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## White light-emitting diodes of GaN-based $\text{Sr}_2\text{SiO}_4:\text{Eu}$ and the luminescent properties

Joung Kyu Park,<sup>a)</sup> Mi Ae Lim, Chang Hae Kim, and Hee Dong Park  
*Advanced Materials Division, KRICT, Taejon 305-600, Korea*

Joon Taik Park  
*Department of Chemistry, KAIST, Taejon 305-600, Korea*

Se Young Choi  
*Department of Ceramic Engineering, Yonsei University, Seoul 120-749, Korea*

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We have synthesized a  $\text{Eu}^{2+}$ -activated  $\text{Sr}_2\text{SiO}_4$  yellow phosphor and investigated an attempt to develop white light-emitting diodes (LEDs) by combining it with a GaN blue LED chip. Two distinct emission bands from the GaN-based LED and the  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  phosphor are clearly observed at 400 nm and at around 550 nm, respectively. These two emission bands combine to give a spectrum that appears white to the naked eye. Our results showed that GaN (400-nm chip)-based  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  exhibits a better luminous efficiency than that of the industrially available product InGaN (460-nm chip)-based YAG:Ce. © 2003 American Institute of Physics.  
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The white light-emitting diodes (LEDs) composed of InGaN blue LEDs and a yellow YAG:Ce phosphor have been investigated extensively due to their applications, such as back-lighting for liquid crystal displays and incandescent lamps. These applications are particularly useful for saving electric power owing to the lower energy consumption of LEDs.<sup>1,2</sup> In addition, there have been some detailed studies on the integration of the blue InGaN LED and the yellow YAG phosphor, as this creates white light from a combination of a blue LED emission (460 nm) and a broadband yellow YAG phosphor.<sup>3,4</sup> However, very few efficient new yellow phosphors have actually been discovered, besides the YAG:Ce phosphor and the organic luminescent materials.

In the present work, we have synthesized an  $\text{Eu}^{2+}$ -activated  $\text{Sr}_2\text{SiO}_4$  yellow phosphor and investigated in an attempt to develop white LEDs through the integration of the GaN blue LED chip ( $\lambda_{\text{em}}=400$  nm) and the  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  phosphor into a single package. As shown in this study, the GaN (400-nm chip)-based  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  white LED exhibits higher luminous efficiency compared with that of the commercially available InGaN (460-nm chip)-based YAG:Ce white LED.

In order to successfully synthesize exact stoichiometric compounds with fine particles and low agglomeration particles, a polymeric complex method using citric acid and ethylene glycol was used. The starting materials used in the polymeric complex method were  $\text{Sr}(\text{NO}_3)_2$ , tetraethyl orthosilicate (TEOS) and  $\text{Eu}_2\text{O}_3$ . Obtained from a high-purity chemicals laboratory, the materials had 99.9% purity. To prepare appropriate solutions, these raw materials were dissolved in distilled water and nitric acid, and then the required amount of each solution was collected on a quartz plate. Consequently, the mixture of citric acid and ethylene glycol (2.5 mol/10 mol ratio) was then added to the plate.

The solution was dried at 120 °C until a transparent solution was obtained. It was then reheated to 200 °C to initiate a condensation reaction that would produce a viscous polymeric resin. The resin was heat-treated at 350 °C to form a charcoal-like porous foam; it was successively milled and then fired in a tubular furnace at 1350 °C for 3 h. At this time the gas flow was adjusted to yield a mixture of 4 volumes of nitrogen to 1 volume of hydrogen. The powder samples were confirmed to be an  $\alpha'$ - $\text{Sr}_2\text{SiO}_4$  single phase with an orthorhombic structure. The luminescent characteristics of fired samples were obtained by a Perkin-Elmer LS-50 luminescence spectrometer with a flash lamp ( $\Delta v^{1/2}=10$   $\mu\text{s}$ ) as the excitation source. To compare the white luminescent LEDs between YAG:Ce and  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  phosphors, white luminescence conversion LEDs were fabricated. Based on the standard LED technology, GaN (400-nm chip)-based  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  white LEDs were encapsulated in a transparent epoxy resin. In the case of the commercially available YAG:Ce phosphor, however, the InGaN (460-nm chip) was used because its 460-nm blue emission was used as an optical excitation of the YAG phosphor. The relative emission spectra of a GaN-based  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  and InGaN-based YAG:Ce LED under a forward bias of 20 mA was measured using a 50-cm single-grating monochromator.

