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FAST TRACK COMMUNICATION

Intense violet-blue emitting $(CaCl_2/SiO_2):Eu^{2+}$ phosphor powders for applications in UV-LED based phototherapy illuminators

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Abstract
An intense violet–blue emitting $(CaCl_2/SiO_2):Eu^{2+}$ phosphor with a composition of 25% $CaCl_2$ and 75% SiO_2 is prepared by a solid state reaction. The phosphor emits at 427 nm with a narrow bandwidth of 21 nm. The photoluminescence (PL) intensities and fluorescence lifetimes are studied as a function of Eu^{2+} concentrations. It is observed that the PL intensity of $(CaCl_2/SiO_2):Eu^{2+}$ can be 30% higher than that of commercial $Sr_2P_2O_7:Eu^{2+}$ phosphor under 395 nm excitation. $(CaCl_2/SiO_2):Eu^{2+}$ would be a promising new phosphor for converting near-ultraviolet radiation to violet–blue emission for a novel phototherapy illuminator using a near-ultraviolet (∼395 nm) light emitting diode as the excitation source.

1. Introduction

It is known that ultraviolet (UV) (220–400 nm) and violet–blue (400–450 nm) radiation have been extensively used in many applications such as sterilization, drinking water purifiers, phototherapy and photocopying [1–5]. For the treatment of hyperbilirubinemia [6], commonly known as infant jaundice, phototherapy has been found to be quite effective. Specific wavelengths of light from special fluorescent lamps penetrate the patient's skin where the light breaks down bilirubin into nontoxic water-soluble components that are then excreted in the urine. Wavelengths close to UV are most effective in breaking down bilirubin. However, UV radiation may have adverse effects, especially for infants. Hence, a source emitting in a narrow band just above 400 nm and having no UV component (violet–blue) is desired [7]. The most conventional way of obtaining the violet–blue radiation source is to use a low-pressure Hg discharge and then convert the 254 nm emission to the desired wavelength using phosphors. Violet–blue $Sr_2P_2O_7:Eu^{2+}$ phosphor is suitable for this purpose with an emission band peaking at 420 nm and the full width at half maximum (FWHM) of 30 nm under 254 nm excitation [8, 9]. The development of GaN based near-UV (∼395 nm) light emitting diode (LED) for converting the near UV radiation to violet–blue emission using phosphors could be an ideal way. Due to a small Stokes shift between excitation and emission photon energies, a novel high light-conversion efficiency phototherapy illuminator in this way is expected. This combination containing a LED as a pumping source also benefits from nontoxicity, reliability and safety, etc. However, $Sr_2P_2O_7:Eu^{2+}$ does not match near-UV LEDs very well; new

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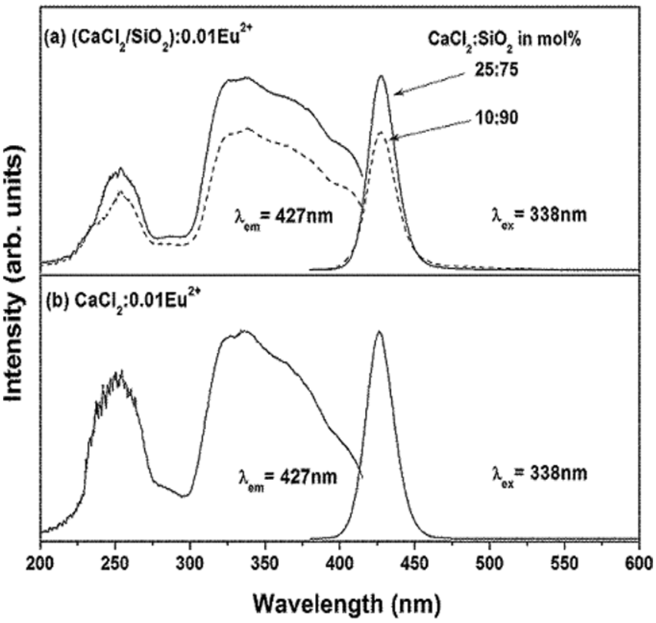

Figure 1. PL and PLE spectra of $(CaCl_2/SiO_2) : 0.01Eu^{2+}$ (*a*) and $CaCl_2 : 0.01Eu^{2+}$ (*b*).

violet–blue phosphors better matching near-UV LEDs are, therefore, needed.

