Composition and structure design of three-layered composite phosphors for high color rendering chip-on-board light-emitting diode devices

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Received: December 24, 2020; Revised: January 30, 2021; Accepted: February 23, 2021

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Abstract: A three-layered phosphor structure was designed and prepared by the spin coating of BaSi₂N₂O₂:Eu (cyan-emitting) and (Sr,Ca)AlSiN₃:Eu (red-emitting) phosphor films on the yellow-emitting Y₃Al₅O₁₂:Ce (YAG:Ce) phosphor ceramic synthesized by the solid-state reaction under vacuum sintering. In order to achieve high color rendering lighting, the influence of the composition and structure of the three-layered phosphors on the optical, thermal, and electrical properties of the chip-on-board (COB) packaged white-light-emitting diodes (WLEDs) was studied systematically. The WLED with the structure of “red+cyan+yellow” (R+C+Y) three-layered phosphor generated neutral white light and had a luminous efficacy of 75 lm/W, the fidelity index (R_f) of 93, the gamut index (R_g) of 97, and the correlated color temperature (CCT) of 3852 K. Under the excitation of laser diode (LD), the layer-structured phosphor yielded the white light with a luminous efficacy of 120 lm/W, color rendering index (CRI) of 90, and CCT of 5988 K. The result indicates that the three-layered phosphor structure is a promising candidate to achieve high color rendering and high luminous efficacy lighting.

Keywords: three-layered composite phosphor; structure design; high color rendering; luminous efficacy

1 Introduction

Solid-state lighting devices based on white-light-emitting

diodes (WLEDs) have replaced traditional incandescent and fluorescent lamps in the market due to their advantages of long lifespan, environmental friendliness, high reliability, and high efficiency [1]. To meet the requirements of some special applications, such as automobile headlamp, ocean lighting, and long-distance street lighting, the state-of-the-art white-light illumination systems are developing towards high power and high brightness. Recently, laser diodes (LDs) have become

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attractive excitation sources to achieve high brightness and high-quality white light if combined with phosphors, because the external quantum efficiency of LDs increases linearly as a function of operating current without the problem of “efficiency droop” [2,3].

A typical approach to obtain high-power white light is to combine high-brightness blue light-emitting diodes (LEDs) or LDs with appropriate yellow phosphor converters [4–6]. The thermally robust phosphor ceramics are believed to be the best choice of phosphor converters, compared to their counterparts including phosphor powders, phosphor in glass, and single crystals [7,8]. The phosphor ceramics possess superior advantages, such as (i) strong mechanical properties, (ii) easy control of light scattering via component and porosity regulation, and (iii) much less degradation in luminous efficacy and color shift [5,9,10]. Also, the great microstructures (such as grain sizes, grain boundaries, pores, secondary phase, and surface structure) and optical property (emission wavelength, transmittance, etc.) tunability let phosphor ceramics get more freedom of performance design [11–14]. The highly efficient $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ (YAG:Ce) ceramic phosphors have been investigated extensively, and they often manifest high efficiency but suffer from low color rendering index (CRI) value, which indicates that the white light produced by using YAG:Ce is not accepted for general lighting. An effective method to obtain high CRI is to co-doping ions (Pr^{3+} , Cr^{3+} , Mn^{2+} , etc.) or partial substitute of Y^{3+} by different ions (Gd^{3+} , etc.) in YAG:Ce to add red spectral components in its spectrum, but usually with a sacrifice in luminous efficacy [15–19]. Alternatively, composite phosphor ceramics consisting of both red- and yellow-emitting phosphors are expected to realize high color rendering lighting. Pricha *et al.* [20] prepared $\text{CaAlSiN}_3:\text{Eu}$ and YAG:Ce double-layered composite ceramics. However, the composite ceramics had severe interfacial chemical interactions because of the composition difference between these two phosphors. To overcome this interfacial reaction problem, it would be a good way to coat a red phosphor film on the YAG:Ce ceramic. Many red phosphors with excellent performance have been studied recently [21,22]. Among these red phosphors, $(\text{Sr,Ca})\text{AlSiN}_3:\text{Eu}$ is considered as the ideal red-emitting phosphor for high-power LEDs (hp-LEDs) or LDs because it has wide excitation and emission bands, as well as high thermal quenching temperatures [23–25].

