-x}Ga_x)₅O₁₂:Ce³⁺) phosphor has been widely used as a conventional white LED.^{1,2} Comparative investigation on the synthesis of YAG:Ce³⁺ has been extensively performed because yellow phosphor is still the best phosphor for the white LED commercial market.^{3,6} YAG:Ce³⁺ phosphor that is excited by a blue GaN diode produces a yellow emission and results in white light as seen by human eyes. However, the color rendering of this white LED is scant in the red color. For high color rendering, the red phosphor must be modified in a white LED. One promising red phosphor that is excitable by blue light is calcium sulfide doped with Eu²⁺ (CaS:Eu²⁺).⁷⁻⁹ A red emission from Eu²⁺ is characterized by the transitions between the ⁸S_{7/2} (4f⁷) ground state and the ²T_{2g} (4f⁶5d) excited state under a calcium sulfide crystal field.¹⁰ The partial replacement of Ca by Sr causes a blue-shift of the emission peak, which is strongly associated with the change of the crystal-field strength.¹¹ Preparation methods that use rare earth ions as codopants have been extensively investigated to improve the luminescence of CaS:Eu²⁺. However, these studies have focused on the persistent or thermo-luminescence properties.^{8,9,12-14} The luminescence properties of CaS:Eu²⁺ fabricated with the GaN LED are very limited. In the present study, we prepared silicon and gallium-coactivated CaS:Eu²⁺ phosphor by conventional method and investigated the incorporation effects of these ions on the luminescence properties. Then we packed the synthesized phosphor on a GaN chip and characterized the emitted light.

Experimental

The initial materials (purity > 99.9%) were CaCO₃, Ga₂O₃, SiO₂, Eu₂O₃, S and NH₄F which were purchased from Aldrich; they were taken in stoichiometric proportions. Excess sulfur and a few wt% of NH₄F (flux) were mixed by an agate mortar and pestle and then transferred to capped alumina crucibles. The mixture was fired three times at 900 °C for 3 h under a

N₂/H₂ reducing atmosphere in a tube furnace. Between each firing repetition, the samples were ground with additional sulfur.

The X-ray diffraction (XRD) patterns of the prepared phosphor were measured using a D/MAX-2200 Ultima diffractometer (Rigaku) with a graphite monochromator and Cu K α radiation ($\lambda = 0.1541$ nm). To measure the luminescence and excitation spectra, the phosphor was irradiated with the light from a 1000-W Xe lamp (working power, 400 W; Oriel) passing through an Oriel MS257 monochromator. The spectra were measured at 90° with an ARC 0.5-m Czerny-Turner monochromator equipped with a cooled Hamamatsu R-933-14 PM tube. The luminescence quantum yield, defined by

$$Q = \frac{\text{number of photons emitted}}{\text{number of photons absorbed}}$$

was determined using a previously described method.¹⁵ The recorded spectra for the quantum yield were corrected for the spectral response of the system using an Oriel 45-W quartz tungsten halogen lamp standard. All measurements were repeated three times. No significant experimental error was found.

To fabricate phosphor-converted LEDs, a blue GaN LED chip (350 × 350 μ m, South Epi) was used as a pumping source on which the lead frame was packed. The prepared phosphors, sieved under $\phi = 20$ μ m, were mixed with epoxy at various weight percentages and then were cast on the lead frame. After treatment under vacuum to remove air bubbles, the phosphor-cast LED was dried at 80 °C for 12 h. For the fabricated LEDs, the Commission International de L'Eclairage (CIE) chromaticity coordinates were recorded with a Minolta BM-7.

Results and Discussion

XRD. X-ray powder diffraction data were collected for CaS:0.01Eu²⁺, 0.1Ga³⁺, xSi⁴⁺, yGa³⁺ with various x and y values. As shown in Figure 1, for x = 0 and y = 0, and x = 0.1 and y = 0, the patterns were coincident with oldhamite CaS

lines (ICSD # 28902). For $x = 0$ and $y = 0.1$, however, several weak satellite lines appeared as minor lines (noted by symbols * and \times). Note that the satellite lines noted by * and \times were coincident with the main lines of α -Ga₂S₃ (ICSD # 488) and β -Ga_{1.33}S₂ (ICSD # 25568), respectively. With increasing x , the intensities of these satellite lines decreased and at $x = 0.1$, the sample formed almost single phase with cubic crystal structure of $Fm\bar{3}m$.¹⁶ This suggested that the addition of a suitable Si⁴⁺ concentration enhanced the crystallinity of the phosphor and therefore increased the luminescence intensity of CaS:Eu²⁺. However, the excess of Si⁴⁺ ions above the optimum concentration might act as a quencher.

