Near-ultraviolet excitable orange-yellow Sr$_3$(Al$_2$O$_5$)Cl$_2$:Eu$^{2+}$ phosphor for potential application in light-emitting diodes

Yu-Sheng Tang,$^{1}$ Shu-Fen Hu,$^{2,a}$ Wei-Chih Ke,$^3$ Chun Che Lin,$^3$ Nitin C. Bagkar,$^3$ and Ru-Shi Liu$^{3,a}$

$^1$Institute of Electro-optical Science and Technology, National Taiwan Normal University, Taipei 116, Taiwan
$^2$Department of Physics, National Taiwan Normal University, Taipei 116, Taiwan
$^3$Department of Chemistry, National Taiwan University, Taipei 106, Taiwan

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Sr$_3$(Al$_2$O$_5$)Cl$_2$ phosphor doped with Eu$^{2+}$ was prepared by a soli-state reaction. This phosphor emits a broad orange-yellow luminescence with a peak wavelength of 620 nm and a full width at half maximum of about 175 nm under near-ultraviolet (NUV) excitation at ~400 nm. Yellow light-emitting diodes (LEDs) for general lighting were fabricated by combining Sr$_3$(Al$_2$O$_5$)Cl$_2$:Eu$^{2+}$ phosphor with an NUV chip. The phosphor-converted LEDs had a color temperature of about 2300 K and their color rendering index was 74. © 2008 American Institute of Physics.

Solid-state lighting, which utilizes light-emitting diodes (LEDs) for illumination, has attracted much interest in recent years. LED-based white light sources have a longer lifetime, higher energy efficiency, greater reliability, and more environmental friendly characteristics than conventional incandescent and fluorescent lamps. The present strategy for producing white light is to combine blue LED with yellow phosphor. The CRI. The other involves codoping ions such as Eu$^2+$ or Eu$^3+$ that were synthesized herein match those of pure Sr$_3$(Al$_2$O$_5$)Cl$_2$ (Ref. 11), indicating the formation of a single phase. Figure 1 plots experimental, calculated, and

![FIG. 1. (Color online) Experimental (crosses), calculated (solid line), and difference (bottom) results of XRD refinement of Sr$_{2.85}$Al$_2$O$_3$:Eu.](http://apl.aip.org/apl/)

$^{a}$Authors to whom correspondence should be addressed. Electronic addresses: sfhu.hu@gmail.com and rsliu@ntu.edu.tw.

SrCl$_2$·6H$_2$O, SrCO$_3$, Al$_2$O$_3$, and Eu$_2$O$_3$ as raw materials. The molar ratio of Sr:Al:Cl:Eu was 3−x:2:2:x. Stoichiometric homogeneous mixtures of highly pure raw materials were obtained by thorough grinding and then sintering in a reductive atmosphere at 1300 °C for 3 h in a 5% H$_2$/95% N$_2$ gas mixture. The crystal structure and phase purity of the synthesized samples were identified by x-ray diffraction (XRD) analysis using an X’Pert PRO advanced automatic diffractometer with Cu Kα radiation operated at 45 kV and 40 mA. The photoluminescence (PL) of the samples was measured using a FluoroMax-3 FluoroMax-P. Thermal quenching and activation energy were studied using a heating apparatus (THMS-600) in combination with PL equipment. The size of the phosphor particles was measured using a particle size analyzer. The mean size was around 5 μm.

XRD patterns of the Sr$_{3-x}$(Al$_2$O$_3$)Cl$_2$:Eu$_x$ (x=0.05, 0.1, 0.15, and 0.2) that were synthesized herein match those of pure Sr$_3$(Al$_2$O$_5$)Cl$_2$ (Ref. 11), indicating the formation of a single phase. Figure 1 plots experimental, calculated, and...
difference results of the XRD refinement of Sr2.85(Al2O3)Cl2:Eu0.15 at room temperature, obtained using GSAS program. Sr2.85(Al2O3)Cl2:Eu0.15 crystallizes as an orthorhombic structure (presented in the inset of Fig. 1) with a space group of $P2_12_12_1$ and lattice constants of $a=9.4017(5)\,Å$, $b=9.4044(4)\,Å$, $c=9.4036(4)\,Å$, and $v$ (cell volume)=$831.44(7)\,Å^3$. All of the observed peaks satisfy the reflection condition, $\chi^2=3.03$, $R_p=8.37\%$, and $R_{wp}=6.54\%$. The lattice constants clearly drop as the amount of Eu$^{2+}$ dopant in the samples, which occupies the Sr sites in the structure, increases.13

Figure 2 presents the excitation [photoluminescence excitation (PLE); $\lambda_{em}=620\,nm$] and emission (PL; $\lambda_{ex}=400\,nm$) spectra of Sr3-x(Al2O3)Cl2:Eu$_x$ ($x=0.05$, 0.1, 0.15, and 0.2) with various Eu$^{2+}$ contents. The excitation spectra have a broad peak between 300 and 400 nm, which corresponds to the $4f$-$5d$ transition of Eu$^{2+}$ ions.10 The phosphors emit orange-yellow luminescence with a peak wavelength of 620 nm. The peak positions were slightly redshifted as the Eu$^{2+}$ content in the crystal structure increases.13

As the concentration of Eu$^{2+}$ ions increases, the distance between Eu$^{2+}$ ions decreases, favoring the nonradiative pathway energy transfer from Eu$^{2+}$ ions. Therefore, the critical distance between Eu$^{2+}$ ions for energy transfer was calculated using the relation that was proposed by Blasse and Grabmaier,17

$$R_c = 2 \left[ \frac{3V}{4\pi x N} \right]^{1/3},$$

where $V$ is the volume of the unit cell, $x_c$ is the critical concentration of the activator ion, and $Z$ is the number of formula units per unit cell. For Sr3(Al2O3)Cl2 host, when $N=12(Z=3)$, $x_c=0.15$, and $V=831.44\,Å^3$, the obtained $R_c$ value is 9.6 Å. $R_c$ can be thought of as a multipolar interaction.