Nowadays, a new concept named “full-spectrum

lighting” (FSL), which mimics the spectrum of natural sunlight, has attracted more and more attention [26]. Full spectrum is defined as the spectral wavelength covering all visible regions with a small amount of ultraviolet and infrared light, and the spectrum should be continuous without extremely disproportionate peaks and troughs. However, except for the red composition often reported by researchers, the cyan gap in the 480–520 nm region also restricts the development of FSL in YAG:Ce phosphor ceramic [27–32]. Hence, a cyan phosphor is important to achieve FSL [33]. $\text{BaSi}_2\text{N}_2\text{O}_2:\text{Eu}$, which possesses an emission band centered at ~ 495 nm (full width at half maxima (FWHM) ≈ 32 nm), is an excellent cyan phosphor due to its high quantum efficiency [34].

In this work, to realize high color rendering, the red-emitting $(\text{Sr,Ca})\text{AlSiN}_3:\text{Eu}$ and the cyan-emitting $\text{BaSi}_2\text{N}_2\text{O}_2:\text{Eu}$ phosphors were chosen, and their films were coated on the YAG:Ce phosphor ceramic. The influence of the concentration of phosphor films and the phosphor ceramics of the three-layered phosphor on optical, thermal, and electrical properties of the packaged WLEDs was systematically investigated. Also, the effect of different stacking structures on the composite phosphor was studied at a specific concentration of the three phosphors. Furthermore, the optimal three-layered composite phosphor was combined with a blue LD to evaluate its suitability in laser-driven lighting. IES TM-30-15 evaluation system, in which the fidelity index (R_f) and the gamut index (R_g) are used to evaluate the color rendering of the light simultaneously, was used in the evaluation of the white LED devices.

2 Experimental

2.1 Fabrication of three-layered phosphors

The transparent YAG:Ce phosphor ceramic was fabricated by the solid-state reaction and vacuum sintering method. High purity powders of Y_2O_3 (99.999%, Fujian Changting Golden Dragon Co., Ltd., China), $\alpha\text{-Al}_2\text{O}_3$ (99.99%, Taimei Chemicals Co., Ltd., China), and CeO_2 (99.995%, Fujian Changting Golden Dragon Co., Ltd., China) were weighted according to the chemical formula $(\text{Ce}_x\text{Y}_{1-x})_3\text{Al}_5\text{O}_{12}$ ($x = 0.0005, 0.001, 0.0015$), and no sintering aids were added. After ball-milled in ethanol for 12 h at a rotation speed of 279 r/min, the slurry was dried at 70 °C in the oven.

The obtained powder was sieved through a 200-mesh screen, calcined at 600 °C in air for 4 h, dry pressed into green bodies ($\Phi = 20$ mm), and then cold isostatically pressed under a pressure of 250 MPa. The green bodies were sintered at 1780 °C in the vacuum of 5.0×10^{-5} Pa for 10 h and air-annealed in the oven at 1450 °C for 10 h. The phosphor ceramic was polished to the different thicknesses by a polyurethane polishing machine with diamond micronized powder as polishing slurry for further measurements and preparation of three-layered phosphors.

