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A novel orange phosphor of Eu^{2+}-activated calcium chlorosilicate for white light-emitting diodes

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Abstract

Novel orange phosphor of Eu^{2+}-activated calcium chlorosilicate was synthesized at 1273 K by conventional solid-state reactions under reductive atmosphere and investigated by means of photoluminescence excitation, diffuse reflectance and emission spectroscopies. These results show that this phosphor can be efficiently excited by the incident light of 300–450 nm, well matched with the emission band of 395 nm-emitting InGaN chip, and emits an intense orange light peaking at 585 nm. By combining this phosphor with a 395 nm-emitting InGaN chip, an intense orange light-emitting diode (LED) was fabricated. Under 20 mA forward-bias current, its CIE chromaticity coordinates are (0.486, 0.446). The dependence of as-fabricated orange LED on forward-bias current indicates that it shows excellent chromaticity stability and luminance saturation. These results show that this Eu^{2+}-activated calcium chlorosilicate is a promising orange-emitting phosphor for near-ultraviolet (UV) InGaN-based white LED.

Keywords: Chlorosilicate phosphors; Light-emitting diode; Luminescence

1. Introduction

Since Nakamura and his co-workers [1] fabricated a blue-emitting GaInN light-emitting diode (LED) in 1994, more and more interests were focused on white light-emitting diodes (WLEDs) because they have a great number of important applications in backlight of the liquid crystal display (LCD), automobile light and solid-state lighting, etc., due to high efficiency, lower energy consumption, good reliability and long lifetime. As earlier introduced by Nichia, the WLEDs were composed of blue LED emitting at 460 nm and phosphor such as cerium-doped yttrium aluminum garnet (YAG:Ce) giving a yellow emission being excited by blue LED. However, it has a poor color quality of CRI $<$ 80 due to the serious scarcity of red light. Another alternative approach is n-UV chip combined with red/green/blue tricolor phosphors, which is expected to own a series of advantages, such as high CRI $>$ 80, high color independence of devices on n-UV chip and more luminous efficiency, etc.

In recent years, the studies on tricolor phosphors suitable for near-ultraviolet (UV) excitation have been attracting more attention for fabricating WLED with n-UV chip for white lighting. Nowadays, $Sr_4Al_{14}O_{25}$:Eu^{2+} was used as blue phosphor for UV-LEDs [2]. Eu^{2+} and Mn^{2+} codoped $Ba_3MgSi_2O_8$ combined with UV-LED showed warm and stable white light [3]. Y_2O_2S:Eu^{3+} and CaS:Eu^{3+} currently used as the red inorganic phosphors for near-UV GaN-based LEDs. However, their luminescent efficiency is lower than that of the green (such as ZnS:Cu^{+}/Al^{3+}) and blue (such as $BaMgAl_{10}O_{17}$:Eu^{2+}) ones [4]. What is more, their stability is not high enough, and their decomposition products (such as sulfide gas) are harmful to environment. Therefore, it is urgent to seek for novel and efficient red phosphors for LED application that can be excited by around 400 nm irradiation. However, only a few red inorganic fluorescence compounds, $(Li_{0.333}Na_{0.334}K_{0.333})Eu(MoO_4)_2$ [5], $(Na_{0.92}Li_{0.08})(Y_{0.8}Gd_{0.2})$-$TiO_4$:$Eu^{3+}$ [6] and Y_2O_3:Eu, Bi [7], have been reported to the efficient red component with application in UV-LED.

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However, the absorption band of Eu^{3+} is almost predominating at 394 nm in most matrix and also very narrow, whose full-width at half-maxim (FWHM) is less than several nanometers, hardly accommodated to even smaller extent with the excursion of emission band of near-UV-emitting InGaN chip.

