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Original research article

Near ultraviolet excited white light emitting diode (WLED) based on the blue $LiCaPO_4:Eu^{2+}$ phosphor

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ABSTRACT

One near ultraviolet (NUV) chip coated with tricolor phosphors to fabricate the white light emitting diode (WLED) has been attractive widely. In this paper, the blue emitting $LiCaPO_4:Eu^{2+}$, together with the red $CaSiAlN_3$: Eu^{2+} and the green (Sr, Ba)SiO_4: Eu^{2+} phosphor, is selected as the tricolor components for the NUV excited WLED preparation. The as-prepared WLED exhibits good luminescent performances with the color rendering index (Ra) of 88.6, the correlation color temperature of 3351 K, the lumen efficiency of 77.05 lm/W, and the color coordinates located at (0.4399, 0.4389). It is worth mentioning that the blue-light of the warm WLED succeeds to keep away from the hazard zone centered at 450 nm. Furthermore, a full spectrum warm WLED with the color rendering index (CRI) of 95.8 is fabricated by adding the fourth component as the $Sr_5(PO_4)_3Cl:Eu^{2+}$ phosphor. The prepared full spectrum WLED achieves the performance index of museum lighting.

1. Introduction

The white light emitting diode (WLED) has the advantages like high energy-efficiency, good life-durability, and environmental friendliness in comparison to the conventional light sources, so it is a promising green solid-state lighting source [1,2]. The commercial WLED lamps use the blue LED (InGaN) chip coated with the cerium-doped yttrium aluminum garnet (YAG: Ce^{3+}) yellow phosphors [3,4]. However, this type of WLED emits insufficient red light but excess blue light, and thereof has a high color temperature and a low color-rendering index [5]. Especially, the excess blue light will make eyes uncomfortable, and thus it is not suitable for indoor lighting [6–10]. A large quantity of literatures have reported that, the potential blue light hazards of light sources are bad for health, such as retina damage [11–13], clock disorders [14], and mental health [15]. Brainard et al. even found that the high-energy blue light hazards would lead to a breast cancer in women [10]. Therefore, it is significant to develop the WLED with good performances suitable for indoor lighting, including the proper blue emission intensity, the low color temperature and the high color rendering index.

In recent years, one near ultraviolet (NUV) chip coated with tricolor phosphors to fabricate the WLED has been attractive widely. There are many commercial phosphors for the NUV excited WLED, such as $BaMgAl_{10}O_{17}:Eu^{2+}$ [16] and $LiSrPO_4:Eu^{2+}$ [17] for the blue, $SrAl_2O_4:Eu^{2+}$ [18] and (Ba, $Sr)_2SiO_4$: Eu^{2+} [19] for the green, and (Sr, Ca) $AlSiN_3$: Eu^{2+} [20] for the red.

For the blue-emitting phosphors excited by the NUV light, phosphates of formula $ABPO_4$, where A is a mono-valent cation and B a divalent cation, have emerged as important optical materials because of their excellent thermal and hydrolytic stabilities [21,17]. $ABPO_4:Eu^{2+}$ (A = Li, Na and K; B = Mg, Ca, Sr and Ba) phosphors [22–26] have been widely studied. Among them, the

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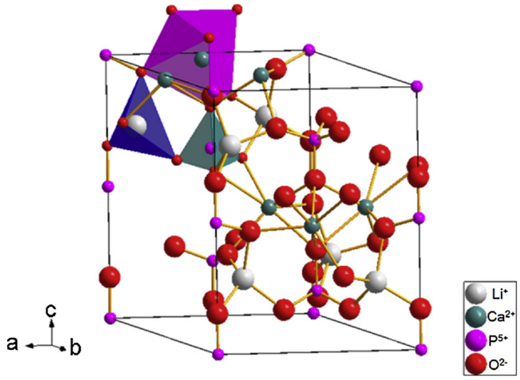

Fig. 1. The crystal structure diagram of $LiCaPO_4$ (ICSD-66387).

$LiCaPO_4:Eu^{2+}$ phosphor has an excellent NUV excitation profile and achieves a quantum efficiency of 88% under the excitation of 400 nm [27].