Herein, we report a heterogeneous luminescent material of $(CaCl_2/SiO_2) : Eu^{2+}$, which can emit at 427 nm with a narrower and stronger emitting band in comparison with $Sr_2P_2O_7 : Eu^{2+}$ under near-UV excitation. In 1975, Lehmann reported efficient photoluminescence (PL) in $(CaCl_2/SiO_2) : Eu^{2+}$ phosphor in which the composition ratio of $CaCl_2$ to SiO_2 was fixed at 10 : 90 [10, 11]. Recently, we have studied the effect of $CaCl_2/SiO_2$ ratios on the violet–blue emission intensities and determined the optimum ratio to be about 25 : 75. It is observed at this ratio that the PL intensity of Eu^{2+} in $(CaCl_2)_{25}/(SiO_2)_{75}$ is 55% stronger than that in $(CaCl_2)_{10}/(SiO_2)_{90}$, as shown in figure 1(*a*) under 328 nm excitation and 30% stronger than that in $Sr_2P_2O_7 : Eu^{2+}$ under near-UV excitation at 395 nm, as shown in figure 4. In this work, we have thus prepared $(CaCl_2)_{25}/(SiO_2)_{75} : Eu^{2+}$ phosphor and studied its PL properties and temperature stabilities.

2. Experimental

Synthesis of the powder samples was conducted by using a two-process solid state reaction. The starting materials, analytical grade, CaO, SiO_2, NH_4Cl (100% excess) and Eu_2O_3 were homogenized for 1 h and calcined at 1273 K for 2 h in air. The NH_4Cl reacts with CaO and Eu_2O_3 to form the halides *in situ*; all the excess of NH_4Cl not used sublimes out of the container during firing. The calcined powders were ground, extra NH_4Cl (100% excess) added and sintered at 1273 K for 2 h in a CO reducing atmosphere. After firing and cooling, the powder phosphors were washed in water to remove any free halide. When dry, they were free flowing powders, stable in air, water, alkaline solutions and acids with the only exception of strong hydrofluoric acid. The concentration of Eu^{2+} was varied from 0.1 to 3 mol%. $Sr_2P_2O_7 : 0.02Eu^{2+}$ and $CaCl_2 : 0.01Eu^{2+}$ phosphors for comparing with $(CaCl_2/SiO_2) : Eu^{2+}$ were synthesized by the process as described in [11] and [12], respectively. The structure of sintered samples was identified by x-ray powder diffractometry (XRD, Rigaku D/M AX-2500 V). The measurements of PL and PL excitation (PLE) spectra were performed by using a Hitachi F4500 fluorescent spectrometer equipped with a 150 W xenon lamp under a working voltage of 700 V. The excitation and emission slits were set at 2.5 and 1.0 nm. The diffuse reflectance measurements are performed using the same spectrometer with $BaSO_4$ powder as a reflectance standard. In fluorescence lifetime measurements, the third harmonic (355 nm) of a Nd-YAG laser (Spectra-Physics, GCR 130) was used as an excitation source, and the signals were detected with a Tektronix digital oscilloscope (TDS 3052). All the above measurements were performed at room temperature. In addition, an He–Cd laser at 325 nm was used to obtain the temperature-dependent PL (40–280 °C) spectra which were performed using a LABRAM-UV Raman microspectrometer (Jobin Yvon).

3. Results and discussion

XRD patterns of Eu^{2+} doped $CaCl_2/SiO_2$ phosphors show only lines corresponding to the α-quartz of SiO_2. Whatever else is present must be either amorphous or in amounts too small to be detected by routine x-ray analysis.

PL and PLE spectra of $(CaCl_2/SiO_2) : 0.01Eu^{2+}$ with the molar ratio of $CaCl_2$ to SiO_2 being 25 : 75 and 10 : 90 are presented in figure 1(*a*). The PL spectra show a similar violet–blue emission band peaking at 427 nm with an FWHM of 21 nm and the PL intensity of Eu^{2+} in $(CaCl_2)_{25}/(SiO_2)_{75}$ can be about 155% of that in $(CaCl_2)_{10}/(SiO_2)_{90}$. Compared with the common FWHM value, 50–100 nm, of Eu^{2+} ions in most phosphor materials, this value is smaller, indicating the weak interaction of Eu^{2+} ions with the host material of $CaCl_2/SiO_2$ [13]. PL and PLE spectra of hygroscopic $CaCl_2 : 0.01Eu^{2+}$ without SiO_2 are also shown in figure 1(*b*). By comparison, the emission band of Eu^{2+} ions originating from the allowed 5d–4f transition in $(CaCl_2/SiO_2) : 0.01Eu^{2+}$ is similar to that in $CaCl_2 : 0.01Eu^{2+}$ without SiO_2, showing that adding SiO_2 did not change the crystal surroundings of Eu^{2+} in $CaCl_2$. Moreover, it is found that the $(CaCl_2/SiO_2) : 0.01Eu^{2+}$ is stable in air, water and alkaline solutions due to the fact that hygroscopic $CaCl_2$ is protected by surrounding SiO_2. From figure 1, it is also observed that the PLE spectra of all samples are composed of several bands, which originate from the parity allowed $4f^7 – 4f^6 5d$ transitions of Eu^{2+} ions and the PLE band in both $CaCl_2 : 0.01Eu^{2+}$ and $(CaCl_2/SiO_2) : 0.01Eu^{2+}$ phosphors can extend to 425 nm covering almost the full near-UV region showing that $(CaCl_2/SiO_2) : Eu^{2+}$ is a promising phosphor suitable for excitation by GaN based near-UV LED and can also be applied as a short wavelength blue component to white LED technology.