Eu^{2+} ion is a kind of well-known activated ion, the emission of Eu^{2+} is very strongly dependent on the host lattice and can be shifted from the UV to the red region of the electromagnetic spectrum [8]. Since the $4f \rightarrow 5d$ transition is an allowed dipole transition, the absorption and emission of Eu^{2+} are characterized as very efficient broadbands in many hosts, which makes Eu^{2+}-doped phosphors good candidates for photonic sources [9].

Eu^{2+}-activated alkali earth halide and silicate compound luminescence materials were synthesized by Leete and Mckeag [10]. Alkali earth halide and silicate compound both are effective hosts as luminescence matrices. Their complex compound, alkali earth chlorosilicate crystal has lower synthesis temperature and higher physical chemistry stability [11]. Therefore, Eu^{2+}-activated chlorosilicates are also expected to be suitable luminescent materials for UV-LEDs.

Recently, a few studies on Eu^{2+}-activated chlorosilicates phosphors for UV-LEDs were reported. Under near-UV excitation, $Ba_5SiO_4Cl_6{:}Eu^{2+}$ phosphor emitted an intense blue light [12], $Sr_8(Si_4O_{12})Cl_8{:}Eu^{2+}$ phosphor gave a bluish-green emission [13] and $Ca_8Mg(SiO_4)_4Cl_2{:}Eu^{2+}$ phosphor had a high green luminescence [14].

In our unpublished work, we have synthesized the Eu^{2+}-doped $Ca_5(SiO_4)_2F_2$ phosphors emitting green visible light (506 nm). Because the broadband absorption and the emission of Eu^{2+} are very strongly dependent on the host lattice, it is expected that the emission of Eu^{2+} shifts to red region when F is substituted by Cl, due to the smaller electronegative value. In the present paper, novel orange phosphor of Eu^{2+}-activated calcium chlorosilicate was synthesized and the luminescent properties of Eu^{2+} in calcium chlorosilicate were studied. An intense orange-emitting LED was fabricated by combining this phosphor with a 395 nm-emitting InGaN chip for the purpose of investigating the optical properties of phosphors in device.

2. Experimental

Powder samples with the general composition $4CaO \cdot CaCl_2 \cdot 2SiO_2$(CSC) and $4CaO \cdot CaCl_2 \cdot 2SiO_2 \cdot 0.075\, Eu_2O_3$(8% excessive $CaCl_2$ added as flux) (CSCE) were prepared by conventional solid-state reaction technique according to Ref. [15]. The starting materials were $CaCO_3$ (A.R.), SiO_2 (A.R.), anhydrous $CaCl_2$ (A.R.) and Eu_2O_3 (99.99%). The raw materials were thoroughly mixed in an agate mortar by grinding and subsequently sintered at 1273 K in reductive atmosphere (25% H_2/75% N_2), followed by an additional grinding. The phase purity of the as-prepared phosphor was investigated by X-ray powder diffraction spectroscopy (XRD) with a Rigaku D/max 2200 vpc X-ray Diffractometer with Cu$K\alpha$ radiation at 40 kV and 30 mA. The XRD patterns were collected in the range $10° \leqslant 2\theta \leqslant 70°$.

The diffuse reflection spectra of the samples were measured by a Cary 5000UV-Vis-NIR spectrophotometer equipped with double out-of-plane littrow monochromator, using $BaSO_4$ as a standard in the measurements. The measurements of photoluminescence and photoluminescence excitation spectra of CSCE were measured by a Fluorolog-3 spectrofluorometer (Jobin Yvon Inc/specx) equipped with a 450 W Xe light source and double excitation monochromators. The phosphor was precoated on an n-UV LED chip with 395 nm emission based on standard LED technology. The spectra and the CIE color coordinates of as-fabricated LED were determined by the LED-1100 Spectral/Goniometric Analyzer from Labsphere Inc. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Phase characterization

