

Yellow-emitting $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$ phosphor for white-light-emitting diodes and yellow-light-emitting diodes

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In this letter, a yellow-emitting $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$ phosphor is reported. Through transitions of $5d \rightarrow 4f$ (${}^2F_{7/2}$ and ${}^2F_{5/2}$) in Ce^{3+} , the phosphor showed a very broad and strong yellow emission under near ultraviolet (UV) or blue light excitation. The energy levels of Ce^{3+} in Sr_3SiO_5 were suggested from its absorption and excitation spectra. White light could be obtained by combining this phosphor with 460 or 405 nm light-emitting diodes (LEDs) [(x, y) = (0.3086, 0.3167) or (0.3173, 0.3103)]. Additionally, a yellow LED was fabricated using a near-UV LED (380 nm chip) with $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$. © 2007 American Institute of Physics. [DOI: 10.1063/1.2432947]

In recent years, light-emitting diodes (LEDs) have been extensively spotlighted as illumination light sources as well as components in display devices since the initial development of white LEDs was known.¹⁻⁴ In particular, white LEDs have excellent properties such as their low level of power consumption and their long life. Moreover, they have an environment benefit in that they do not use mercury in comparison to fluorescent lamps.⁵ Therefore, the white LEDs are expected to enable new concepts in lighting field. There are basically two methods for generating white light using LEDs.⁶ The first of these is the combining of different colors that are emitted from different LED chips (e.g., red, green, and blue radiation or a complementary combination of color radiation). The second is the combining of emission from a blue or ultraviolet (UV) LED with a longer wavelength that has been downconverted from phosphors. Between the two, white LEDs fabricated by combining blue LEDs with a yellow-emitting phosphor have attracted much interest due to the easy fabrication, low cost, and high brightness associated with this combination. However, few stable inorganic yellow phosphors with the exception of $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (YAG:Ce) are known. Therefore, many studies have been performed. Park *et al.*³ and Xie *et al.*⁷ reported $\text{Sr}_3\text{SiO}_5:\text{Eu}^{2+}$ and $\text{Ca-}\alpha\text{-SiAlON}$ phosphors, respectively. It was found that cool white or daylight could not be generated from a white LEDs fabricated with those phosphors, since the peak emission from Eu^{2+} is approximately 570–585 nm. Recently, Xie *et al.* investigated Eu^{2+} -activated Li- α -SiAlON with which a white LED was fabricated, and daylight could be generated from the white LED.⁸ However, the bandwidth of the emission from Eu^{2+} -activated yellow phosphor is narrower than that of YAG:Ce.^{2,3,8} A broad-emission phosphor is needed in two-band white LEDs in order for a white LED to have a good color rendering property.

Oxide materials are chemically stable compared to sulfide materials⁹ and they are easy to synthesize compared to nitride phosphor. In the case of nitride materials, a high nitrogen atmosphere or a high firing temperature is needed.^{7,8} Among the oxide materials, if a silicate is used, the firing temperature cannot be very high (in the region of 1000–1500 °C). Additionally, there is large crystal field

splitting in some silicate hosts for an Eu^{2+} ion,^{2,3} and it can be expected for a Ce^{3+} ion in the silicate. For these reasons, a silicate was chosen as a host material. In this letter, a yellow-emitting Ce^{3+} -activated strontium silicate ($\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$) is reported, whose charge is compensated with Li^+ . Kelsey and Brown reported that a charge-compensated phosphor was brighter than uncompensated phosphor.¹⁰ Li^+ codoping helps to incorporate the Ce^{3+} into Sr^{2+} sites by compensating for the different charges between Ce^{3+} and Sr^{2+} .¹¹ It is believed that there is no yellow emission known from Ce^{3+} in oxide hosts, except for a garnet structure phosphor such as YAG:Ce under blue light excitation.^{12,13} $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$ shows high luminous efficiency under near-UV light as well as under blue light, and emission from this phosphor is broader than that of Eu^{2+} -activated yellow phosphor. Therefore, it can be applicable to white LEDs using either InGaN-based blue LEDs or GaN-based near-UV LEDs.