Fluorescence spectra of  $\text{Sr}_{2-x}\text{SiO}_4:\text{Eu}_x$  samples with different  $\text{Eu}^{2+}$  content are shown in Fig. 1. As can be seen from this figure, the emission spectra show a broadband character, and the fluorescence intensity increases with  $x$ , reaching a maximum at  $x=0.03$  mol. The broadness of the emission band indicates an interaction between the host and the activator, which can be attributed to the presence of an excited electron in an outer shell of the  $\text{Eu}^{2+}$  ion.<sup>5</sup> The emission band at about 520 nm shifts slightly to a longer wavelength with an increase in  $\text{Eu}^{2+}$  concentration. This may be attributed to some changes in the crystal field around  $\text{Eu}^{2+}$  that increased the  $\text{Eu}^{2+}$  concentration. Although the 4f elec-

<sup>a)</sup>Electronic mail: parkjk@pado.kRICT.re.kr

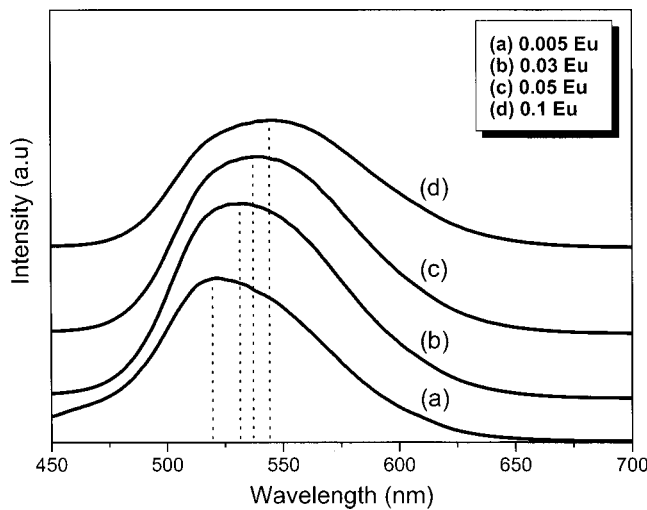


FIG. 1. The  $\text{Eu}^{2+}$  concentration dependence photoluminescence emission spectra of the  $\text{Sr}_2\text{SiO}_4$  system under the 410-nm excitation wavelength.

trons of  $\text{Eu}^{2+}$  are not sensitive to a lattice environment due to the shielding function of the electrons in the outer shell, the  $5d$  electrons are split by the crystal field, which may lead to a shift in its emission peak.

According to Ref. 6, the probability of an energy transfer among  $\text{Eu}^{2+}$  ions increases when the  $\text{Eu}^{2+}$  concentration increases. A nonradiative energy transfer from one  $\text{Eu}^{2+}$  ion to another  $\text{Eu}^{2+}$  ion usually occurs as a result of an exchange interaction, radiation reabsorption or a multipole–multipole interaction. In the case of the  $\text{Eu}^{2+}$  ion, the  $4f^7 \rightarrow 4f^6 5d^1$  transition is allowed, while the exchange interaction is responsible for the energy transfer of forbidden transitions and typical critical distance, which is about  $5 \text{ \AA}$ .<sup>7</sup> It is indicated that the exchange interaction plays no role in the energy transfer between  $\text{Eu}^{2+}$  ions. Since the  $4f \rightarrow 5d$  transition of  $\text{Eu}^{2+}$  is allowed, the energy transfer in the present case will occur only as a result of an electric multipolar interaction. As an increase of  $\text{Eu}^{2+}$  concentration, the distance between  $\text{Eu}^{2+}$  ions becomes less, and the probability of energy transfer among  $\text{Eu}^{2+}$  ions increases. In other words, the probability of  $\text{Eu}^{2+}$  ions at higher levels of  $5d$ , which make an energy transfer to the lower  $5d$  levels of  $\text{Eu}^{2+}$  ions, increases with an increase of  $\text{Eu}^{2+}$  concentration.<sup>6</sup> It makes it possible to shift of emission peak to the longer wavelength with an increase of  $\text{Eu}^{2+}$  concentration.

