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A green-yellow emitting β-Sr_2SiO_4:Eu^{2+} phosphor for near ultraviolet chip white-light-emitting diode

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Abstract: Sr_2SiO_4:xEu^{2+} phosphors were synthesized through the solid-state reaction technique. The crystal phase of Sr_2SiO_4:xEu^{2+} phosphor manipulated by Eu^{2+} concentration was studied. The phase transited from β to α′ in Sr_2SiO_4:xEu^{2+} phosphor with increasing europium concentration. The single β phase was formed as x≤0.005 and changed α′ phase when x>0.01. The emission spectrum of the β-Sr_2SiO_4:Eu^{2+} phosphor consisted of a green-yellow broadband peaking at around 540 nm and a blue band at 470 nm under near ultraviolet excitation. The white LEDs by combining near ultraviolet chips with β-Sr_2SiO_4:Eu^{2+} phosphors were fabricated. The luminous efficiency (15.7 lm/W) was higher than α′-Sr_2SiO_4:Eu^{2+} phosphor white LED.

Keywords: luminescence; silicate; light-emitting diode; rare earths

In recent years, growing interest has been focused on white light emitting diodes (LEDs) for lighting because of their benefits in terms of energy-saving, reliability, maintenance and safety. The white LEDs fabricated with InGaN blue LED chips and yellow phosphors such as conventional $Y_3Al_5O_{12}$:Ce^{3+}, yellow oxynitride or silicate phosphors, have been investigated extensively due to their easy fabrication, low cost and high brightness[1–6]. However, the blue chip based white LEDs have color variation with input power and low reproducibility owing to their strong dependence of white color quality on the amount of phosphor. In comparison with white LEDs fabricated with blue chip and yellow phosphor combination, the GaN near ultraviolet (NUV) LED chip (400 nm) based white LEDs have higher color stability because all the colors are generated by the phosphors. The NUV chip with excitable phosphors therefore is another attractive combination for white light generation. Rare earths doped silicate phosphor is a good candidate for NUV white LED owing its good photoluminescence properties and chemical-physical stabilities[4–10]. As a yellow emitting phosphor, α′-Sr_2SiO_4:Eu^{2+} has been utilized to combine with NUV chips to fabricate white LEDs. The color coordinates were x=0.39, y=0.41, with the color rendering index (CRI) of 68 and the luminous efficiency of 3.8 lm/W[7]. Eu^{2+}-activated Sr_2SiO_4 phosphor has two phases, i.e. α′ and β. The β-Sr_2SiO_4:Eu^{2+} also emits a strong green-yellow band under NUV excitation, exhibiting a promising candidate for white LED phosphor. However, the white LEDs utilizing NUV chips with β-Sr_2SiO_4:Eu^{2+} green-yellow phosphors have scarcely been demonstrated yet.

In this letter, we synthesized Sr_2SiO_4:xEu^{2+} phosphors with various Eu^{2+} concentrations (x) in the range of 0–0.06, and observed that the single β phase was only formed as x≤0.005. With increasing x higher than 0.01, phase transition from β to α′ occurred. To obtain α′-Sr_2SiO_4:Eu^{2+} with Eu^{2+} concentration less than 0.01 to compare the optical properties with single-phased β-Sr_2SiO_4:Eu^{2+}, a small amount of Ba^{2+} was introduced into Sr_2SiO_4 host to replace Sr^{2+} for forming single α′-$Sr_{1.95-x}Ba_{0.05}SiO_4$:$xEu^{2+}$[11]. The photoluminescent properties of β-Sr_2SiO_4:Eu^{2+} were studied as a function of Eu^{2+} concentrations, demonstrating that β-Sr_2SiO_4:0.0035Eu^{2+} had stronger luminescence than α′-Sr_2SiO_4:Eu^{2+} for any Eu^{2+} concentrations with our synthesis method. Finally, the white LEDs by combining NUV chips with the single-phased β-Sr_2SiO_4:Eu^{2+} phosphors were fabricated.

1 Experimental

All the samples were synthesized through the solid-state

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reaction technique. $SrCO_3$ (99%), $BaCO_3$ (99%), SiO_2 (99%), and Eu_2O_3 (99.99%) were employed as the raw materials. These raw materials in the desired ratio were well milled. The mixture was fired at 1280 °C for 4 h in a slightly reducing atmosphere (a mixture of 5% H_2 and 95% N_2) in an electric furnace. The final phase was checked with a conventional X-ray diffraction (XRD) technique. Photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured at room temperature with a Hitachi F-4500 fluorescence spectrophotometer. Based on the standard LED technology, GaN (395 nm chip) based β-Sr_2SiO_4:Eu^{2+} white LEDs were encapsulated in transparent epoxy resin. The color coordinates and the color rendering indices (CIR) as well as the correlated color temperature (T_c) in kelvins of the fabricated white LED were measured using USB4000 Miniature Fiber Optic Spectrometer.