In this paper, the blue emitting $LiCaPO_4:Eu^{2+}$, together with the red $CaSiAlN_3$: Eu^{2+} and the green (Sr, Ba)SiO_4: Eu^{2+} phosphor, is selected as the tricolor components for the NUV excited WLED preparation. A white full spectrum with the low blue hazard efficiency and the high color rendering is obtained.

2. Experiments

A series of phosphors $LiCaPO_4:xEu^{2+}$ (x = 0.005, 0.01, 0.03, 0.05 and 0.07) with different concentrations are prepared by the high-temperature solid-state sintering method. Li_2CO_3(AR), $CaCO_3$(AR), $NH_4H_2PO_4$(AR) and Eu_2O_3(AR) are selected as the raw materials and mixed in a grinding bowl. After homogeneous mixing, they are loaded into a corundum crucible and sintered in a vacuum furnace with 5% H_2/N_2 mixed gas, which are heated at 5℃/min. The temperature rises to 600℃ for 1 h, and then increases to 960℃ for 5 h. After that, it is cooled to the room temperature and ground for further analysis.

3. Results and discussion

3.1. The XRD pattern of the phosphor

As shown in Fig. 1, $LiCaPO_4$ has the trigonal structure with the P31c (159) space group. The unit cell volume and lattice parameters of the matrix are a = b = 7.5247 Å, c = 9.9657 Å, c/a = 1.3244, V = 488.67$Å^3$, and Z = 6. The crystal structure of $LiCaPO_4$ is indexed to ICSD-66387, where the $LiCaPO_4$ is composed of a three dimensional framework of the vertex-sharing LiO_4 and PO_4 tetrahedron, and the Ca^{2+} ions have six contacts to oxygen completing irregular eight-coordinate geometry.

Fig. 2 depicts the XRD patterns of a series of the as-synthesized $LiCaPO_4:xEu^{2+}$ (x = 0.005, 0.01, 0.03, 0.05, and 0.07), and the standard pattern (ICSD-66387) of $LiCaPO_4$ is taken as a reference. The XRD patterns agree well with the reference and the doping of Eu^{2+} ions does not lead to the notable structural variation. The Eu^{2+} ions (r = 0.125 nm with CN = 8) substitutes the Ca^{2+} ions (r = 0.112 nm with CN = 8) in the $LiCaPO_4$ host lattice because these two ions have approximate radiuses.

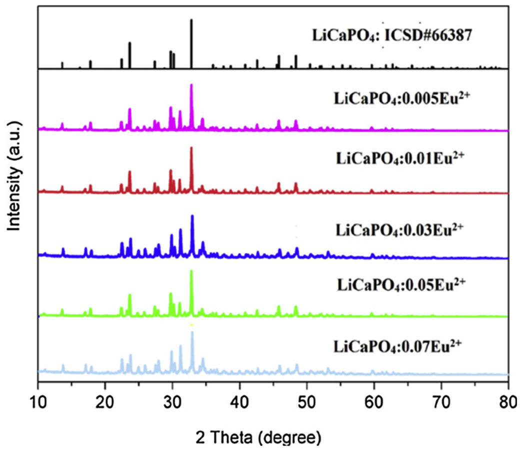

Fig. 2. XRD patterns of the as-prepared samples $LiCaPO_4:xEu^{2+}$ (x = 0.005, 0.01, 0.03, 0.05, and 0.07) and the standard pattern of ICSD-66387.