Luminescence and quantum yield. Figure 2 shows the luminescence spectra of CaS:0.01Eu²⁺, x Si⁴⁺ with different Si⁴⁺ concentrations ($0 \leq x \leq 0.1$). The phosphor, excited at blue light, produced a red emission with a peak at 645 nm. The intensity slightly increased with increasing Si⁴⁺ concentration, and had a maximum at $x = 0.05$. Above this concentration, the intensity decreased with increasing x . When x was below 0.1, the peak position of the red emission from CaS:Eu²⁺, x Si⁴⁺ was nearly independent of the Si⁴⁺ concentration. The Si⁴⁺ ion only slightly affected the luminescence intensity of CaS:Eu²⁺. The excitation spectrum of the 645 nm emission was also measured at room temperature. As illustrated in

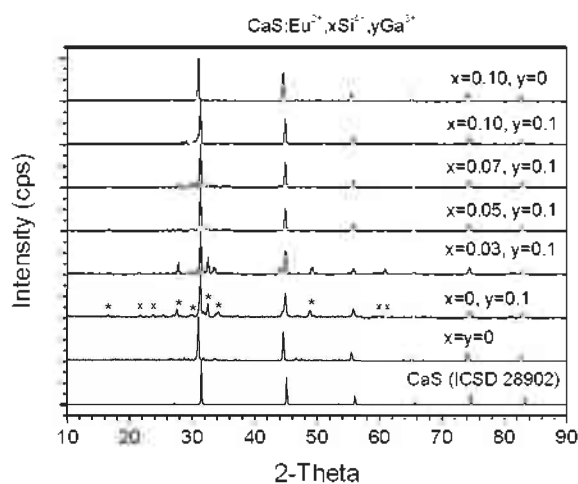


Figure 1. XRD patterns of CaS:0.01Eu²⁺, x Si⁴⁺, y Ga³⁺.

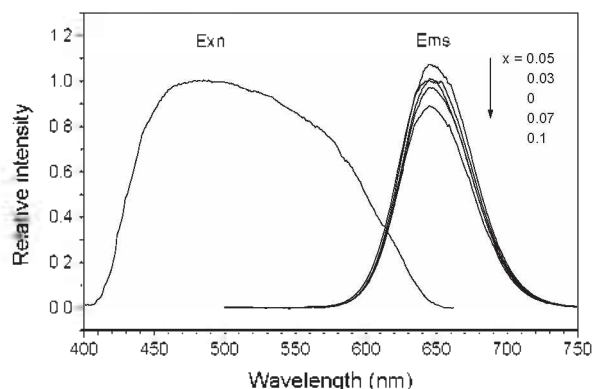


Figure 2. Luminescence spectra of CaS:0.01Eu²⁺, x Si⁴⁺ with $x = 0, 0.03, 0.05, 0.07$ and 0.10 mole; and excitation spectrum of the 645 nm emission ($x = 0$).

Figure 2, the excitation spectrum revealed that the blue GaN LED chip was a suitable pumping source for the red phosphor.

Next, we measured the luminescence spectra of CaS:Eu²⁺, x Si⁴⁺, y Ga³⁺ ($x = 0.05, 0 \leq y \leq 0.4$) by exciting at $\lambda_{\text{exc}} = 460$ nm. As shown in Figure 3, the peak position of the phosphor was affected by the concentration of Ga³⁺. The emission band blue-shifted with increasing concentration. The relative luminescence intensities of the phosphors are illustrated in Figure 4(a). The intensity increased slightly with increasing y , and had a maximum at $y = 0.1$. Above this concentration, the intensity decreased with increasing y . We also investigated the luminescence intensity of CaS:Eu²⁺, x Si⁴⁺, y Ga³⁺ ($0 \leq x \leq 0.1, y = 0.1$) as a function of the Si⁴⁺ concentration. As shown in Figure 4(b), the x dependency of the red luminescence of the Ga³⁺ codoped phosphor was different from that of the Ga³⁺ undoped phosphor. For the phosphor codoped with 0.1 mole of Ga³⁺, the intensity significantly increased with increasing Si⁴⁺ concentration, and had a maximum at $x = 0.05$. At this Si⁴⁺ concentration, the intensity increased by ca. 35% compared to CaS:Eu²⁺. These results revealed that the codoping Si⁴⁺ and Ga³⁺ to CaS:Eu²⁺ cooperatively enhanced the red emission, and that the optimum concentrations of Si⁴⁺ and Ga³⁺ in CaS:Eu²⁺ were approximately 0.05 and 0.1 moles, respectively.