2 Results and discussion

The crystal structure of the Sr_2SiO_4:xEu^{2+} phosphor is confirmed to be the monoclinic β phase when $x \leq 0.005$. The β phase transits to the orthorhombic α′ phase as $x > 0.01$. For x value around 0.01, the sample is a mixture of β and α′ phases. Fig.1 depicts the XRD patterns of Sr_2SiO_4:xEu^{2+} (x=0, 0.005, 0.01 and 0.02) samples. The XRD patterns for x=0 and 0.005 match well with JPCDS 38-0271, i.e. β-Sr_2SiO_4, with JPCDS 39-1256, i.e. α′-Sr_2SiO_4, for x=0.02. It is shown that the crystal phase of the phosphors is Eu^{2+} concentration dependent. All the $Sr_{1.95}Ba_{0.05}SiO_4$:xEu^{2+} samples are α′ phase. The Sr_2SiO_4 crystal lattice may be distorted by addition of Eu^{2+} or Ba^{2+}, leading to the crystal phase transits from β to α′.

Fig.2(a) shows the PL and PLE spectra of β-Sr_2SiO_4: 0.0035Eu^{2+}. The PL spectra consist of a broad blue band at about 470 nm and a broad green-yellow band at around 540 nm. Because the two emission bands overlap each other, the PLE spectra of the two samples monitor at 430 and 590 nm for β-Sr_2SiO_4:0.0035Eu^{2+}, respectively, and 450 and 600 nm for α′-$Sr_{1.95}Ba_{0.05}SiO_4$:0.0035Eu^{2+}, respectively. The PLE spectra monitoring each of the two bands are different, demonstrating that the blue band prefers the shorter wavelength excitation in UV spectral region, and the yellow band is in favor of longer wavelength excitation in NUV and blue region. The intensity ratio of the green-yellow to the blue band thereby increases with increasing excitation wavelengths, as shown in the PL spectra. The PL is dominated by the blue band under 310 nm excitation and by the green-yellow band with a weak shoulder at the blue under 400 nm excitation. In comparison with the PL spectra of the yellow emitting α′-$Sr_{1.95}Ba_{0.05}SiO_4$:0.0035Eu^{2+} phosphor, as shown in Fig.2(b), the emission bands of β-Sr_2SiO_4: 0.0035Eu^{2+} are located at the short wavelength side at the same excitation wavelength with green-yellow luminescence.

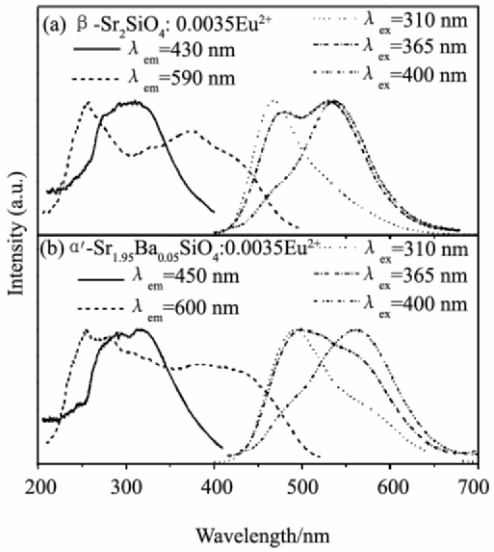

Fig.2 PLE and PL spectra of the β-Sr_2SiO_4:0.0035Eu^{2+} (a) and the α′-$Sr_{1.95}Ba_{0.05}SiO_4$:0.0035Eu^{2+} (b)

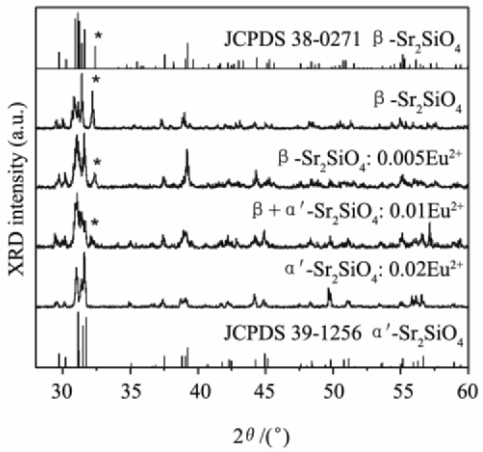

Fig.1 X-ray diffraction patterns of the Sr_2SiO_4:xEu^{2+} (x=0, 0.005, 0.01, 0.02) phosphors