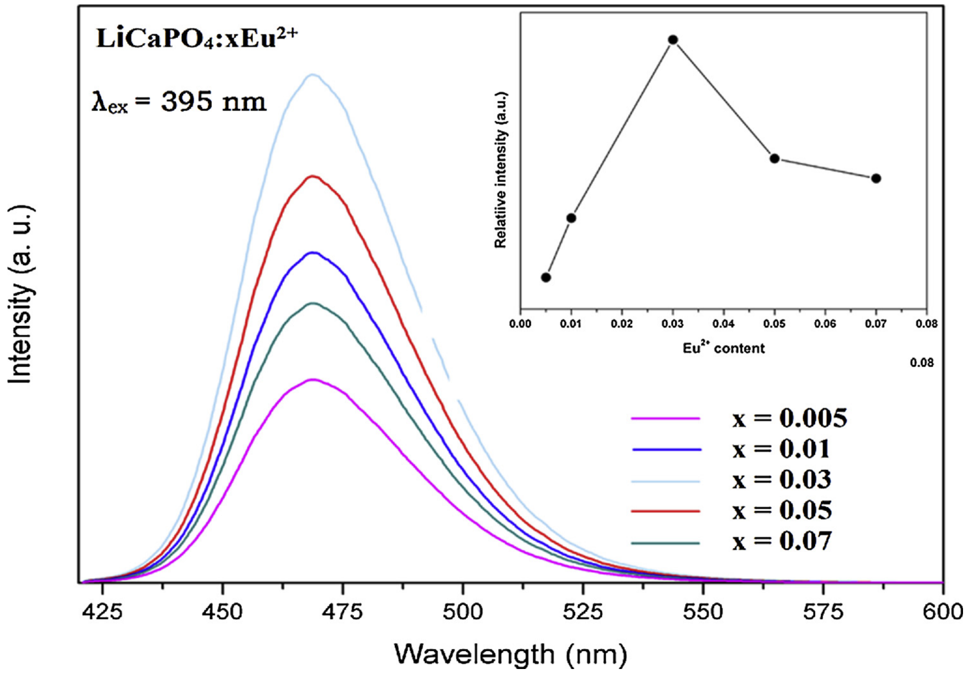

Fig. 3. The emission spectrum of different concentration $LiCa_{1-x}PO_4l:xEu^{2+}$ (λ_{ex} = 395 nm).

3.2. The excited spectrum and the emission spectrum

A series of $LiCaPO_4:Eu^{2+}$ phosphors with different doping concentrations of Eu^{2+} are fabricated and their emission spectra at 395 nm wavelength are tested to analyze the influence of different doping concentrations on the luminescent properties. The emission spectra of different doping concentrations at the 395 nm near-ultraviolet excitation wavelength are shown in Fig. 3.

Under the excitation of 395 nm light, the emission intensity of the samples with different doping concentrations varies with the different concentrations. At x = 0.03, the emission intensity of the samples reaches the maximum, and then decreases with the increase of the concentration because of the concentration quenching of the Eu^{2+} doping ions.

The excitation spectra (λ_{em} = 470 nm) and emission spectra (λ_{ex} = 395 nm) of $LiCa_{0.97}PO_4:0.03Eu^{2+}$ phosphors are shown in Fig. 4. The $LiCa_{0.97}PO_4:0.03Eu^{2+}$ phosphor has a wide excitation range of 220 to 450 nm. The excitation corresponds to the transition of Eu^{2+} ions from the $4F_7$ ($^8S_{7/2}$) ground state to $4f^6 5d^1$. On the other hand, the $LiCa_{0.97}PO_4:0.03Eu^{2+}$ phosphor exhibits a wide and strong blue emission band from 450 to 520 nm centered at 470 nm under 395 nm excitation. The radiation transition of the Eu^{2+} ions in the inset figure in Fig. 4 indicates that, the electron jumps from 4*f* to 5*d* when excited by the NUV light. The electron relaxes to the $4f^6 5d^1$ level in the form of non-radioactive transition, and then transits to $4f^7$ to release blue photons.

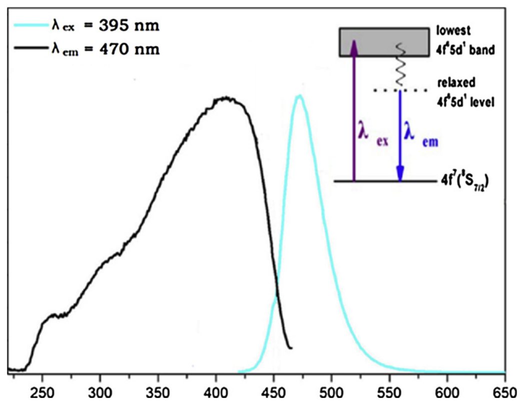

Fig. 4. PLE (λ_{em} = 470 nm) and PL (λ_{ex} = 395 nm) spectra of the $LiCa_{0.97}PO_4:0.03Eu^{2+}$ phosphor; the inset illustrates the energy level diagram of the Eu^{2+} ions in $LiCa_{0.97}PO_4:0.03Eu^{2+}$.