In figure 2, the Eu^{2+} concentration dependence of the PL intensity in $(CaCl_2/SiO_2) : xEu^{2+}$ is depicted (solid squares). It can be seen that the PL intensity initially goes up by increasing the Eu^{2+} concentration from 0.1 mol% up to the

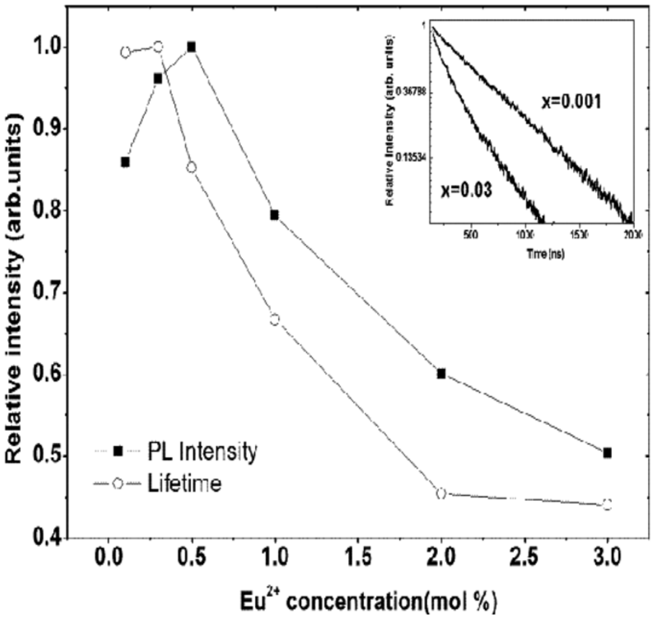

Figure 2. The PL intensities (solid squares) and lifetimes (open circles) of Eu^{2+} in $(CaCl_2/SiO_2):xEu^{2+}$ with varying Eu^{2+} concentrations from 0.1 to 3 mol%. Insets: the decay curves of Eu^{2+} in $(CaCl_2/SiO_2):xEu^{2+}$ for $x = 0.1$ and 3 mol%.

quenching concentration of about 0.5 mol% beyond which the intensity begins to decrease gradually due to the effect of the concentration quenching. The decay curves of the violet–blue fluorescence of Eu^{2+} in $(CaCl_2/SiO_2):xEu^{2+}$ have been measured. The lifetimes are obtained by integrating the decay curves, of which the initial intensities are normalized, as shown in figure 2 (open circles). The decay curves for $x = 0.1$ and 3 mol% as an example are shown in the inset of figure 2. The fluorescence lifetimes are little changed at about 700 ns as the Eu^{2+} concentration is less than 0.3 mol%. They begin to decrease gradually from about 700 to 340 ns with increasing Eu^{2+} concentration from 0.3 to 3 mol%. The variation of the PL intensities and fluorescence lifetimes with the Eu^{2+} concentrations can be understood by the following analysis. At a low doping concentration (<0.5 mol%), the luminescent efficiency is considered to be unchanged because of constant lifetimes. The increase in PL intensity with Eu^{2+} concentration is thus attributed to the enhanced absorbed numbers of the excitation photons by Eu^{2+} ions. When the Eu^{2+} concentration is more than 0.5 mol%, the absorption of excitation photons is considered to be saturated and the PL intensity is governed mainly by the luminescent efficiency of the phosphors, so that the decrease in PL intensity is coinciding with the decrease in the fluorescence lifetime for $x > 0.5$ mol%, as shown in figure 2. The occurrence of absorption saturation for the excitation is confirmed by the diffuse reflection spectra of $(CaCl_2/SiO_2):xEu^{2+}$, as shown in figure 3. For pure $CaCl_2/SiO_2$, there is almost a reflectance platform appearing in the wavelength range 200–600 nm. When Eu^{2+} ions are doped, absorption bands appear in the wavelength range 330–450 nm, attributed to 4f–5d transition of Eu^{2+} ions. The absorption enhances with increasing Eu^{2+} content and tends to be saturated when the concentration of Eu^{2+} is higher than 0.5 mol%.