A yellow-emitting $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$ phosphor was synthesized via a solid-state reaction method. The raw materials used in the synthesis of the phosphor were as follows: SrCO_3 (Aldrich, 99.995%), CeO_2 (Aldrich, 99.999%), SiO_2 (Kojundo Chem, 99.9%), and Li_2CO_3 (Aldrich, 99.99%). Li was used to compensate for the imbalance of charges resulting from the substitution of a Ce^{3+} ion for a Sr^{2+} ion. After the ingredients were mixed thoroughly using ethanol as a solvent for mixing, the mixture was fired at a temperature above 1250 °C in a reducing atmosphere. After these procedures, the phosphor was yellow in body color due to presence of the Ce^{3+} ion in Sr_3SiO_5 . In order to investigate its luminescent properties, photoluminescence (PL) and photoluminescence excitation (PLE) were characterized with a DARSA PRO 5100 PL System (Professional Scientific Instrument Co., Korea) using a xenon lamp (500 W) at room temperature. The excitation was performed with 460 nm radiation corresponding to a blue light. White LEDs were fabricated using InGaN-based blue LEDs (460 nm chip) and GaN-based deep-blue LEDs (405 nm chip). Their optical properties were evaluated under a forward bias of 20 mA at room temperature and an integrating sphere was used to obtain their luminous efficiencies.

The absorption spectra of Sr_3SiO_5 and Ce^{3+} -doped Sr_3SiO_5 phosphor are depicted in Fig. 1. As shown in this figure, $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$ can absorb light efficiently from

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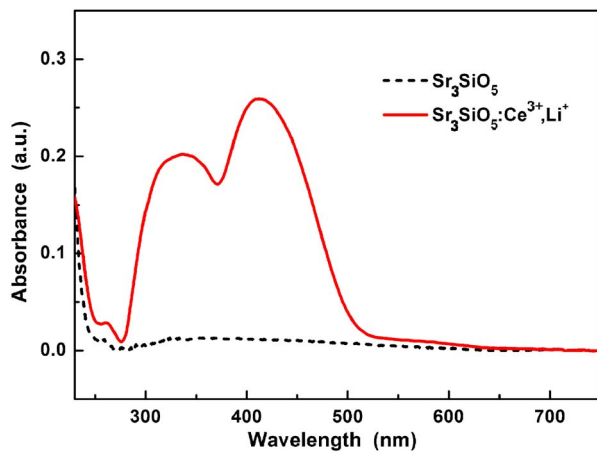


FIG. 1. (Color online) Absorption spectra of Sr_3SiO_5 (host material, dotted line) and $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$ (phosphor, solid line).

near UV to blue. However, undoped Sr_3SiO_5 , whose body color is white, showed no absorption in the spectral region from near UV to visible light. It is obvious from Fig. 1 that the yellow emission of the phosphor is attributed to the allowed transition from $5d$ to $4f$ (${}^2F_{7/2}$ and ${}^2F_{5/2}$) of the activator Ce^{3+} ion.

The emission from Ce^{3+} is usually characterized by a fast decay time.¹⁴ $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$ showed a very fast decay time (nearly 56 ns) from a measurement of this. From the PL measurement at 7 K, it was verified that the emission band is composed of two sub-bands located at 562 nm (λ_1) and 505 nm (λ_2) with an energy difference $\Delta E=2008\text{ cm}^{-1}$, which is in agreement with the theoretical difference between ${}^2F_{7/2}$ and ${}^2F_{5/2}$ levels ($\sim 2000\text{ cm}^{-1}$).¹⁵ Both a fast decay time and a broad band consisting of two sub-bands also indicate that the yellow emission of the phosphor is attributed to the allowed transition of $5d \rightarrow 4f$ of Ce^{3+} .¹⁴

Figure 2 shows the PL/PLE spectra of $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$. The excitation band consists of two broad bands which ascribe to $4f \rightarrow {}^2D_{3/2}$ and $4f \rightarrow {}^2D_{5/2}$. The excitation band ranges from approximately 250 to 500 nm and shows a strong intensity near 415 nm. $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$ showed a strong broad emission at 465–700 nm under about 360–460 nm excitation. Due to a broad yellow emission and intense excitation band present in the visible spectral region, $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$ can be applicable to white LEDs pumped

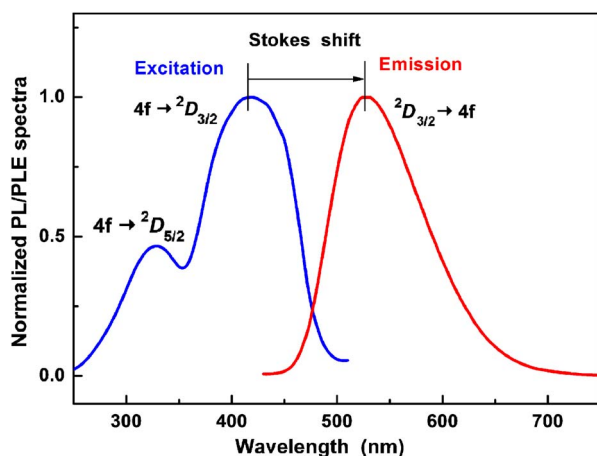


FIG. 2. (Color online) Normalized PL and PLE spectra of $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$.