The cyan and red phosphor films were prepared by the spin coating method. $\text{BaSi}_2\text{N}_2\text{O}_2\text{:Eu}$ phosphor, $(\text{Sr,Ca})\text{AlSiN}_3\text{:Eu}$ phosphor (Yantai Bright Photoelectric Material Co., Ltd., China), glue A (mixture of epoxy resin and benzyl alcohol, 5351A, Shanghai Huitian New Material Co., Ltd., China), and glue B (mixture of triethylenetriamine and water, 5351 B, Shanghai Huitian New Material Co., Ltd., China) are commercially available. Curing reaction can occur after mixing glues A and B, which can facilitate films curing and molding. The cyan film has the mass ratio of glue A:glue B:($\text{BaSi}_2\text{N}_2\text{O}_2\text{:Eu}$) of 1:1:0.05, 1:1:0.07, and 1:1:0.09, and the red film has the mass ratio of glue A:glue B:($(\text{Sr,Ca})\text{AlSiN}_3\text{:Eu}$) of 1:1:0.01, 1:1:0.02, and 1:1:0.03. The $\text{BaSi}_2\text{N}_2\text{O}_2\text{:Eu}$, glue A, and glue B were mixed with a glass rod in a mixing pot. After defoaming in a vacuum defoamer, the mixture was evenly dripped on the rotating glass substrate, and the thickness of the final film can be changed by adjusting the rotation time and speed. The glass substrate coated with the mixture was put in the oven at 80 °C for 20 min and at 150 °C for another 20 min to reach a compact film. Then the phosphor film was scraped off with a scraper from bottom to top of the substrate without any damage for further tests and preparation of three-layered phosphors. The $(\text{Sr,Ca})\text{AlSiN}_3\text{:Eu}$ red phosphor films were prepared in the same way. The $\text{BaSi}_2\text{N}_2\text{O}_2\text{:Eu}$ film, $(\text{Sr,Ca})\text{AlSiN}_3\text{:Eu}$ film, and YAG:Ce ceramic were stacked in different orders to prepare different three-layered phosphor structures. Similar to the previous film preparation, the different composite phosphors were prepared by spin-coating a mixture of phosphor and glues onto a ceramic or another phosphor film on the ceramic rather than a glass substrate.

2.2 Characterization

The surface morphologies of the phosphor ceramic and phosphor films were characterized by a field emission

scanning electron microscope (FESEM, SU-8220, Hitachi, Japan), equipped with an energy dispersive X-ray spectroscope (EDS). The total transmittances of the ceramic and films over the wavelength ranging from 250 to 800 nm were recorded by an ultraviolet–visible–near infrared (UV–Vis–NIR) spectrophotometer (Cary 5000, Varian Medical System Inc., USA). The room-temperature photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured by the fluorescence spectrophotometer (FS5, Edinburgh Instruments, USA). Another fluorescence spectrophotometer (F-4600, Hitachi, Japan) equipped with a xenon lamp as the excitation source was used to measure the temperature-dependent PL and PLE spectra in the temperature range from 25 to 225 °C. In order to optimize the luminous performance of LEDs, YAG:Ce ceramic (Y), cyan phosphor film (C), and red phosphor film (R) were combined in six different three-layer structures (e.g., the “C+R+Y” means that C is attached directly to LEDs and Y is far away from the LEDs). These phosphors were then combined with chip-on-board (COB) LED devices to fabricate WLEDs. The electroluminescent properties, such as the electroluminescence (EL) spectrum, luminous flux, luminous efficacy, R_t , R_g , and correlated color temperature (CCT) of the WLEDs, were tested using a spectroradiometer with an integrating sphere (HASS-2000, Hangzhou, China). The optical properties of the composite phosphor with the C+R+Y structure under the laser excitation were measured by a sphere-spectroradiometer which is equipped with an integrating sphere (Labsphere Inc., USA), a charge-coupled device (CCD) spectrometer (HR4000, Ocean Optics, USA), and a high-power blue laser light source with adjustable output power.

3 Results and discussion

Figure 1(a) shows the surface morphology of the YAG:Ce sample. It can be seen that YAG:Ce ceramic has regular grains with an average grain size of ~ 5 μm . A number of closed pores are present in the sample. Although these pores as light scattering centers will decrease the transmittance of the sample, they are beneficial to improving the conversion efficiency of phosphor ceramics by increasing the interaction between incident blue light and the ceramic, which results in more blue light being absorbed [35]. The fractured

Fig. 1 FESEM morphologies of (a) YAG:Ce ceramic, (b) $\text{BaSi}_2\text{N}_2\text{O}_2\text{:Eu}$ film, and (c) $(\text{Sr,Ca})\text{AlSiN}_3\text{:Eu}$ film. (d) The total transmittance of phosphor mentioned above.

surfaces of the $\text{BaSi}_2\text{N}_2\text{O}_2\text{:Eu}$ and $(\text{Sr,Ca})\text{AlSiN}_3\text{:Eu}$ phosphor films are shown in Figs. 1(b) and 1(c). The micron-sized phosphor particles, which have been circled in the graphs, are loosely dispersed in the polymer matrix. As seen in Fig. 1(d), both the ceramic and phosphor films have good optical transmittance (the thicknesses of YAG:Ce ceramic, $(\text{Sr,Ca})\text{AlSiN}_3\text{:Eu}$ red film, and $\text{BaSi}_2\text{N}_2\text{O}_2\text{:Eu}$ cyan film are 1, 0.4, and 0.4 mm, respectively), which is beneficial to the entry of the blue excitation light and the extraction of the emitted light.