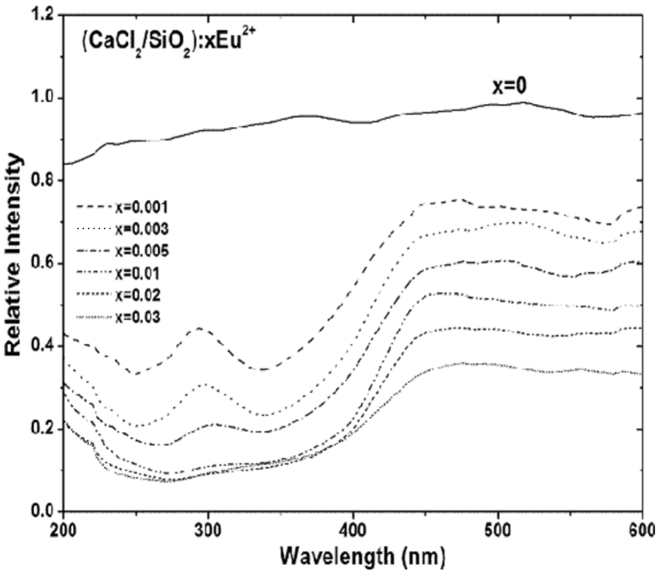

Figure 3. Diffuse reflection spectra of Eu^{2+} in $(CaCl_2/SiO_2):xEu^{2+}$ with varying Eu^{2+} concentrations.

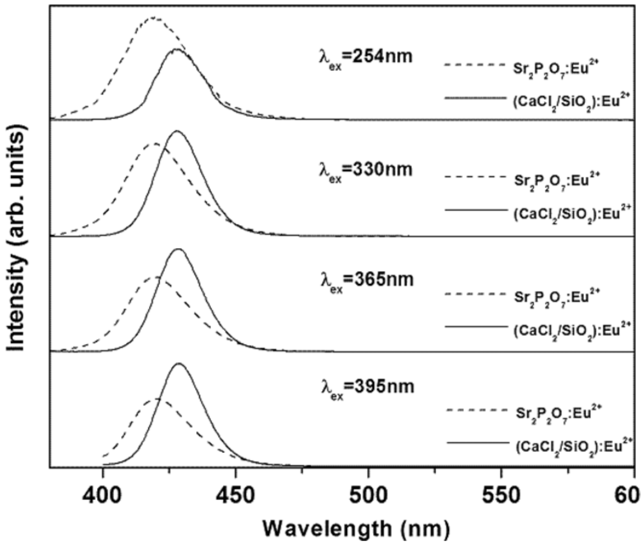

Figure 4. The PL spectra of $(CaCl_2/SiO_2):0.05Eu^{2+}$ and $Sr_2P_2O_7:0.02Eu^{2+}$.

$Sr_2P_2O_7:Eu^{2+}$ phosphor is known as a violet–blue phosphor used in the field of photocopying lamps and phototherapy illuminators, especially for the treatment of hyperbilirubinemia [8]. Moreover, the $Sr_2P_2O_7:Eu^{2+}$, Mn^{2+} phosphor has been reported to be a candidate for blue–orange phosphors for the application of near-UV chip-based white LEDs [14, 15]. The PL spectra of $Sr_2P_2O_7:0.02Eu^{2+}$ and $(CaCl_2/SiO_2):0.05Eu^{2+}$ are shown in figure 4. The emission peak of $(CaCl_2/SiO_2):0.05Eu^{2+}$ phosphor is located in a slightly lower energy position than Eu^{2+} in $Sr_2P_2O_7$ (420 nm). The relative emission intensity in $(CaCl_2/SiO_2):0.05Eu^{2+}$ is about 55%, 85%, 105% and 130% as that in $Sr_2P_2O_7:0.02Eu^{2+}$ for excitation at 254 nm, 330 nm, 365 nm and 395 nm, respectively. The PL comparison is performed by exciting the different phosphor powders with the same excitation source. As we know, the PL intensity is proportional to the absorbed number of the excitation light and luminescent efficiency.

