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Characterization and Photoluminescence Properties of Eu^{3+} Doped $3\text{CdO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{SiO}_2$ Amorphous System for White Light-Emitting Diodes

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A new phosphor, Eu^{3+} doped $3\text{CdO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{SiO}_2$ (CAS: Eu^{3+}), is prepared by a convenient sol–gel method. Under excitation either into the $^5\text{L}_6$ state with 394 nm or the $^5\text{D}_2$ state with 464 nm, the phosphor gives a red emission at 610 nm originating from the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu^{3+} . The luminescence properties compared with $\text{YAG}:\text{Ce}^{3+}$ and $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ are studied. The red emission of CAS: Eu^{3+} is about 3 times stronger than that of commercial $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$. The high color saturation (the chromaticity index is $x = 0.6209$, $y = 0.3461$) and the low thermal quenching effect make phosphor CAS: Eu^{3+} a promising candidate for the phosphor-converted white LEDs.

InGaN-based white light-emitting diodes (LEDs) have drawn much attention due to their valuable applications, such as white light sources to replace traditional incandescent and fluorescent lamps, backlights for portable electronics, medical, and architecture lightings, etc.^{1,2} White LEDs have been commendably realized using $\text{YAG}:\text{Ce}^{3+}$ as a broadband yellow phosphor coated on the blue InGaN chip.³ However, such a combination exhibits a poor color rendering index (<80) because of the lack of a red light component (above 600 nm).⁴ Another way to generate warm white light with high color rendering index and color reproducibility is to combine an UV chip with red, green, and blue (RGB) phosphors.^{5,6} Efficient red-emitting phosphors are necessary for both of these methods. Nitridosilicate shows orange-red emission and has high quantum efficiency and very low thermal quenching, which makes it an encouraging red phosphor for use in white light-emitting diodes.⁷ In the past several years, however, only a small number of nitridosilicates have been synthesized due to the scarcity of appropriate synthesis methods, the limitation of high cost and sensitivity of raw materials.^{8,9} Therefore, it is urgent to develop new red or orange-red phosphors that can be well coupled with the blue ($\lambda \approx 460$ nm) or near UV ($\lambda \approx 400$ nm) LEDs using inexpensive and efficient method.

Eu^{3+} is a preferable choice as an activator ion with red emission via the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition at about 611 nm, which has been used in most commercial red phosphors.^{10,11} In this paper, we report a new red amorphous material, Eu^{3+} doped $3\text{CdO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{SiO}_2$ amorphous system (CAS: Eu^{3+}), synthesized by the sol–gel method. The CAS: Eu^{3+} phosphor can be

effectively excited by near-UV (about 394 nm) and blue (about 464 nm) light, which is suitable for use in white LEDs.

Cadmium nitrate ($\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$) and aluminum nitrate ($\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$) were predissolved in 8.5 mL of ethanol and an equimolar amount of tetraethyl orthosilicate (TEOS) was added under vigorous stirring. Hydrolysis took place upon addition of distilled water and the final molar ratio of TEOS: ethanol:water was 1:12:4. A small amount of HNO_3 was added as a catalyst, and the pH value of the mixture was adjusted to 2. Then the desired amount of europium nitrate, $\text{Eu}(\text{NO}_3)_3$ (mol concentration varying from 0.1 to 0.4) was poured into the precursor solution. Transparent sols were obtained after stirring for several hours. Transparent gels could be obtained by drying the sols at 60 °C for 1 to 2 days. The obtained gels were fully ground and annealed at 900 °C for 3 h in air to produce the final samples. The structural characterization was analyzed by X-ray diffraction (XRD; Rigaku D/max-IIB) spectra with the $\text{Cu K}\alpha$ line of 0.15405 Å. The photoluminescence (PL) and PL excitation (PLE) spectra were measured using a Hitachi F-4500 fluorescence spectrophotometer.

The XRD patterns of all samples show the absence of crystalline. No diffraction peak is observed in the XRD pattern due to the amorphous structure of the samples, and the addition of Eu^{3+} does not alter the amorphous nature of the powders (see Figure S1 in the Supporting Information).

The PL and PLE spectra of CAS: Eu^{3+} are presented in Figure 1. The PLE spectrum monitored at 611 nm shows characteristic intraconfigurational 4f–4f transitions of Eu^{3+} . The $^7\text{F}_0 \rightarrow ^5\text{L}_6$ (394 nm) and $^7\text{F}_0 \rightarrow ^5\text{D}_2$ (464 nm) excitation lines as well as a broad charge-transfer (CT) band centering at 254 nm in the UV region are the strongest absorptions. The PL spectra show a strong emission line at 611 nm and a weak emission at 590 nm, which arise from the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transitions