Fig.3 (a) and (b) present the PL spectra of the Sr_2SiO_4: xEu^{2+} samples with different Eu^{2+} concentrations under 310 and 400 nm excitations, respectively. The PL spectra under 310 nm excitation are dominated by a blue band at 470 nm with a tail on the longer-wavelength side for Eu^{2+} concentration x<0.01. As Eu^{2+} concentration increases over 0.01, the blue band shifts to the longer wavelength side around 490 nm and a yellow band appears around 570 nm. Under 400 nm excitation, the PL spectra are dominated by a green-yellow band around 540 nm with a weak shoulder around 470 nm for x<0.01. For x>0.01, the 570 nm yellow bands dominate the spectra. It clearly exhibits that the emission peak shifts in the PL spectra as x exceeds 0.01 for both 310 and 400 nm excitations.

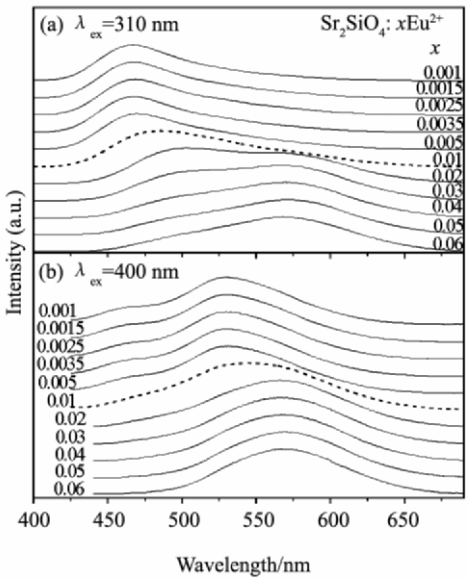

Fig.3 PL spectra of Sr_2SiO_4:$x$$Eu^{2+}$ under 310 nm (a) and 400 nm (b) excitation wavelength

Both XRD and PL spectra suggest that 0.01 is a critical concentration of Eu^{2+} at which the luminescent properties are given by both β and α′ phases. The spectral shift with x values is the response of crystal phase transition from β to α′. The emission bands remain at the same positions as the x value changes in the same phase, i.e., the emission band position is phase dependent.

Two Eu^{2+} emission bands are observed in both β and α′ Sr_2SiO_4:Eu^{2+}. It is known that there are two different strontium sites, denoting Sr(I) and Sr(II), in α′-Sr_2SiO_4 with equal amounts in the lattice. Sr(I) has ten oxygen coordinates and Sr(II) surrounded by nine oxygen ions. The shorter-wavelength emission is attributed to Eu^{2+} on Sr(II) sites; whereas the longer-wavelength emission to the Eu^{2+} on Sr(I) sites[12]. In the α′→β phase transition a rotation of SiO_4 tetrahedra occurs, so that polyhedra lose their mirror symmetry, and each pair of symmetrical Sr–O bonds splits into a shorter and a longer bond, keeping their average length approximately constant. An overall increase of the Sr–O bond valence is produced[11]. It may result in the strength of the crystal field around Sr^{2+} ions in β phase stronger than that in α′ phase. Therefore, the emission bands shift to the short-wavelength side. The excitation wavelength dependence of the emission bands (Fig.2) can also be reasonably attributed to the different properties of the two Sr^{2+} sites.

Fig.4 gives the dependence of relative PL integrated intensities of β-Sr_2SiO_4:$x$$Eu^{2+}$, α′-$Sr_2SiO_4$:$x$$Eu^{2+}$ and α′-$Sr_{1.95}Ba_{0.05}SiO_4$:$x$$Eu^{2+}$ on Eu^{2+} concentration under 400 nm excitation. The optimal composition, at which the maximal luminescence is recorded, is found to be β-Sr_2SiO_4: 0.0035Eu^{2+}.