The X-ray diffraction pattern of CSCE is shown in Fig. 1. For the obtained phase, it is carefully observed that there are no peaks of raw materials besides small amount of calcium orthosilicate impurity phase. It is initially expected that the CSCE will be isomorphic to $Ca_5(SiO_4)_2F_2$, due to the similar chemical properties. But the obtained phase does not agree with JCPDS 29-0324, indicating its structure is different from $Ca_5(SiO_4)_2F_2$. It is also found that the main phase does not agree with any JCPDS available. What is more, the XRD patterns of samples with various Eu concentrations (1–5%) have been measured too. The results show that different Eu

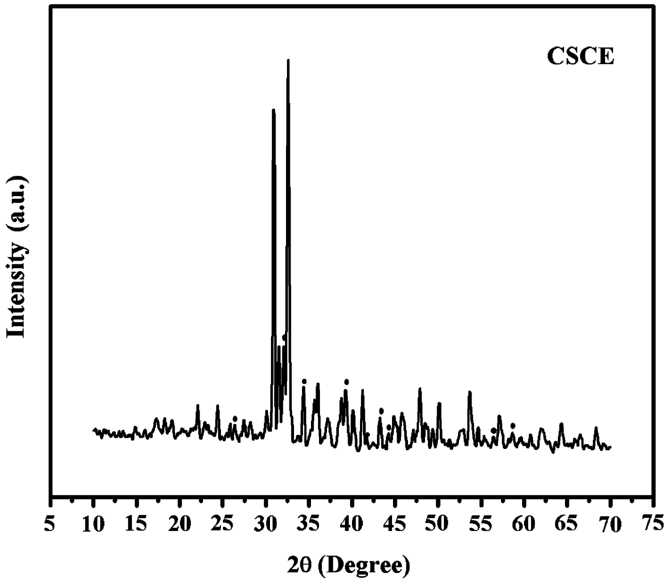

Fig. 1. XRD pattern of CSCE phosphor (filled circle for calcium orthosilicate impurity phase).

concentrations do not result in new other phase except the unknown main phase. Consequently, we speculate that the obtained unknown phase is likely to be a new phase. With respect to this point, a further study is still being carried on.

3.2. Photoluminescent properties of CSCE

Fig. 2 shows the diffuse reflection spectra of CSC and CSCE. For pure CSC, the onset of reflectance is around 200 nm, and it increases steeply until up to 250 nm, then a reflectance platform appears in the wavelength range of 300–800 nm. When Eu^{2+} ions are doped, it can be seen in the curves (b) of Fig. 2 that there are several obvious absorption bands in the wavelength range of 280–500 nm, attributed to $4f \rightarrow 5d$ transition of Eu^{2+} ions.

The excitation and emission spectra of CSCE phosphor are shown in Fig. 3. The excitation spectrum exhibits a broadband between 250 and 500 nm with four peaks around 275, 320, 372 and 426 nm, which are attributed to the $4f \rightarrow 5d$ transition of Eu^{2+} and consistent with the diffuse reflectance spectra as presented in Fig. 3. For the emission spectrum, an asymmetric broadband predominating at around 585 nm with the FWHM about 153 nm is ascribed to $5d \rightarrow 4f$ allowed transition of Eu^{2+} ions. Furthermore, a shoulder at around 505 nm is also observed, owing to the emission of Eu^{2+} in small amount of calcium orthsilicate impurity phase [16].

The excitation and emission spectra indicate that this phosphor can be effectively excited by UV (395 nm) and exhibits an intense orange light, nicely fitting in with the widely applied UV LED chips.