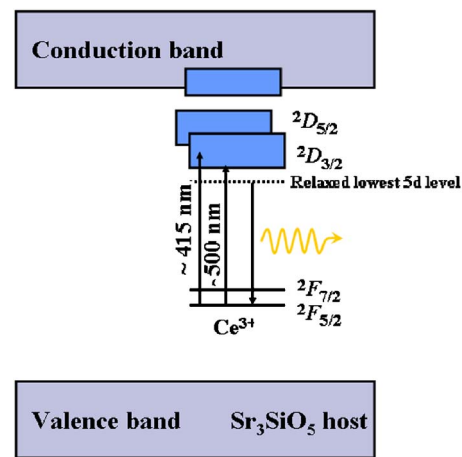


FIG. 3. (Color online) Schematic diagram of the energy levels of Ce^{3+} in Sr_3SiO_5 .

by blue LEDs or near-UV LEDs. In the case of a two-band white light using blue LEDs, the wider the emission band of the phosphor, the higher the color rendering index of the white LED. The bandwidth (121.8 nm) of the emission from $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$ is slightly wider than that (116.1 nm) of YAG:Ce. Therefore, it is expected that the white LED using $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$ produces a superior white light that covers a wider range of visible spectrum.

Figure 3 shows a schematic diagram of the energy level of a yellow-emitting $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$ phosphor. The energy level diagram was suggested from spectroscopic analyses of the absorption and PLE spectra. $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$ can show a property of direct excitation under low-energy excitation. An external photon whose energy corresponds to blue light can excite only Ce^{3+} activator, as shown in Fig. 3. Valence electrons cannot be excited to conduction band in this system since the excitation energy is smaller than the band gap energy of the host crystal. The energy of the blue light is in resonance with the magnitude of energy difference between the lowest $5d$ and $4f$ levels. Consequently, the $4f$ electron in Ce^{3+} is excited directly by the external blue light; subsequently, the broad yellow emission of Ce^{3+} is followed by radiative decay from the relaxed lowest $5d$ band to ${}^2F_{7/2}$ or ${}^2F_{5/2}$.

Figure 4 shows the maximum PL intensities of $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$ phosphor samples with different amounts

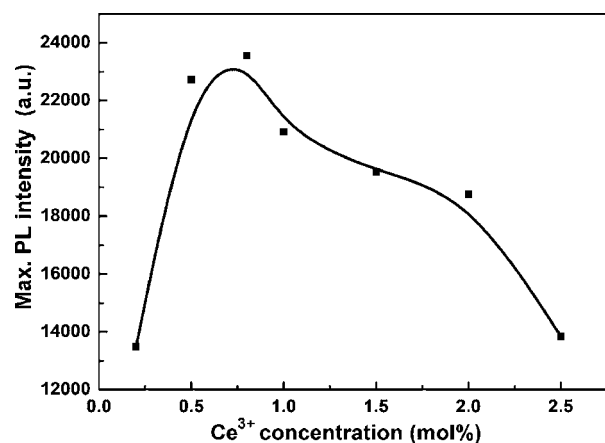


FIG. 4. Maximum PL intensities of $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$ with varying Ce^{3+} concentration.

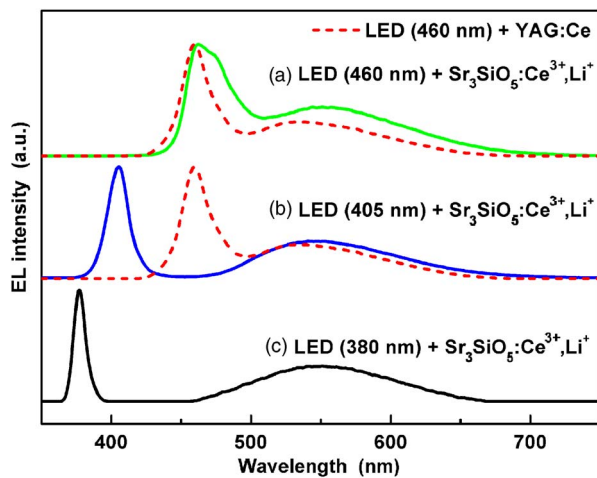


FIG. 5. (Color online) Electroluminescent spectra of white LEDs using (a) 460 nm chip and (b) 405 nm chip and (c) a yellow LED using 380 nm chip measured under a forward bias of 20 mA.