We determined the critical concentration of the Eu²⁺ activator in CaS containing the optimum concentrations of Si⁴⁺ and Ga³⁺. As shown in Figure 5, the intensity of the red luminescence was significantly affected by the concentration of Eu²⁺. In the low concentration region, the intensity of the

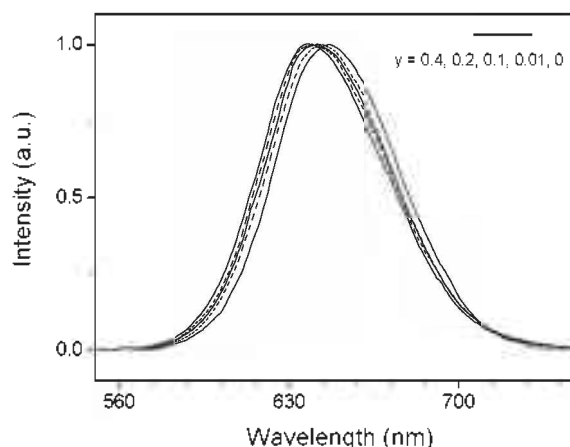


Figure 3. Luminescence spectra of CaS:0.01Eu²⁺,0.05Si⁴⁺, y Ga³⁺ with $y = 0, 0.01, 0.1, 0.2$ and 0.4 ($\lambda_{\text{exc}} = 460$ nm).

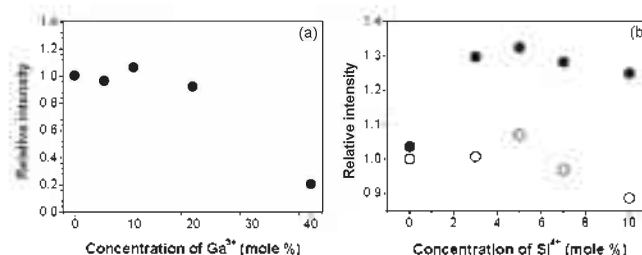


Figure 4. Relative maximum intensity of CaS:0.01Eu²⁺, x Si⁴⁺, y Ga³⁺ ($\lambda_{\text{exc}} = 460$ nm) with (a) $x = 0, 0 \leq y \leq 0.4$ and (b) $0 \leq x \leq 0.1, y = 0$ (open circles) and 0.1 (solid circles).

phosphor was markedly enhanced as z increased to $z = 0.01$. Above this concentration, the intensity decreased gradually with increasing z . The absolute value of the luminescence quantum yield, Q , of CaS:zEu²⁺,Si⁴⁺,Ga³⁺ on the 460 nm excitation was also measured as a function of the Eu²⁺ content (z) at room temperature. As plotted in Figure 5, the Eu²⁺ concentration dependency of the quantum yield was very similar to the case of the luminescence intensity. Q increased as the Eu²⁺ concentration increased, and reached a maximum at $z = 0.01$ moles per mole of CaS : $Q = 10.0\%$ for the 460 nm excitation. Above this concentration of Eu²⁺, Q decreased with increasing the concentration. These results indicated that the critical concentration of Eu²⁺ in CaS containing auxiliary Si⁴⁺ and Ga³⁺ ions was approximately 1 mole%.