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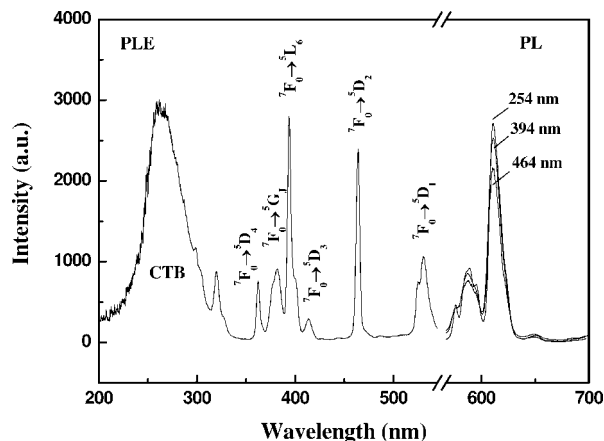


Figure 1. PLE spectrum of CAS:Eu³⁺ monitoring the 611 nm Eu³⁺ emission, and PL spectra under 254, 394, and 464 nm excitation.

TABLE 1: Relative Intensity of the CAS:Eu³⁺ Samples As Functions of Eu³⁺ Concentration and Excitation Wavelength

Eu ³⁺ concentration	emission intensity under different excitation		
	$\lambda_{\text{ex}} = 254 \text{ nm}$	$\lambda_{\text{ex}} = 394 \text{ nm}$	$\lambda_{\text{ex}} = 464 \text{ nm}$
0.1	9.4	7.3	6
0.2	118	65.8	56
0.25	96.8	100	84
0.3	128.8	90	77.3
0.35	138.4	87	72.3
0.4	142.2	85	59.6

of Eu³⁺, respectively. Upon varying the excitation wavelength ($\lambda_{\text{ex}} = 254, 394, \text{ and } 464 \text{ nm}$), there is no significant changes in the emission spectrum except the emission intensity. It is found that CAS:Eu³⁺ phosphor demonstrates high photoluminescent efficiency when the excitation wavelength is 394 or 464 nm. At the 0.25 mol concentration of Eu³⁺, the emission intensity from $\lambda_{\text{ex}} = 394 \text{ nm}$ is nearly the same as that excited by 254 nm. The emission intensity from $\lambda_{\text{ex}} = 464 \text{ nm}$ has a small decrease by about 20% with respect to the emission intensity from $\lambda_{\text{ex}} = 254 \text{ nm}$. Table 1 presents the photoluminescence emission intensity as functions of Eu³⁺ concentration and excitation wavelength. The CAS:Eu³⁺ samples have different quenching concentrations under the excitation at different wavelengths. The emission intensity increases with increasing the Eu³⁺ concentration when the excitation wavelength is 254 nm. The emission intensity excited at 394 and 464 nm light, however, is maximized at 0.25 mol Eu³⁺ concentration. It is indicated that the CAS:0.25 Eu³⁺ phosphor emits efficiently under the near UV (394 nm) and blue (464 nm) light which makes it possible to create white light from a combination of a near-UV or blue InGaN chip.

Typical photoluminescence spectra of the CAS:Eu³⁺ phosphor, together with that of standard YAG:Ce³⁺ as comparison, are shown in Figure 2. The YAG:Ce³⁺ phosphor can be effectively excited by 470 blue light and emits strong yellow fluorescence at 530 nm. However, YAG:Ce³⁺ does almost not absorb near-UV light ($\lambda \approx 400 \text{ nm}$), and its emission is silent under the 400 nm light irradiation. The white light realized by the combination with a blue LED exhibits a poor color rendering index because of the lack of red color component. Compared with YAG:Ce³⁺, the emission of CAS:Eu³⁺ phosphor occurs at a fairly longer wavelength at 611 nm under 394 and 464 nm excitation which perfectly match with the emission wavelength of near-UV/blue GaN-based LEDs.

As a novel red phosphor applying in white-light LEDs with the near-UV/blue GaN-based chips as excitation sources, the

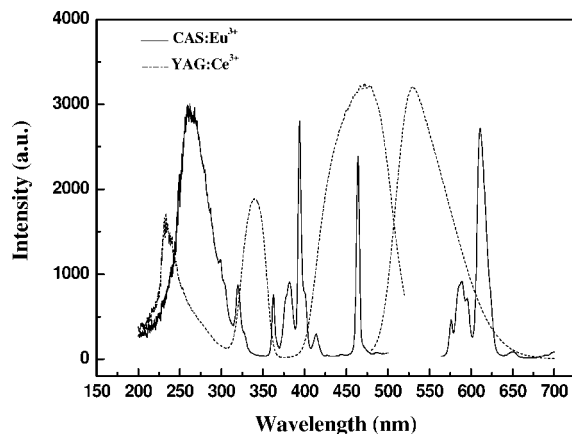


Figure 2. Typical photoluminescence spectra of CAS:Eu³⁺ and YAG:Ce³⁺.