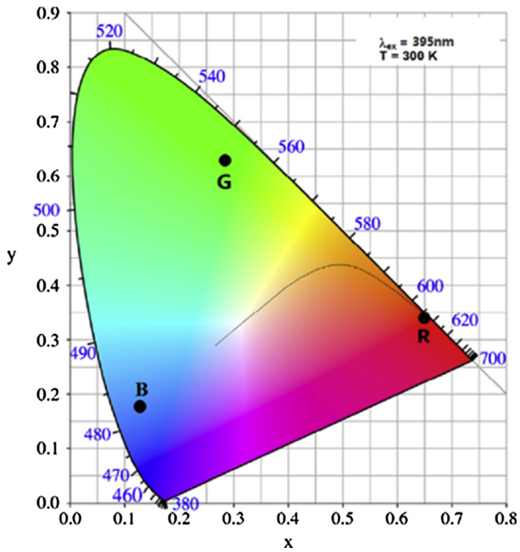

Fig. 5. The CIE chromatic coordinates with three phosphors, including Point R for (Sr, Ca)$AlSiN_3$:Eu^{2+}, Point G for (Ba,Sr)$_2SiO_4$:Eu^{2+} and Point B for $LiCaPO_4$:Eu^{2+}.

3.3. Preparation of the NUV excited WLED

A NUV excited WLED is fabricated by using the 395 nm InGaN chip coated with the red (Sr, Ca) $AlSiN_3$: Eu^{2+}, the green (Ba, Sr)$_2SiO_4$: Eu^{2+}, and the blue $LiCaPO_4$: Eu^{2+} phosphors. The corresponding CIE chromaticity coordinates in Fig. 5 are at R (0.642, 0.360) for the red phosphor, G (0.283, 0.640) for the green phosphor and B (0.125, 0.175) for the blue phosphor respectively.

The emission spectrum of the as-prepared warm WLED is shown in Fig. 6. The color rendering index (Ra) is 88.6; the correlation color temperature is 3351 K, and the color coordinates of the emitted light (in Fig. 7) are located at (0.4399, 0.4389) and the lumen efficiency is 77.05 lm/W. It is worth mentioning that the blue-light region of the warm WLED succeeds to minimize the impact of the blue-light hazard zone centered at 450 nm.

3.4. The full spectrum warm WLED with the high CRI

A full spectrum warm WLED with the color rendering index (CRI) higher than 95 is important in the museums and other special spaces, which requires a strong ability to restore the color of objects. In this paper, a high Ra full spectrum WLED is fabricated by using the 395-nm near-UV chip coated with $Sr_5(PO_4)_3Cl$:Eu^{2+}, $LiCaPO_4$:Eu^{2+}, (Ba, Sr)$_2SiO_4$:Eu^{2+}, and (Sr, Ca)$AlSiN_3$:Eu^{2+} phosphors. The emission spectra of four kinds of phosphors at 395-nm (in Fig. 8) are distributed widely from 420 to 650 nm.

The emission spectrum of the as-fabricated full-spectrum WLED is shown in Fig. 9. The correlation color temperature is 3527 K; the color coordinate is (0.4125, 0.4067); the luminous efficiency is 40.31 lm/W, and the color rendering index Ra reaches as high as 95.8. Therefore, the as-prepared full spectrum WLED has an excellent color rendering performance.

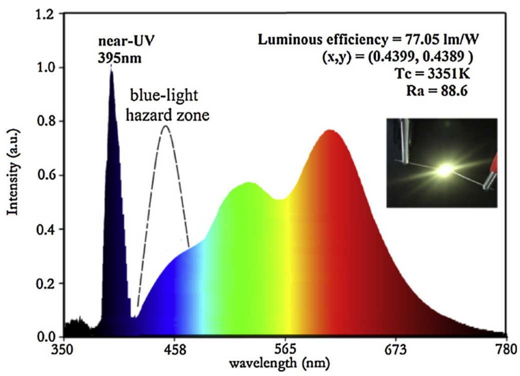

Fig. 6. The emission spectra of the WLED fabricated by the three phosphors with UV-Chips.