At the critical concentration of Eu²⁺, the quantum yield of Si⁴⁺ and Ga³⁺-uncodoped CaS was only 3.0%. The improvement of luminescence efficiency by very small quantities of Si⁴⁺ and Ga³⁺ codopants can be associated with not only the improvement of the crystallinity of the phosphor but also the charge and size mismatches between the codopant and the host cation. The charge mismatch resulted in the creation of the charge compensating cation vacancy (CCV). The CCV situated around the activator lowered the local site-symmetry of the activator. The size mismatch has been more extensively tested for trivalent rare earth ions as a main perturbation.^{17,18} The incorporation of the codoping ion with smaller effective

ionic size and larger electronegativity in host lattice also gave rise to a reduction in the site-symmetry, distortions and/or stress in the neighboring activator. The codoping Si⁴⁺ ion with smaller size (26 pm) and larger electronegativity (1.90), compared with Ca²⁺ (100 pm, 1.00) and Ga³⁺ (62 pm, 1.81) ions, possibly gave rise to a stronger effect on the enhancement of the luminescence.

Device characterization. Optimized CaS:Eu²⁺,Si⁴⁺,Ga³⁺ phosphors were fabricated with blue GaN LEDs. The PL spectrum of the fabricated white LED was measured while applying 3.35-3.68 V at a constant current of 10 mA. Figure 6 shows a typical PL spectrum of one of the fabricated LED devices. The PL spectrum consisted of two bands: the sharp band peaking at 460 nm due to an emission from the pumping GaN diode, and a broad band peaking at 641 nm due to an emission from the red phosphor. The CIE 1931 chromaticity of the optimized phosphor with different weight percentages is shown in Figure 7. The chromaticity index (x, y) varied from (0.1433, 0.0402) for the naked GaN chip to (0.3813, 0.1542) for the 6 wt% phosphor blended with epoxy. The observed chromaticities of the fabricated LEDs varied along the line, connecting the blue LED ($\lambda_{\text{ems}} = 460$ nm) and the red phosphor chromaticity points. The results suggested that the prepared phosphor might be a potential red phosphor for a high-rendering white LED.

Conclusion

The addition of Si⁴⁺ and Ga³⁺ strikingly enhanced the luminescence intensity of CaS:Eu²⁺ synthesized by the solid-state reaction at 900 °C. The maximum intensity of red phosphor was obtained when 0.10 mol% of Eu²⁺, 5.0 mol% of Si⁴⁺ and 10 mol% of Ga³⁺ were used as dopants. The chromaticity index of the phosphor-fabricated GaN LED was (0.2412, 0.0882) for 2 wt% and (0.3813, 0.1542) for 6 wt% of phosphor.

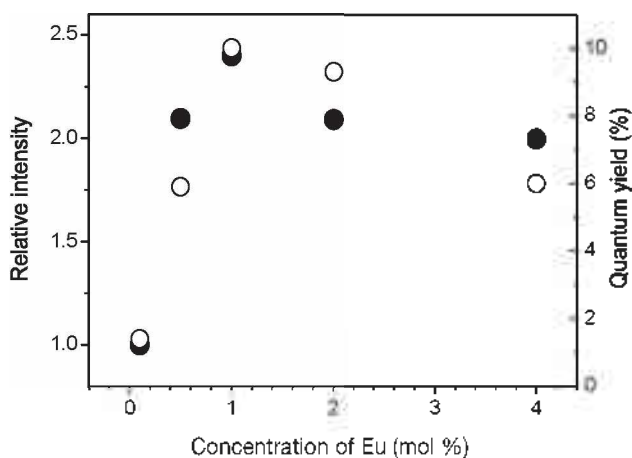


Figure 5. Relative maximum intensity (●) and absolute quantum yield (○) of CaS:zEu²⁺, 0.05Si⁴⁺, 0.1Ga³⁺ ($\lambda_{\text{exc}} = 460$ nm).

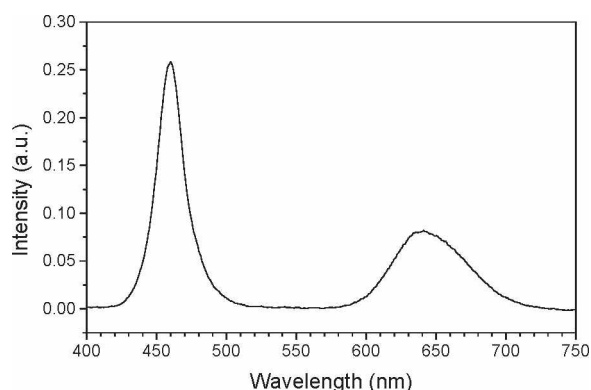


Figure 6. PL spectrum of phosphor-fabricated GaN LED.