Figure 2 shows the PLE and PL spectra of YAG:Ce ceramics, $\text{BaSi}_2\text{N}_2\text{O}_2\text{:Eu}$ films, and $(\text{Sr,Ca})\text{AlSiN}_3\text{:Eu}$ films with different concentrations. The illustrations are photographs of the corresponding phosphor ceramic or films. As seen from Fig. 2(a), two absorption bands at 340 and 460 nm can be found, which can be attributed to $4f \rightarrow 5d_2$ and $4f \rightarrow 5d_1$ transitions of Ce^{3+} , respectively. A broad emission band, assigned to the transition of the $5d$ excited state to $^2F_{5/2}$ and $^2F_{7/2}$ ground states, can be found [6,15,36]. It can be seen that the emission intensity of the YAG:Ce ceramic increases with the increase of the Ce^{3+} concentration. As shown in Fig. 2(b), $\text{BaSi}_2\text{N}_2\text{O}_2\text{:Eu}$ phosphor films yield a broad excitation ranging from 250 to 475 nm,

corresponding to the $4f^7 (8S_{7/2}) \rightarrow 4f^6 5d^1$ transition of Eu, and a narrow emission band with the peak position at 492 nm. The PL intensity increases with increasing concentration of phosphor in the film [33]. When the Eu ions are doped in $(\text{Sr,Ca})\text{AlSiN}_3$, the emission peak which can be attributed to the transition of $4f^6 5d^1 \rightarrow 4f^7$ is located at 634 nm [37–40]. The PL intensity is obviously enhanced with the increase of the phosphor concentration. The PL/PLE spectra of the YAG:Ce ceramic, $\text{BaSi}_2\text{N}_2\text{O}_2\text{:Eu}$, and $(\text{Sr,Ca})\text{AlSiN}_3\text{:Eu}$ phosphor films under the excitation of 460 nm are compared in Fig. 2(d). The cyan and yellow emissions can be reabsorbed by the red phosphor due to the large spectral overlap between the excitation spectrum of $(\text{Sr,Ca})\text{AlSiN}_3\text{:Eu}$ and the emission spectra of $\text{BaSi}_2\text{N}_2\text{O}_2\text{:Eu}$ and YAG:Ce. Also, YAG:Ce can convert the emission of the cyan phosphor to yellow light. Therefore, it is necessary to optimize the structure of the three-layered phosphors to reach the optimal optical properties (high luminous efficacy and color rendering). Ce^{3+} almost displays a single exponential fluorescent decay model with a typical lifetime of about 65 ns (Fig. 2(e)). As shown in Figs. 2(f) and 2(g), when Eu^{2+} is doped in $\text{BaSi}_2\text{N}_2\text{O}_2$ and $(\text{Sr,Ca})\text{AlSiN}_3$, their fluorescence lifetime (τ) are 12.7 and 8.7 μs , respectively.

Fig. 2 PLE and PL spectra of (a) YAG:Ce ceramics, (b) BaSi₂N₂O₂:Eu films, and (c) (Sr,Ca)AlSiN₃:Eu films with different concentrations. (d) Normalized PL spectra of the above three phosphors under the 460 nm blue light excitation. Fluorescent decay curves for (e) YAG:Ce ceramic, (f) BaSi₂N₂O₂:Eu film, and (g) (Sr,Ca)AlSiN₃:Eu film.

One of the key parameters to evaluate phosphor used for WLEDs is the thermal stability $I_x \cdot \tau / I_{RT}$. Figure 3 shows the temperature-dependent PL spectra of YAG:Ce ceramic, BaSi₂N₂O₂:Eu film, and (Sr,Ca)AlSiN₃:Eu film under 460 nm excitation. The thermal stability is defined as the ratio of the PL intensity at high temperatures to that at the room temperature (Fig. 3(d)). The YAG:Ce ceramic shows the excellent thermal stability. With the increase of the temperature, the PL intensity decreases slightly, and it can maintain 92.5% at 225 °C. The red shift of the emission peak is also observed, which is mainly caused by reabsorption of the high-energy part of the emission [41]. It indicates the phosphor ceramic can maintain the luminous