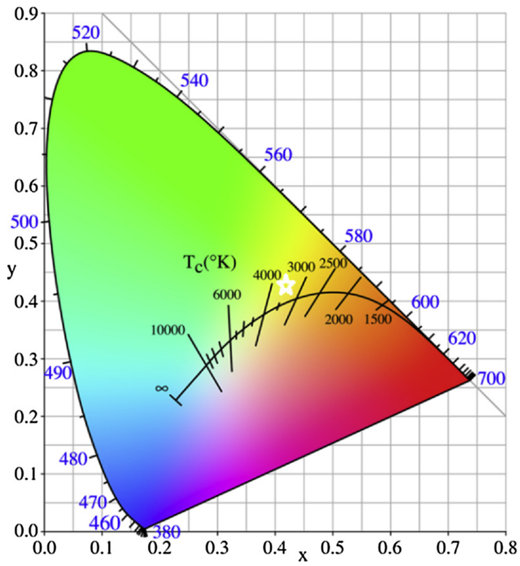

Fig. 7. The position of the WLED fabricated by the three phosphors excited by near-UV chips on CIE.

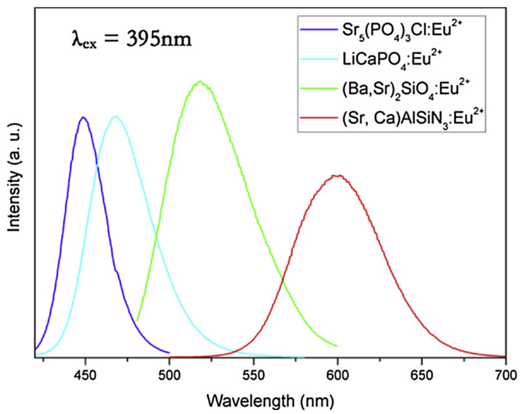

Fig. 8. The emission spectra of $Sr_5(PO_4)_3Cl:Eu^{2+}$, $LiCaPO_4:Eu^{2+}$, $(Ba,Sr)_2SiO_4:Eu^{2+}$ and $(Sr, Ca)AlSiN_3:Eu^{2+}$phosphors (λ_{ex} = 395 nm).

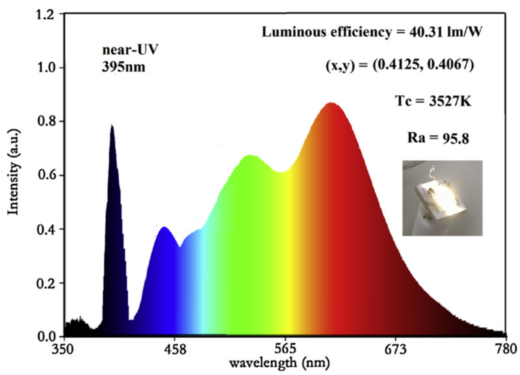

Fig. 9. The emission spectrum of the full-spectrum warm WLED.

4. Conclusion

In order to obtain the high-performance NUV excited WLED, the $LiCaPO_4:Eu^{2+}$ phosphor with an excellent excitation profile in the near UV range is synthesized and optimized. A NUV excited warm WLED is prepared by using the 395 nm InGaN chip coated with the red (Sr, Ca) $AlSiN_3$: Eu^{2+}, the green (Ba, $Sr)_2SiO_4$: Eu^{2+}, and the blue $LiCaPO_4$: Eu^{2+} phosphors. The color rendering index (Ra) is

88.6; the correlation color temperature is 3351 K; the color coordinates are located at (0.4399, 0.4389); and the lumen efficiency is 77.05 lm/W. It is worth mentioning that the blue-light region of the warm WLED succeeds to minimize the impact of the blue-light hazard zone centered at 450 nm. In addition, a full spectrum warm WLED with the color rendering index (CRI) of 95.8 is fabricated by using the 395-nm near-UV chip coated with the $Sr_5(PO_4)_3Cl:Eu^{2+}$, $LiCaPO_4:Eu^{2+}$, (Ba, $Sr)_2SiO_4:Eu^{2+}$, and (Sr, $Ca)AlSiN_3:Eu^{2+}$ phosphors. The correlation color temperature is 3527 K; the color coordinate is (0.4125, 0.4067); and the luminous efficiency is 40.31 lm/W.

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