of Ce^{3+} . $\text{Sr}_{3-2x}\text{SiO}_5:x\text{Ce}^{3+},x\text{Li}^+$ phosphor samples showed a maximum emission intensity when the amount of Ce^{3+} was 0.8 mol % ($x=0.024$). When the Ce^{3+} content exceeded $x=0.024$, concentration quenching occurred. According to Dexter's theory,¹⁶ the probability of energy transfer from a sensitizer to an activator via dipole-dipole interaction is given by

$$P_{\text{sa}}(dd) = \frac{3\hbar^4 c^4 Q_A}{4\pi R^6 n^4 \tau_s} \left(\frac{\varepsilon}{\kappa^{1/2} \varepsilon_c} \right)^4 \int \frac{f_s(E) F_A(E)}{E^4} dE. \quad (1)$$

From this equation, the critical distance R_c can be represented as follows:¹⁷

$$R_c^6 = 0.63 \times 10^{28} \frac{4.8 \times 10^{-16} P_A}{E^4} \int f_s(E) F_A(E) dE, \quad (2)$$

where P_A is the oscillator strength of the transition. The oscillator strength of the Ce^{3+} ions was taken as 0.01.¹⁷ The values of E and the spectral overlap $\int f_s(E) F_A(E) dE$ can be derived from the normalized PL and PLE spectra. From the spectra, the values of E and the spectral overlap are 2.603 eV and 0.033 eV^{-1} , respectively. From Eq. (2) the value of R_c for the energy transfer was calculated as 16.7 Å. When the critical distance was calculated using the critical concentration, a value of 17.2 Å was obtained. This was consistent with the value (16.7 Å) obtained from the normalized PL/PLE spectra.

Figure 5 shows the relative emission spectra of white LEDs measured under a forward bias of 20 mA. White LEDs were fabricated by combining blue LEDs (InGaN-based 460 nm emitting and GaN-based 405 nm emitting chips) with $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$. A yellow LED was also fabricated by using a near-UV LED (GaN-based 380 nm emitting chip) and the aforementioned phosphor. Each fabricated white LED was compared with white LEDs fabricated using commercial YAG:Ce. As shown in Figs. 5(a) and 5(b), white light can be generated from a combination of $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$ with 460 nm InGaN-based LEDs or a combination of $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$ with 405 nm GaN-based LEDs. In the case of YAG:Ce, since excitation efficiency of YAG:Ce is low under 405 nm excitation, it is difficult for YAG:Ce to be applied to 405 nm GaN-based white LED. However, both

460 nm InGaN-based and 405 nm GaN-based white LEDs using $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$ generated bright white light. These two white LEDs showed luminous efficiencies of 31.7 and 25.0 lm/W, respectively. (For white LEDs using commercial YAG:Ce, luminous efficiency was 23.5 lm/W).

The Commission Internationale de l'Eclairage (CIE) color coordinates of the InGaN-based white LEDs were (0.3086, 0.3176) and the color rendering index, R_a , was 81. Those of GaN-based white LEDs showed (0.3173, 0.3103) and the R_a value was 69. For the GaN-based white LEDs, the low R_a was due to the weak emission of the visible light in the red region and the region between 430 and 465 nm. In this case, R_a is not satisfactory for an application to a light source for a building interior; however, it is acceptable for an application as a backlight in mobile phones, or as exterior light, for example.

In addition, when $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$ was coated onto a 380 nm GaN-based near-UV LED, the LED showed a bright yellow light (Fig. 5). $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$ can be applied to a near-UV LED unlike YAG:Ce whose PL intensity is very weak under excitation of near-UV light. If this phosphor is coated onto a near-UV LED together with red, green, and blue phosphors, it can show excellent white light property because deficient regions in the visible spectrum will be compensated by the broad yellow emission from this phosphor. Consequently, this yellow-emitting $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$ phosphor can be applied to a variety of LEDs from blue LEDs (460 or 405 nm chips) to near-UV LEDs (380 nm chip).

In summary, a yellow-emitting $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$ phosphor was synthesized and luminescent properties of this phosphor were investigated. When the LEDs with emission wavelength of 460 or 405 nm were coated with this phosphor, white light was generated. Blue LED-pumped white LEDs coated with $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$ showed excellent white light (efficiency=31.7 lm/W, $R_a=81$, $T_c=6857$ K). $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$ also showed a strong yellow emission under excitation of near-UV LEDs (380 nm). This indicates that $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$ is a promising phosphor applicable to near-UV LEDs as well as blue LEDs.

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