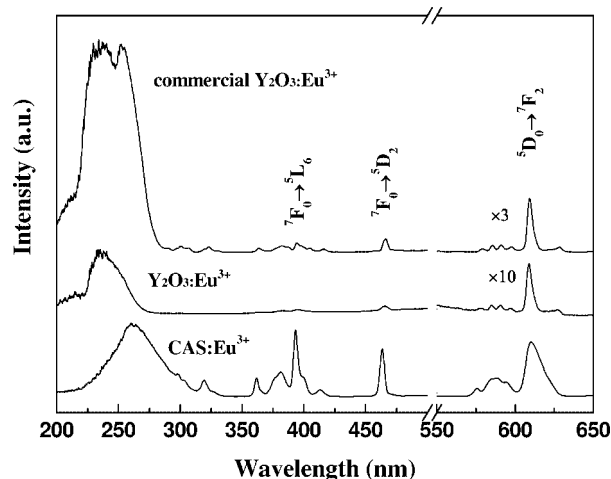


Figure 3. PLE spectra monitoring the $^5D_0 \rightarrow ^7F_2$ red emission and PL spectra under 394 nm excitation of Eu³⁺ doped CAS, Y₂O₃ and commercial Y₂O₃.

PLE spectrum monitoring the $^5D_0 \rightarrow ^7F_2$ red emission and the PL spectrum upon 394 nm excitation into the 5L_6 state in the present synthesized CAS:Eu³⁺ phosphor are compared with those of the conventional Y₂O₃:Eu³⁺ red phosphor, as shown in Figure 3. The PLE spectrum of Y₂O₃:Eu³⁺ depicts two weak $^7F_0 \rightarrow ^5L_6$ (394 nm) and $^7F_0 \rightarrow ^5D_2$ (464 nm) excitation lines and a strong CT band. The CAS:Eu³⁺ phosphor gets very strong $^7F_0 \rightarrow ^5L_6$ and $^7F_0 \rightarrow ^5D_2$ excitation peaks, either of which is almost 10 times stronger than that of Y₂O₃:Eu³⁺. Under the strong 395 nm excitation, the red emission of CAS:Eu³⁺ is about 10 times stronger than that of Y₂O₃:Eu³⁺. Even compared with commercial Y₂₃:Eu³⁺, the $^5D_0 \rightarrow ^7F_2$ intensity of CAS:Eu³⁺ still exceeds that of commercial Y₂O₃:Eu³⁺ by 3 times.

The Commission International de l'Eclairage (CIE) chromaticity coordinates of CAS:Eu³⁺ phosphor are shown in the inset of Figure 4. The chromaticity coordinates of the CAS:Eu³⁺ phosphor are $x = 0.6209$ and $y = 0.3461$, while the index of YAG:Ce³⁺ is (0.461, 0.525). The characteristic index of CAS:Eu³⁺ with high color saturation indicates that white light is possibly generated by coupling with a UV LED and BG phosphors or with a blue LED and a suitable green phosphor together. It is generally required that phosphors for white LEDs should have low thermal quenching for avoiding the changes in chromaticity and brightness of white LEDs.¹² One can see from Figure 4, with increasing temperature up to 130 °C, the normalized emission intensity of the YAG:Ce³⁺ phosphor is

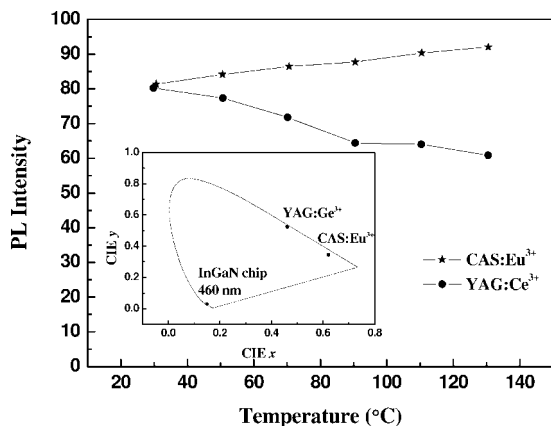


Figure 4. Temperature dependence of the emission intensity of CAS:Eu³⁺ and YAG:Ce³⁺ phosphors. Inset shows CIE chromaticity coordinates of CAS:Eu³⁺.

decreased to 76%. However, the emission intensity of the CAS:Eu³⁺ phosphor does not decrease at all. On the contrary, it is increased to 116% of the initial value. It indicates that the CAS:Eu³⁺ phosphor has a more stable structure than the YAG:Ce³⁺ phosphor when compared to that of the emission intensity with increasing temperature (see Figure S2 in the Supporting Information), and the CAS:Eu³⁺ phosphor has a comparatively low temperature quenching effect.

In conclusion, a new excellent red phosphor CAS:Eu³⁺ is prepared by the sol–gel method. The phosphor is effectively excited by near-UV (about 394 nm) and blue (about 464 nm) light, respectively, and gives a red emission at 611 nm which is competitive (≈ 3 times) with that of commercial Y₂O₃:Eu³⁺. In addition, the high color saturation and low thermal quenching

show that this phosphor is a potential candidate for white-light LED applications.

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Supporting Information Available: Additional XRD pattern of CAS:Eu³⁺ and emission spectra of CAS:Eu³⁺ and YAG:Ce³⁺. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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