Additionally, the emission intensity ($I$) per activator of Sr3(Al2O3)Cl2:Eu$^{2+}$ phosphors is given by the following equation:18

$$I/I_0 = K[1 + \beta(x)^{Q/3}]^{-1},$$

where $x$ is the concentration of the activator and $K$ and $\beta$ are the constants for a given excitation (Ex=400 nm) and host structure. The inset of Fig. 3 plots log($\lambda x$) versus log($I/I_0$), which is linear with a gradient of $-1.08$, which is the value of $\beta$. The value of $Q$ calculated from Eq. (3) was found to approximately about six. $Q$ values of 6, 8, and 10 mean dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interaction, respectively, indicating that the dipole-dipole interaction is the main mechanism of concentration quenching of the Eu$^{2+}$-doped Sr3(Al2O3)Cl2 phosphor.19

![FIG. 2. (Color online) Excitation ($\lambda_{em}=620\,nm$) and emission ($\lambda_{ex}=400\,nm$) of Sr3-x(Al2O3)Cl2:Eu$_x$ ($x=0.05$, 0.1, 0.15, 0.2) with three deconvoluted Gaussian peaks; the inset shows decay curve of the 620 nm emission for the Sr2.85(Al2O3)Cl2:Eu0.15.](image)

![FIG. 3. Emission intensity of Sr3(Al2O3)Cl2:Eu phosphors as a function of Eu$^{2+}$ concentration; the inset plots log($\lambda x$) versus log($I/I_0$) of Sr3-x(Al2O3)Cl2:Eu$_x$ phosphor.](image)
Recently, many authors have studied the thermal quenching of phosphors. Figure 4 presents the thermal quenching of the luminescence spectra of Sr$_{2.85}$Al$_2$O$_5$Cl$_2$:Eu$_{0.15}$ at various temperatures from 100 K to room temperature. It reached 10% of its initial value at 200 K and 20% at 250 K; the thermal quenching temperature ($T_{50}$) was found to be 365 K that the temperature at the emission intensity was 50% of its initial value. To understand the thermal quenching behavior at various temperatures, the thermal quenching data were fitted using the Arrhenius equation,$^{10,20}$

$$I(T) = \frac{I_0}{1 + c \exp\left(\frac{-E}{kT}\right)}.$$  

(4)

where $I_0$ is the initial intensity, $I(T)$ is the intensity at a given temperature $T$, $c$ is a constant, $E$ is the activation energy for thermal quenching, and $k$ is Boltzmann’s constant. The inset of Fig. 4 plots of $\ln[I_0/I - 1]$ versus $1/(kT)$, and the activation energy ($E$), which fitted all of the data closely, was 0.06 eV for Sr$_{3-x}$(Al$_2$O$_5$)Cl$_2$:Eu$_x$.

The LEDs were packaged using Sr$_{3-x}$(Al$_2$O$_5$)Cl$_2$:Eu$_x$ phosphor and a NUV chip that emits at 400 nm. The optical properties of LEDs were determined using a 20 mA forward-bias current at room temperature. Table I summarizes the optical properties of the LED and the variation in chromaticity coordinates, CRI, and color temperature for different drive currents were found to be ($x=0.0115$, $y=0.0013$), 0.5 and 110 K, respectively.$^5$ Further work to improve the luminescent properties of this phosphor and produce white light using various volumes of phosphors are currently being undertaken.

In summary, orange-yellow phosphors Sr$_{3-x}$(Al$_2$O$_5$)Cl$_2$:Eu$_x$ in pure phase were synthesized and characterized that were packaged in a yellow emitting LED with a NUV chip with correlated color temperature (CCT) $\sim$2300 K and CRI $\sim$74. Additionally, the variations in the Commission Internationale de l’Éclairage (CIE) parameters, color temperature, and CRI of LED with drive current are discussed. The luminescent properties were studied to identify potential applications of NUV LED.

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**TABLE I.** The CIE chromaticity points, domain wavelength, color temperature, and the CRI at various drive currents.

<table>
<thead>
<tr>
<th>Drive current (mA)</th>
<th>$x$</th>
<th>$y$</th>
<th>$W_C$ (nm)</th>
<th>CCT (K)</th>
<th>CRI</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.5167</td>
<td>0.4366</td>
<td>585</td>
<td>2234</td>
<td>73.7</td>
</tr>
<tr>
<td>30</td>
<td>0.5119</td>
<td>0.4374</td>
<td>585</td>
<td>2286</td>
<td>74.1</td>
</tr>
<tr>
<td>40</td>
<td>0.5097</td>
<td>0.4374</td>
<td>585</td>
<td>2307</td>
<td>73.8</td>
</tr>
<tr>
<td>50</td>
<td>0.5103</td>
<td>0.4367</td>
<td>585</td>
<td>2297</td>
<td>73.9</td>
</tr>
<tr>
<td>60</td>
<td>0.5052</td>
<td>0.4361</td>
<td>585</td>
<td>2344</td>
<td>74.2</td>
</tr>
</tbody>
</table>