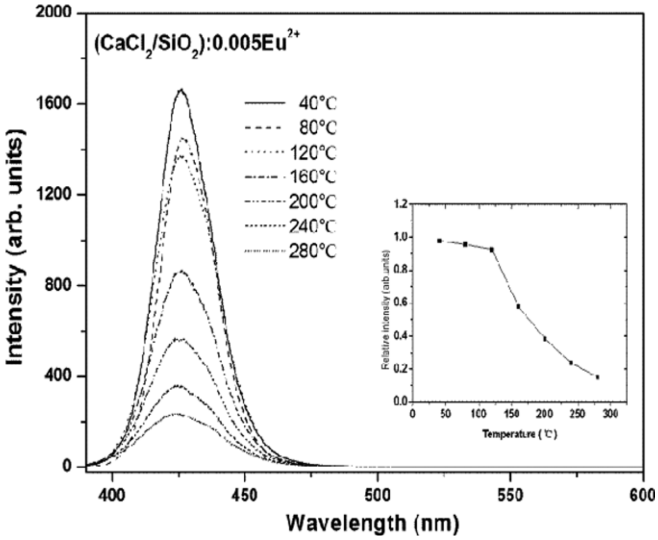

Figure 5. The PL spectra of $(CaCl_2/SiO_2) : 0.005Eu^{2+}$ at various temperatures in the range 40–280 °C. Inset shows the relative emission intensity of $(CaCl_2/SiO_2) : 0.005Eu^{2+}$ as a function of temperature.

There is an optimal concentration of luminescence centres for maximum PL. In this work, commercial $Sr_2P_2O_7$ phosphor with an optimal Eu^{2+}concentration of 2 mol% is selected as a normal phosphor. We observed that the PL intensity upon 395 nm excitation of the synthesized compound can be 30% higher than that of commercial $Sr_2P_2O_7 : 2\%\ Eu^{2+}$. We think that the difference in the PL intensity is mainly the result of different optical absorbance at 395 nm. The absorption tail of $Sr_2P_2O_7 : 2\%\ Eu^{2+}$ is located at the higher energy side of that of the new phosphor $(CaCl_2/SiO_2) : Eu^{2+}$, leading to less absorbance at 395 nm. In addition, $(CaCl_2/SiO_2) : Eu^2$ whose FWHM is 21 nm shows a purer colour than $Sr_2P_2O_7 : Eu^{2+}$ (FWHM is 30 nm). Hence, $(CaCl_2/SiO_2) : Eu^{2+}$ is more suitable to be combined with the GaN based near-UV LED for the application of high light-conversion efficiency phototherapy illuminators.

The thermal quenching property of the $(CaCl_2/SiO_2) : Eu^{2+}$ phosphor is also investigated. Figure 5 shows the luminescent spectra of $(CaCl_2/SiO_2) : 0.005Eu^{2+}$ at various temperatures in the range 40–280 °C. One can see that the $(CaCl_2/SiO_2) : Eu^{2+}$ (0.5 mol%) phosphor has a weak thermal quenching effect at temperatures lower than 120 °C. With increasing temperature up to 160 °C, the emission intensity of $(CaCl_2/SiO_2) : Eu^{2+}$ is decreased to 59% of the initial value. To further improve its high temperature thermal stability, an advanced material preparation method is currently under investigation.

4. Conclusions

An intense narrow violet–blue emission band is obtained in $(CaCl_2/SiO_2) : Eu^{2+}$ phosphor with the composition of 25% $CaCl_2$ and 75% SiO_2 prepared by solid state reaction. The phosphor exhibits an emission peak at 427 nm with an FWHM of 21 nm. The optimum concentration of Eu^{2+} in $(CaCl_2/SiO_2) : Eu^{2+}$ is determined to be 0.5 mol%. $(CaCl_2/SiO_2) : Eu^{2+}$ shows a weak thermal quenching effect at temperatures lower than 120 °C. The PL intensity of $(CaCl_2/SiO_2) : Eu^{2+}$ can be 30% higher than that of $Sr_2P_2O_7 : Eu^{2+}$ phosphor under 395 nm excitation. By using a near-ultraviolet(∼395 nm) LED as an excitation source, $(CaCl_2/SiO_2) : Eu^{2+}$ would be a very promising phosphor for converting the near-UV radiation to violet–blue emission for a novel high light-conversion efficiency phototherapy illuminator.

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