efficacy and color stability when used as the color converter. It is worthwhile to mention that the emission intensity of BaSi₂N₂O₂:Eu or (Sr,Ca)AlSiN₃:Eu phosphor film decreases with the increase of the temperature due to the thermal quenching, which is caused by excited state electrons going back to the ground state in a non-radiative process [42]. The insets in Figs. 3(b) and 3(c) are the temperature-dependent PL spectra of these two phosphors without the mixtures of A and B glues, and they exhibit the same trend as the spectra of the corresponding phosphor films. The PL intensity of BaSi₂N₂O₂:Eu drops to 57.8% when the temperature rises to 225 °C, and the PL intensity of (Sr,Ca)AlSiN₃:Eu phosphor film can maintain 66.7% of its initial value.

Fig. 3 Temperature-dependent PL spectra of (a) YAG:Ce ceramic, (b) (Sr,Ca)AlSiN₃:Eu film, and (c) BaSi₂N₂O₂:Eu film. (d) Thermal stability of the five types of phosphors with the increasing temperature from 25 to 225 °C. The insets in (b) and (c) are the corresponding PL spectra of the phosphor without the mixtures of A and B glues.

Also, the emission peak blue shifts slightly as the temperature increases due to the thermally activated phonon-assisted tunneling, which can be described in terms of the thermal back-transfer from the lower energy excited states to the higher energy excited states with the assistance of thermal active phonons [43].

In order to screen the optimal spectral composition, the cyan and red films with different phosphor concentrations were combined with YAG:Ce ceramics with different Ce³⁺ concentrations to investigate their optical properties under the excitation of the COB packaged 460 nm blue light (Table 1). Similar to the previous film preparation, the different composite phosphors were prepared by spin-coating a mixture of phosphor and glues onto a ceramic or another phosphor film on the ceramics rather than a glass substrate. The R+C+Y structure was used for measurements. The addition of the red-emitting component is useful to improve the color rendering, but human eye sensitivity is low in the red spectral region. So, it is quite difficult to obtain a high luminous efficacy and high color rendering simultaneously. Also, when the concentration of cyan and red phosphor films increases, luminous

efficacy of the composite phosphor decreases due to their low thermal conductivities. The luminous efficacies of five combinations are higher than 70 lm/W, of which only two concentration combinations have R_f and R_g greater than 90. When the concentration of the red phosphor film is 1:1:0.01, the color temperature is between 3500 and 5000 K, which is often used and suitable for indoor lighting. Only the sample with the red concentration of 1:1:0.01 (the mass ratio of glue A: glue B:((Sr,Ca)AlSiN₃:Eu)), cyan phosphor concentration of 1:1:0.07 (the mass ratio of glue A: glue B:(BaSi₂N₂O₂:Eu), and Ce³⁺ concentration in YAG of 0.1 at% has a relatively high luminous efficacy (75 lm/W). So, this concentration combination was chosen for further testing.

Figure 4 shows the EL spectra of WLEDs using different structures of three-layered phosphors. The input power of the blue LED was 1.5 W. It is known that the red phosphor film can absorb the emission light of cyan and yellow phosphors, and the yellow phosphor can absorb the emission of the cyan phosphor, which will decrease the luminous efficacy and affect the color rendition of WLEDs (Fig. 3(d)). In order to improve the color rendering of WLEDs effectively, the red and

Table 1 Optical properties of the COB packaged WLEDs with different concentrations of red and cyan phosphor films under the excitation of 460 nm blue LEDs with an input power of 1.5 W