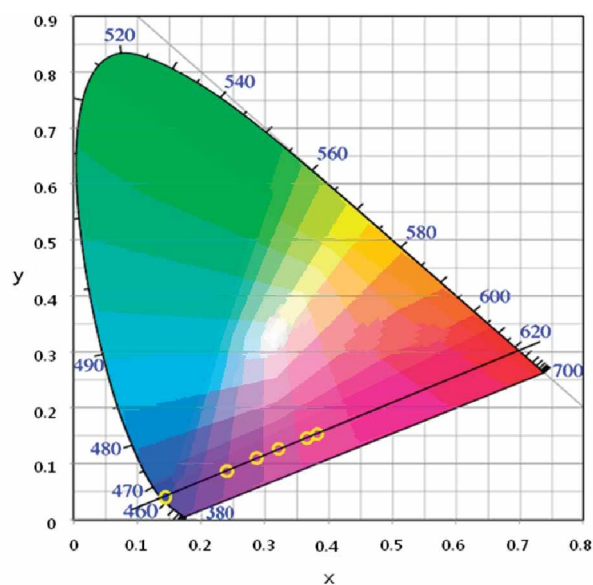


Figure 7. CIE indexes of GaN LED fabricated with various wt% of CaS:0.01Eu²⁺, 0.05Si⁴⁺, 0.1Ga³⁺ (circles from left to right: 0, 2, 3, 4, 5 and 6 wt%).

Acknowledgments. This study was supported by Chungnam National University.

References

1. Nakamura, S.; Fasol, G. *The Blue Laser Diode: GaN Based Light Emitters and Lasers*; Springer: Berlin, 1997.
2. Mueller-Mach, R.; Mueller, G. O.; Krames, M. R.; Trottier, T. *IEEE J. Sel. Top. Quantum Electron* **2002**, *8*, 339.
3. Pan, Y.; Wu, M.; Su, Q. *Mater. Sci. Eng. B* **2004**, *106*, 251.
4. Jia, D.; Wang, Y.; Guo, X.; Li, K.; Zou, Y. K.; Jia, W. *J. Electrochem. Soc.* **2007**, *154*, J1.
5. Yang, Z.; Li, X.; Yang, Y.; Li, X. *J. Lumin.* **2007**, *122-123*, 707.
6. Jang, H. S.; Im, W. B.; Lee, D. C.; Jeon, D. Y.; Kim, S. S. *J. Lumin.* **2007**, *126*, 371.
7. Shionoya, S. *Phosphor Handbook*; Shionoya, S.; Yen, W. M., Eds.; CRC Press: New York, 1999; Ch. 3.
8. Guo, C.; Huang, D.; Su, Q. *Mater. Sci. Eng. B* **2006**, *130*, 189.
9. Jia, D.; Wang, X.-J. *Optical Mater.* **2007**, *30*, 375.
10. Rubio, O. J. *J. Phys. Chem. Solid* **1991**, *52*, 101.
11. Sung, H.-J.; Cho, Y.-S.; Huh, Y.-D.; Do, Y. R. *Bull. Korean Chem. Soc.* **2007**, *28*, 1280.
12. Jia, D.; Jia, W.; Evans, D. R.; Dennis, W. M.; Liu, H.; Zhu, J.; Yen, W. M. *J. Appl. Phys.* **2000**, *88*, 3402.
13. Jia, D. *J. Electrochem. Soc.* **2006**, *153*, H198.
14. Kim, K. N.; Kim, J.-M.; Choi, K. J.; Park, J. K.; Kim, C. H. *J. Am. Ceram. Soc.* **2006**, *89*, 3413.
15. Kim, K.-B.; Kim, Y.-I.; Chun, H.-G.; Cho, T.-Y.; Jung, J.-S.; Kang, J.-G. *Chem. Mater.* **2002**, *14*, 5045.
16. Guentert, O. J.; Faessler, A. Z. *Kristallogr. Kristallgeom. Kristallphys. Kristallchem.* **1956**, *107*, 357.
17. Antic-Fidancev, E.; Hölsä, J.; Lastusaari, M.; Lupei, A. *Phys. Rev. B* **2001**, *64*, 195108.
18. Liu, X.; Han, K.; Gu, M.; Xiao, L.; Ni, C.; Huang, S.; Liu, B. *Solid State Comm.* **2007**, *142*, 680.