3.3. Fabricate LED with CSCE

To obtain a highly efficient orange component for LED, an intense orange light-emitting LED was fabricated by combining CSCE phosphor with a 395 nm-emitting InGaN chip. Fig. 4 shows the electroluminescence spectra of naked UV LED (curve 1) and the fabricated PC-LED (curve 2) combined with CSCE phosphor under 20 mA forward-bias current. Comparatively, the peak at 395 nm is attributed to the emission of InGaN chip and the broadband at 616 nm is due to the emissions of CSCE. Bright orange light from the LED is observed by naked eyes. From two curves, it is obviously observed that the near violet light of naked n-UV-LED chip at 395 nm is absorbed dramatically by CSCE (curve 2) and simultaneously down-converted into an intensive orange light around 616 nm. Compared with CSCE phosphor, it is surprising that maximum emission peak of LED-based CSCE shifts from 585 to 616 nm. With regard to this phenomenon, we speculate interaction between CSCE and resin may occur. It is because phosphor and resin were solidified with each other for a few hours at

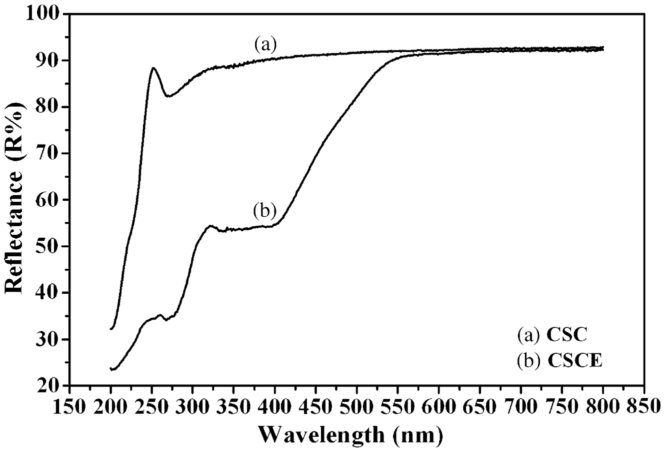

Fig. 2. The diffuse reflection spectra of CSC and CSCE.

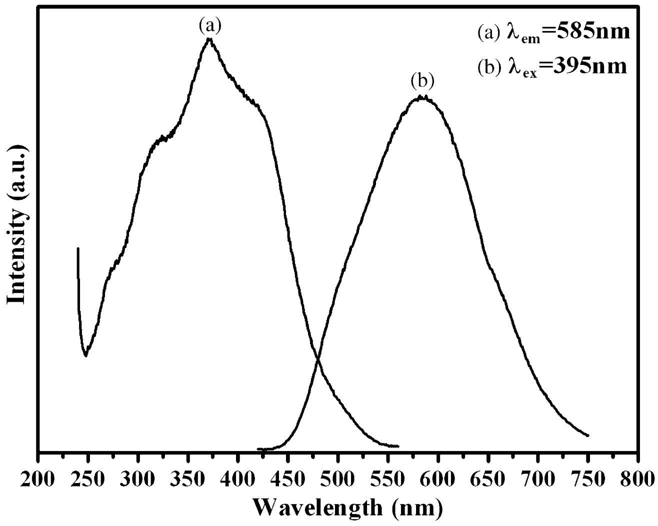

Fig. 3. Photoluminescence excitation spectra ((a) $\lambda_{em} = 585$ nm) and emission spectrum ((b) $\lambda_{ex} = 395$ nm) of CSCE.

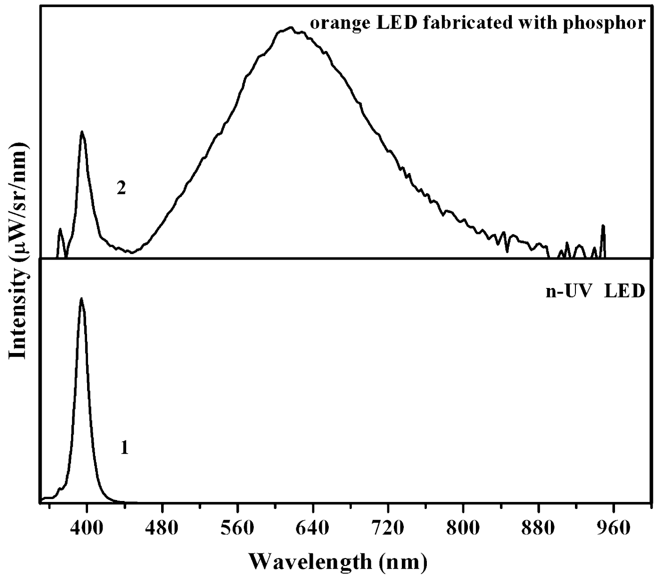

Fig. 4. The electroluminescence spectra of naked UV LED (curve 1) and the fabricated PC-LED (curve 2) combined with CSCE phosphor under 20 mA forward-bias current.