Mass ratio of glue A:glue B: ((Sr,Ca)AlSiN ₃ :Eu)	Mass ratio of glue A:glue B: (BaSi ₂ N ₂ O ₂ :Eu)	Concentration of Ce ³⁺ in YAG	Luminous efficacy (lm/W)	Color coordinates (x, y)	CCT (K)	(R _f , R _g)
1:1:0.01	1:1:0.05	0.05 at%	72	(0.37, 0.40)	4380	(92, 95)
1:1:0.01	1:1:0.05	0.1 at%	77	(0.40, 0.42)	3866	(88, 90)
1:1:0.01	1:1:0.05	0.15 at%	79	(0.40, 0.44)	3825	(87, 91)
1:1:0.01	1:1:0.07	0.05 at%	68	(0.36, 0.40)	4721	(90, 95)
1:1:0.01	1:1:0.07	0.1 at%	75	(0.39, 0.42)	3852	(93, 97)
1:1:0.01	1:1:0.07	0.15 at%	72	(0.40, 0.42)	3886	(87, 91)
1:1:0.01	1:1:0.09	0.05 at%	62	(0.35, 0.41)	4898	(83, 92)
1:1:0.01	1:1:0.09	0.1 at%	68	(0.38, 0.42)	4193	(90, 100)
1:1:0.01	1:1:0.09	0.15 at%	57	(0.33, 0.35)	5408	(94, 104)
1:1:0.02	1:1:0.05	0.05 at%	60	(0.40, 0.36)	3257	(90, 110)
1:1:0.02	1:1:0.05	0.1 at%	62	(0.43, 0.40)	3027	(92, 105)
1:1:0.02	1:1:0.05	0.15 at%	57	(0.43, 0.38)	2877	(88, 110)
1:1:0.02	1:1:0.07	0.05 at%	53	(0.41, 0.36)	3181	(89, 110)
1:1:0.02	1:1:0.07	0.1 at%	58	(0.43, 0.39)	3014	(93, 106)
1:1:0.02	1:1:0.07	0.15 at%	57	(0.44, 0.39)	2877	(90, 108)
1:1:0.02	1:1:0.09	0.05 at%	47	(0.42, 0.38)	3127	(82, 107)
1:1:0.02	1:1:0.09	0.1 at%	53	(0.43, 0.38)	3081	(88, 106)
1:1:0.02	1:1:0.09	0.15 at%	49	(0.26, 0.50)	3004	(88, 113)
1:1:0.03	1:1:0.05	0.05 at%	52	(0.44, 0.37)	2615	(87, 114)
1:1:0.03	1:1:0.05	0.1 at%	57	(0.45, 0.37)	2481	(88, 111)
1:1:0.03	1:1:0.05	0.15 at%	54	(0.46, 0.39)	2471	(86, 110)
1:1:0.03	1:1:0.07	0.05 at%	45	(0.27, 0.50)	2562	(84, 116)
1:1:0.03	1:1:0.07	0.1 at%	52	(0.45, 0.37)	2634	(86, 116)
1:1:0.03	1:1:0.07	0.15 at%	50	(0.46, 0.38)	2469	(86, 113)
1:1:0.03	1:1:0.09	0.05 at%	39	(0.43, 0.35)	2539	(78, 117)
1:1:0.03	1:1:0.09	0.1 at%	46	(0.44, 0.36)	2485	(82, 118)
1:1:0.03	1:1:0.09	0.15 at%	41	(0.45, 0.36)	2405	(84, 117)

Fig. 4 EL spectra of WLEDs with different structures of three-layered phosphors: (a) R+C+Y, (b) R+Y+C, (c) C+R+Y, (d) C+R+Y, (e) Y+R+C, and (f) Y+C+R.

cyan phosphor films, which are used to supplement the spectral component of YAG:Ce, should be placed close to the blue LED. As seen from the EL spectra of these composite phosphors with different structures in Fig. 4, the structures of R+C+Y (Fig. 4(a)) and C+R+Y (Fig. 4(c)) can fill the cyan and red light gaps. However, the WLED with the structure of C+R+Y has low color rendering. For the R+C+Y structure used for high-power lighting devices in reflection geometry, the YAG:Ce phosphor ceramic will contact with the heat sink substrate, enabling to dissipate the heat generated by the phosphor films and itself.