As already mentioned in Fig. 1, the shifting of the emission band to a longer wavelength with an increase of the  $\text{SiO}_2$  content is also observed. Table I presents the main ex-

TABLE I. Spectral parameters of the  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  for various  $\text{SiO}_2$  content.

	Excitation maximum (nm)	Emission maximum (nm)	Stokes shift ( $\text{cm}^{-1}$ )	CFS ( $\text{cm}^{-1}$ )
Sample A (Sr/Si=2/0.5)	332, 382	523	7057	3943
Sample B (Sr/Si=2/0.8)	332, 384	527	7067	4079
Sample C (Sr/Si=2/1.0)	332, 387	533	7078	4281
Sample D (Sr/Si=2/1.3)	332, 394	555	7363	4730

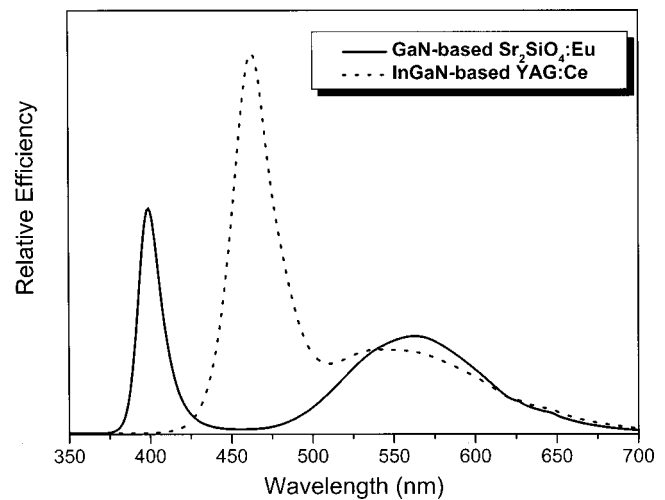


FIG. 2. Relative emission spectra of a white-emitting InGaN-based YAG:Ce LED and GaN-based  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  LED under a 20-mA drive current.

citation peaks, the emission peaks, the Stokes shift and the crystal field splitting (CFS). The excitation spectrum of sample A (Sr/Si=2/0.5) consists of two bands peaking around 332 and 382 nm, these two bands have almost merged and broadened so that the excitation spectrum appears as a broad single band. In addition, the emission band of sample A shows a single broad band maximizing at 523 nm, with the Stokes shift of around  $7057 \text{ cm}^{-1}$ , and the CFS is  $3943 \text{ cm}^{-1}$ . The emission band in sample D (Sr/Si=2/1.3), on the other hand, was observed at 555 nm. This, compared to other samples, is located at a longer wavelength accompanied by increases of the Stokes shift and CFS energy. It should be noted that the shift of the emission band to a longer wavelength occurs as the  $\text{SiO}_2$  content increases. The shift of the  $\text{Eu}^{2+}$  emission band depends on the host lattice, covalency, and the strength of the crystal field.<sup>8</sup> The increase of the  $\text{SiO}_2$  content indicates an increasing degree of covalency. As covalency increases, the interaction between the electrons is reduced, so that they spread out over wider orbitals.<sup>9</sup> Consequently, an increase in the covalency will reduce the energy difference between the ground state  $4f^7$  and the excited state  $4f^6 5d^1$ , so that there will be more splitting of the  $t_{2g}$  and  $e_g$  levels (which means a larger CFS). This increase in covalency may lead to the shifting of the emission band to a longer wavelength.