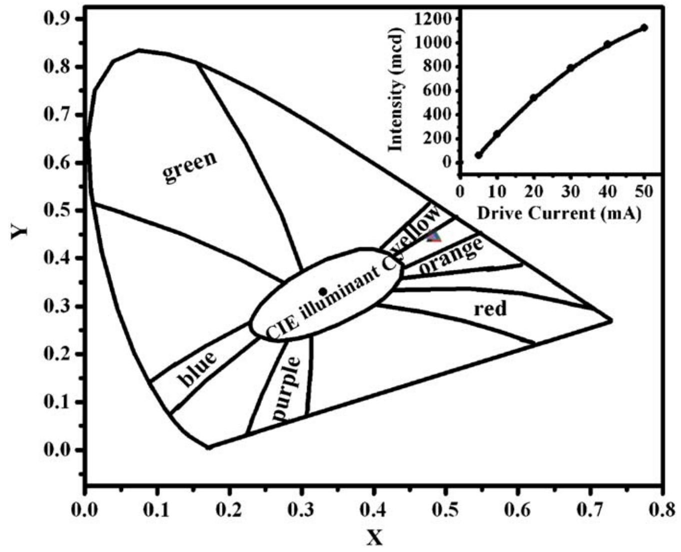

Fig. 5. The CIE coordinates of as-synthesized and orange LED-based CSCE under $I_F = 5.0$, 10, 20, 30, 40, 50 mA in the CIE 1931 chromaticity diagram. The inset shows the dependence of the emission intensity on forward-bias currents.

150 °C in the process of LED fabrication. Further research is being carried on.

Fig. 5 shows the CIE coordinates of as-synthesized and orange LED-based CSCE under $I_F = 5.0$, 10, 20, 30, 40, 50 mA in the CIE 1931 chromaticity diagram. The inset shows the dependence of the emission intensity on forward-bias currents. In general, the operating voltage and the drive current of LED are approximately 3.6 V and 20 mA, respectively. Under 20 mA forward-bias current, the CIE chromaticity coordinates of the LED-based CSCE are (0.486, 0.446). As the drive current increases from 5 to 50 mA, there are no significant changes in the emission spectra except the emission intensity and the FWHM of the emission band, which are 171, 175, 172, 174, 177 and 178 nm, respectively. The x value of color coordinates decreases slightly, approximately difference percentage of -0.6% and the y value of color coordinates increases slightly, approximately difference percentage of 1.6%. The change of FWHM results in the tiny variation of CIE coordinates. At the same time, the luminous intensity of the fabricated orange LED almost linearly increases and there is no significant saturation or quenching phenomenon even the operating current is over 50 mA. The dependence of as-fabricated orange LED on forward-bias current shows that it presents excellent chromaticity stability and luminance saturation, indicating that CSCE is a promising orange-emitting phosphor for near-UV InGaN-based white LED.

4. Conclusions

In the present work, novel orange CSCE phosphor was synthesized. It is an excellent phosphor for n-UV LED due to broad excitation band near the UV range and intense emission. Furthermore, orange phosphor-converted LED was successfully fabricated by precoating CSCE phosphor onto 395 nm-emitting InGaN chip. The as-fabricated orange LED shows excellent chromaticity stability and luminance saturation as forward-bias current varies. It is believed to be a good orange phosphor candidate for creating white light in phosphor-converted white LEDs.

Acknowledgments

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