The Commission Internationale De L'Eclairage (CIE) chromaticity coordinates of WLEDs fabricated by using YAG:Ce ceramic and different structures of three-layered phosphors are shown in Fig. 5(a). In the composite phosphors, the thicknesses of YAG:Ce ceramic, (Sr,Ca)AlSiN₃:Eu red film, and BaSi₂N₂O₂:Eu cyan film are 1.0, 0.4, and 0.4 mm, respectively. It can be seen that the color coordinates of all the WLEDs based on composite phosphor fall in the white light area. When the YAG:Ce phosphor ceramic or the cyan phosphor film is close to the blue LEDs, the obtained light is far from the black body radiation line and no longer white. In addition, the CCT value also changes when the structure of three-layered phosphors is different (Table 2). The obtained white light based on the structure of R+C+Y is closest to the blackbody line and can be used for neutral white light illumination. As shown in Fig. 5(b), although the surface temperature of the three-layered phosphors is higher than that of YAG:Ce, all of them are lower than 67 °C when they are excited by the blue LED, indicating that WLEDs using these composite phosphors can remain relatively high luminous efficacy while they work. As shown in Fig. 5(c), with the decrease of the YAG:Ce ceramic thickness in the R+C+Y structured composite phosphor, the color rendering and CCT of the WLED increase, and the luminous efficacy decreases. The emission light changes from warm light to cold light (Fig. 5(d)), approaching the blackbody radiation line, which is attributed to the different proportion of red, yellow, and cyan in the emitted light caused by the changed thickness of the ceramic. It is worth noting that the color coordinates of different structures can be closest to the blackbody line and can be used for neutral white light illumination by changing the thicknesses and concentrations of the cyan, yellow, and red phosphors. This result just provides a solution for phosphors with

Fig. 5 (a) CIE chromaticity coordinates of WLEDs using YAG:Ce ceramic and different structures of the three-layered phosphors and T_c in (a) indicates the color temperature of the point; (b) the surface temperature of WLEDs in operation; (c) luminous efficacy, R_g , R_f , CCT, and (d) CIE chromaticity coordinates of WLEDs based on the R+C+Y three-layered phosphor with different YAG:Ce ceramic thicknesses under the excitation of 460 nm blue LEDs with an input power of 1.5 W.

specific thickness and concentration to change their color temperature and luminous efficacy by transforming

Table 2 Optical properties of the COB packaged WLEDs with different structures of three-layered phosphors under the excitation of 460 nm blue LEDs with an input power of 1.5 W

Structure of three-layered phosphor	Luminous flux (lm)	Luminous efficacy (lm/W)	Color coordinates (x, y)	CCT (K)	(R _r , R _g)
R+C+Y	106	75	(0.39, 0.42)	3852	(93, 97)
R+Y+C	128	90	(0.42, 0.44)	3573	(83, 92)
C+R+Y	112	77	(0.37, 0.43)	4489	(85, 88)
C+Y+R	133	89	(0.37, 0.46)	4691	(78, 80)
Y+R+C	146	100	(0.42, 0.47)	3809	(76, 78)
Y+C+R	151	106	(0.41, 0.48)	3972	(75, 80)

the stack structure purposefully. By using this CIE chromaticity diagram, we can design the WLED devices with specific properties.

The luminous flux, luminous efficacy, and CCT of the WLEDs based on the R+C+Y three-layered phosphor as a function of incident pump power are demonstrated in Fig. 6. The luminous flux increases linearly with increasing the pump power, and it reaches a saturation threshold at 3.5 W. The surface temperature of the three-layered phosphors can be up to 121 °C when the pump power is 4.44 W (Fig. 6(b)), so thermal quenching is the main reason for luminance saturation which leads to the decrease of luminous flux. Perhaps the thermal conductivity of the films is too low to dissipate the generated heat, so that the heat is accumulated and the temperature of the phosphors rises. The CCT value nearly does not change with the increase of the pump power, indicating that the white light is maintained. When LEDs are used for lighting, they will face a variety of extreme environmental conditions, such as long-term exposure to sun and rain, thunder and lightning, and large temperature changes, etc. Therefore, the variation EL spectra of R+C+Y three-layered samples before and after high-temperature and high-humidity (85 °C/RH 85%) test for 6 days were tested (Fig. 6(c)). After the test, the films still adhere to the ceramic and no change can be found in the composite phosphor. However, the EL intensity decreases after the test, which may be attributed to the hydrolysis of phosphors in the film.