The relative emission spectra of the white-emitting InGaN (460-nm chip)-based YAG:Ce LED and the GaN (400-nm chip)-based  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  LED are shown in Fig. 2. In the case of the InGaN-based YAG:Ce LED and the YAG:Ce phosphor are clearly resolved at 460 nm and at around 550 nm, respectively. On the other hand, the GaN-based  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  LED shows two bands at 400 and 560 nm. The 400-nm emission band is due to a radiative recombination from a GaN active layer. This blue emission was used as an optical transition of the  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  phosphor. The 560-nm emission band is ascribed to a radiative recombination of  $\text{Eu}^{2+}$  impurity ions in the  $\text{Sr}_2\text{SiO}_4$  host matrix. It is presumed that energy from the 400-nm excitation band may be trapped at the  $\text{Eu}^{2+}$  ion, emitting a yellow emission at 560 nm. These two emission bands combine to give a spectrum

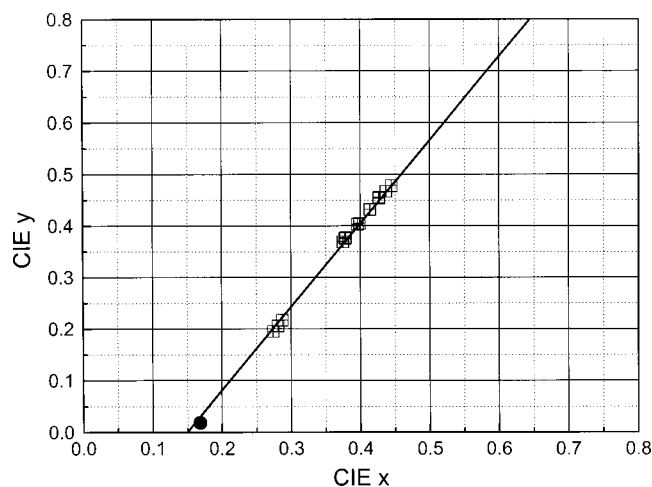


FIG. 3. CIE chromaticity points of GaN-based  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  LED and of the corresponding GaN LED. The chromaticity points of GaN-based  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  LED (marked by square), produced by varying the  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  concentration, are on the straight line connecting the chromaticity point of GaN LED (marked by a closed circle).

that appears white to the naked eye. The luminous efficiency of GaN-based  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  measured from these results is about 3.8 lm/W, which is higher than that of the industrially available InGaN-based YAG:Ce (in this case, 2 lm/W).

A wide range of whitish colors can be realized by fabricating GaN-based LED with different amounts of  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  concentration. The CIE chromaticity of GaN-based LED with different amounts of  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  concentration is shown in Fig. 3. As the concentration of  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  increases, the color shifts from blue to yellow. In addition, the chromaticity coordinates are close to the straight line interconnecting the points of the blue pump and the yellow

phosphor. The color rendering index (CRI) of a GaN-based  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  white LED packaged in a standard epoxy lamp configuration with a reflecting cup with a CIE chromaticity ( $x=0.39$ ,  $y=0.41$ ) is 68. This value is lower than that of the industrially available InGaN-based YAG:Ce (CRI=80). However, we have recently obtained evidence for the possibility of further improvements in the CRI by optimizing the peak wavelength of the main yellow emission.

In summary, we have synthesized an  $\text{Eu}^{2+}$ -activated  $\text{Sr}_2\text{SiO}_4$  yellow phosphor, and investigated its luminescent properties in an attempt to develop white LEDs by integrating the GaN blue LED chip and the  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  phosphor; the combination of a blue LED emitting (400 nm) and a broadband yellow  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  phosphor creates white line. The main emission peak shifts to a longer wavelength as the  $\text{SiO}_2$  content increases. This may be understood in terms of the degree of covalency and crystal field splitting of the  $5d^1$  configuration. The white GaN-based  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  developed in this work showed a higher luminous efficiency compared with the industrially available InGaN-based YAG:Ce.

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