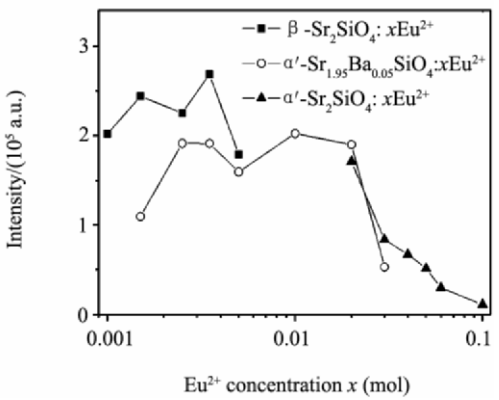

Fig.4 Emission intensities of Eu^{2+} fluorescence as a function of Eu^{2+} concentration in Sr_2SiO_4:Eu^{2+} and $Sr_{1.95}Ba_{0.05}SiO_4$:Eu^{2+} phosphors (emission intensity is measured under excitation at 400 nm)

It is also observed that both α′-Sr_2SiO_4:$x$$Eu^{2+}$ and α′-$Sr_{1.95}Ba_{0.05}SiO_4$:$x$$Eu^{2+}$ have strong luminescence for x=0.02. The PL intensities gradually reduce as x further increases, owing to the concentration quenching. At low Eu^{2+} concentration of x≤0.005, pure α′ phase is formed only in $Sr_{1.95}Ba_{0.05}SiO_4$:$x$$Eu^{2+}$ but not in Sr_2SiO_4:$x$$Eu^{2+}$. One reason is that the addition of Ba results in the lattice distortion and defects, which compete with luminescent centers in absorbing the excitation energies, and thus reduces the luminescent intensity in comparison with β-Sr_2SiO_4:$x$$Eu^{2+}$. At high Eu^{2+} concentration of x>0.01, concentration quenching occurs both in α′-Sr_2SiO_4:$x$$Eu^{2+}$ and α′-$Sr_{1.95}Ba_{0.05}SiO_4$:$x$$Eu^{2+}$. Therefore, the maximal luminescent intensity occurs in β-Sr_2SiO_4:$x$$Eu^{2+}$ system.

As a result of the strong PL emission, the β-Sr_2SiO_4:0.0035Eu^{2+} sample is selected to fabricate LEDs using the NUV InGaN chip. The emission spectrum of the white LEDs measured under a forward-bias current of 20 mA is shown in Fig.5. The color coordinates are x=0.32, y=0.40 with the color temperature of 6045 K and the color

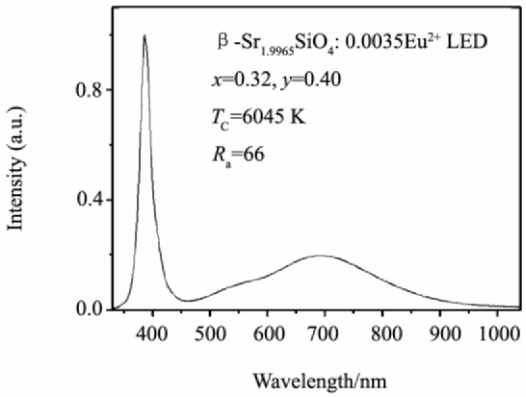

Fig.5 PL spectra of white InGaN-based β-Sr_2SiO_4:0.0035Eu^{2+} LED under 20 mA forward-bias drive current

rendering index (CRI) of 66. The luminous efficiency is 15.7 lm/W, higher than that (3.8 lm/W) fabricated with NUV chip and α′-Sr_2SiO_4:Eu^{2+} phosphor[7]. The two-color emitting β-Sr_2SiO_4:Eu^{2+} phosphor has great potentials in solid sate lighting if an orange or red phosphor is added to improve the color coordinates and color rendering index.

3 Conclusion

Green-yellow β-Sr_2SiO_4:Eu^{2+} phosphors were synthesized and concentration manipulated crystal phase in Sr_2SiO_4:xEu^{2+} were observed. The single β phase was only formed at $x \leq 0.005$, and α′ single phase at $x > 0.01$. Different emission bands were observed when Eu^{2+} replaced Sr(I) and Sr(II) sites, corresponding to 540 and 470 nm bands in β-Sr_2SiO_4:Eu^{2+}, respectively and 570 and 490 nm bands in α′-Sr_2SiO_4:Eu^{2+}, respectively. As a consequence, a spectral shifted to longer wavelength side in Sr_2SiO_4:xEu^{2+} when Eu^{2+} concentrations higher than 0.01 was observed. The luminescent intensity of β-Sr_2SiO_4:xEu^{2+} was higher than α′-Sr_2SiO_4:xEu^{2+} and α′-$Sr_{1.95}Ba_{0.05}SiO_4$:xEu^{2+} under excitation at 400 nm. Therefore, the luminous efficiency of the β-Sr_2SiO_4:Eu^{2+} phosphors white LED was higher than the α′-Sr_2SiO_4:Eu^{2+} phosphors white LED. The β-Sr_2SiO_4:Eu^{2+} phosphor could be a good candidate for generating white light in phosphor-converted white LEDs.

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