In order to evaluate the potential of this composite phosphor for laser lighting, optical properties of the R+C+Y structured composite phosphor under the blue laser excitation were also measured. The blue laser

Fig. 6 (a) Luminous flux, luminous efficacy, and CCT of WLEDs based on the R+C+Y three-layered phosphor; (b) the surface temperature as a function of incident pump power; and (c) EL spectra of the R+C+Y three-layered phosphor before and after high-temperature and high-humidity test for 6 days.

power density was $0.92 \text{ W} \cdot \text{mm}^{-2}$. As seen from Fig. 7(a), the values of luminous efficacy, CRI, and CCT of the white light are 120 lm/W, 90, and 5988 K, respectively. Big differences in the luminous efficacy and CCT of the “R+C+Y” three-layer phosphor have been found under LED excitation and under LD excitation. When the composite phosphor is excited by a high-power blue laser instead of a blue LED, the power density is higher and therefore more blue light is transmitted. The blue light is not converted and passes through the phosphor to participate in the final white light, so the color temperature and luminous efficacy of the obtained

Fig. 7 (a) Emission spectrum of R+C+Y structured three-layered phosphor under the excitation of 450 nm blue laser with a laser power density of $0.92 \text{ W}\cdot\text{mm}^{-2}$. The inset shows the luminous flux as a function of blue laser power density and the photograph of the composite phosphor after the excitation of blue laser. (b) SEM morphology of the damaged area. EDS analyses of spectra: (c) 1 in (b) and (d) 2 in (b).

white light are higher than when the composite phosphor is excited by LEDs. The inset in Fig. 7(a) shows the luminous flux of the R+C+Y structured phosphor as a function of the blue laser power density. The luminous flux reaches its maximum at $0.92 \text{ W}\cdot\text{mm}^{-2}$, and decreases abruptly at $1.2 \text{ W}\cdot\text{mm}^{-2}$. The sharp decrease can be ascribed to the carbonization of the phosphor films when they are pumped by the blue laser. As shown in the inset of Fig. 7(a), two black spots on the composite phosphor where the blue laser excites can be observed. Obvious pits can be observed in the damaged area (Fig. 7(b)). According to the EDS results in Figs. 7(c) and 7(d), the elements in the pits are C, O, and Si, and the undamaged area outside the pits contains more C. Because C in the damaged area is released into the air in the form of CO_2 after combining with O in the air under the excitation of high-power density blue laser. Therefore, the phosphor film containing organic binders is not suitable for laser lighting, and all inorganic color converters with high thermal stability or thermal conductivity need to be developed.

4 Conclusions

In this work, to realize high color rendering lighting, we

proposed coating both the cyan-emitting $\text{BaSi}_2\text{N}_2\text{O}_2\text{:Eu}$ and red-emitting $(\text{Sr,Ca})\text{AlSiN}_3\text{:Eu}$ phosphor films on the yellow-emitting YAG:Ce phosphor ceramic. The optimal composition of the cyan film, red film, and yellow ceramic was 1:1:0.07 (the mass ratio of glue A:glue B:($\text{BaSi}_2\text{N}_2\text{O}_2\text{:Eu}$)), 1:1:0.01 (the mass ratio of glue A:glue B:($(\text{Sr,Ca})\text{AlSiN}_3\text{:Eu}$)), and Ce^{3+} concentration in YAG of 0.1 at%, respectively. Also, the structure or the stacking sequence of the three-layered phosphors had a great influence on the luminous efficacy and color rendering properties of WLEDs. By combining with a COB blue LED, the sample with a structure of R+C+Y three-layered phosphors generated neutral white light with the luminous efficacy of 75 lm/W, R_f of 93, R_g of 97, and CCT of 3852 K. The luminous flux reached a saturation threshold when the incident pump power was 3.5 W, which can be attributed to the thermal quenching of phosphor films. Under the blue laser excitation, the values of luminous efficacy, CRI, and CCT of the white light are 120 lm/W, 90, and 5988 K, respectively. However, the luminance saturation of the same sample was as low as $0.92 \text{ W}\cdot\text{mm}^{-2}$. In our future work, to increase the threshold of luminance saturation, full-inorganic multi-layered phosphors with higher thermal conductivities will be prepared to keep the temperature of the phosphor as low as possible.

Acknowledgements

This work was supported by the National Key R&D Program of China (Grant No. 2017YFB0310500), the National Natural Science Foundation of China (Grant No. 61775226), the Strategic Priority Research Program of Chinese Academy of Sciences (Grant No. XDA22010301), and the key research project of the frontier science of the Chinese Academy of Sciences (No. QYZDB-SSW-JSC022).

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